Reductive Dimerization of CO by a Na/Mg(I) Diamide

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ABSTRACT: Sodium reduction of \([\{\text{SiNDipp}\}Mg]_2\) \([\text{SiNDipp} = \{\text{CH}_2\text{SiMe}_2\text{N(Dipp)}\}_2; \text{Dipp} = 2,6-\text{i-Pr}_2\text{C}_6\text{H}_3]\) provides the Mg(I) species, \([\{\text{SiNDipp}\}Mg\text{Na}]_2\), in which the long Mg−Mg bond (>3.2 Å) is augmented by persistent Na−aryl interactions. Computational assessment indicates that this molecule is best considered to comprise a contiguous tetrametallic core, a viewpoint borne out by its reaction with CO, which results in ethynyldiolate formation mediated by the dissimilar metal centers.

INTRODUCTION

Prior to Jones and co-workers’ isolation of stable guanidinate and β-diketiminate (BDI) derivatives such as compound 1 in 2007 (Chart 1),1−5 experimental studies of low oxidation state Mg(I) derivatives were limited to transient species under low temperature matrix isolation conditions.6 Although more than 25 examples of such compounds have now been described, like 1, a majority conform to the general structural requirement of a bulky monoanionic spectator ligand to provide the requisite kinetic stabilization of the \([\text{Mg−Mg}]^{2+}\) unit against disproportionation to Mg(II) and Mg(0).

Chart 1. Structures of Compounds 1−7

The implementation of an ever more bulky suite of amide and β-diketiminate anions, in harness with a variety of neutral monodentate bases, has, thus, resulted in the isolation of a variety of species comprising four-,7,8 three-,9−15 two-,16 or even asymmetric combinations of four- and three-,17 or three- and two-coordinate magnesium centers.18 The intermetallic distance in these compounds has proved remarkably malleable such that the Mg−Mg bond lengths encompass an unusually wide range, with extremes provided by an N-mesityl BDI variant of 1 \([2, \text{Mg−Mg} 2.808(1) \text{Å}]^8\) and compound 3 \([3.1962(14) \text{Å}]^8\) in which the coordination number of both magnesium atoms in 1 is raised to four through the introduction of two molecules of strongly basic 4-dimethylaminoypyridine (DMAP).7 While this deformability is consistent with a very shallow bond potential energy surface, experimental charge density studies and quantum theory of atoms-in-molecules (QTAIM) calculations revealed that the Mg−Mg bond of compound 1 is not a classical covalent interaction. Rather, a large region of negative Laplacian in the Mg−Mg internuclear region comprises a non-nuclear attractor (NNA) containing 0.8 electrons, in effect electron density that is not associated with a particular nucleus and, hence, distinct from the positions of the magnesium atoms.9,18−20

While a pre-existing \([\text{Mg−Mg}]^{2+}\) unit has also been manipulated to provide further Mg(I) derivatives,21,22 the synthesis of these compounds invariably involves the generation of a salt by reduction of a magnesium(II) halide starting material with either sodium or potassium. The current apotheosis of this approach has very recently been provided by Harder and co-workers’ report that sodium reduction of a magnesium(II) iodide bearing the extraordinarily bulky BDI*...
[BDI* = HC\{t-Bu\}N\{DiPeP\}]2; DiPeP = 2,6-(3-pentyl)-phenyl] ligand provides the remarkable magnesium(0) compound, \([\{\text{BDI}^\text{*}\}MgNa]\2\) (4).\23 Whereas the Mg−Mg separation [5.7792(5) Å] in 4 is too long to represent a binding interaction, the shorter of the Mg−Na distances [3.1216(7) Å] approaches the sum of the ionic radii of the respective group 1 and group 2 metal centers (3.19 Å).\24 Compound 4 also disproportionates in benzene to provide a further Mg(0)-containing species, \([\{\text{BDI}^\text{*}\}MgMgMg\{\text{BDI}^\text{*}\}]\) (5), in which the magnesium atoms were shown by QTAIM to be connected via two NNAs, each with a basis of 0.64 electrons.

An exception to this synthetic approach has been provided by Yang and co-workers’ utilization of doubly reduced α-dimine, phenanthrene-9,10-diimine, and ω-phenylene diamide ligand sets.\10 14 In these cases the redox noninnocent ligands were reduced with excess potassium metal, albeit the reactions were performed in the presence of MgCl2, and so are again driven by the thermodynamically favorable production of an ionic group 1 salt. Charge balance in the resultant Mg(I) species, such as 6, is necessarily maintained by the incorporation of potassium cations. Although these cations interact strongly with the delocalized π system of the planar dianionic spectator ligands, they impose a negligible impact on the bonds between the three-coordinate Mg centers, which are <3 Å in all cases.

In contrast to the unsupported Mg−Mg bonds of compounds 1–3 and 6, a notable feature of compound 4 is the presence of bridging Na−aryl contacts, which presumably play a significant role in the stability of the dimeric molecule.\25 We, and others, have recently observed that similarly persistent Na− and K−aryl interactions provide a defining feature in a number of dimeric potassium diamidoaluminum derivatives.\25 28 In these cases, the integrity of the formal Al(I) centers is maintained by a sterically demanding diamide ligand, such as in the seven-membered cyclic species, \([\{\text{SiN}^\text{Dipp}\}\cdot \text{AlI}]_2\{\{\text{SiN}^\text{Dipp}\}\cdot \text{AlI}\} = \{\text{CH}_2\text{SiMe}_2\text{N}(\text{Dipp})\}_2\;\text{Dipp} = 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3\} (7).\26 Prompted by the robust nature of compounds 4 and 7, in this contribution we show that the thermodynamic preference for heavier group 1 element−aryl interactions\27 30 can provide a strategy to access dinuclear low oxidation state alkaline earth species that circumvent conventional salt elimination.

## RESULTS AND DISCUSSION

Initial DFT calculations were performed to model the sodium and potassium reduction of a neutral magnesium derivative, \([\{\text{SiN}^\text{Dipp}\}\cdot \text{Mg}]_\text{9Na, K} \) (Scheme 1), the sodium-based process was calculated to be more exergonic (M = Na, ΔG = −72.3; M = K, ΔG = −63.7 kcal mol−1).

Encouraged by these results, compound 8 was synthesized by reaction of the aniline pro-ligand, \([\text{SiN}^\text{Dipp}\]H2, with dibutyl magnesium in hexane at room temperature. Although 8 was isolated in analytically pure base-free form by removal of volatiles, it was observed to quickly sequester aromatic solvents. Compound 8 was, thus, characterized as its Mg−η1−benzene and Mg−η1-toluene adducts by X-ray diffraction analysis performed on colorless single crystals isolated by slow evaporation of the respective arene solutions (Figure S14). Guided by the greater theoretical viability of the sodium reduction, a benzene solution of 8 was reacted with an excess of 5 wt % Na/NaCl at room temperature for 12 h, whereupon removal of volatiles and crystallization from toluene solution provided compound 9 as highly air-sensitive bright yellow crystals. The 1H NMR spectrum of compound 9 was characterized by a significant asymmetry across the various \([\text{SiN}^\text{Dipp}\]\) ligand environments. This was particularly apparent in the silylmethyl signals, which appeared as two (6H) singlets at δ 0.52 and −0.21 ppm, and which may be attributed to a loss of the mirror plane of symmetry through the seven-membered magnesium chelate of 8. Notably, these resonances did not display any level of coherence transfer consistent with chemical or conformational exchange in the corresponding EXSY NMR experiment.

The origin of these observations became apparent in a subsequent single crystal X-ray diffraction analysis of compound 9, which confirmed it as a tetranuclear heterobimetallic species in which a pair of \([\text{SiN}^\text{Dipp}\]\)Mg units are bridged by twofold η1-Na-Dipp interactions (Figure 1). Intrinsically to the crystallographic symmetry (P1), the asymmetric unit comprises a racemate, such that the Mg1/Mg2- and Mg3/Mg4-containing molecules describe right- and left-handed helices, respectively. While there are some significant variations across the comparable metric data of both

![Figure 1. ORTEP (30% probability) of the Mg1/Mg2-containing molecule in compound 9. Hydrogen atoms and disordered molecules of solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg1−Mg2 3.2077(10), Mg3−Mg4 3.2124(11), Mg1−Na2 3.7259(13), Mg1−N1 2.0843(18), Mg1−N2 2.0786(19), Mg2−Na2 3.7014(13), Mg2−N3 2.090(2), Mg2−N4 2.0794(19), Mg3−Na3 3.6290(12), Mg4−Na3 3.6691(12), N2−Mg1−N1 109.76(7), N3−Mg2−N4 110.77(8), N5−Mg3−N6 110.03(8), N8−Mg4−N7 110.41(8).](https://doi.org/10.1021/jacs.1c09467)
molecules, their gross constitutions are effectively identical. The most notable features of the structures are the exceptionally long magnesium–magnesium separations \([\text{Mg}_1-\text{Mg}_2 \ 3.2077(10), \ \text{Mg}_3-\text{Mg}_4 \ 3.2124(11) \ \text{Å}]\), which exceed even that reported for compound \(3 \ [3.1962(14) \ \text{Å}]\). Consistent with the attribution of a Mg(I) oxidation level to magnesium, the \(\text{N}--\text{Mg}\) bonds observed in \(9 \ [\text{avg. } 2.0831 \ \text{Å}]\) are more closely commensurate with the \(\text{N}--\text{Mg}\) distances in compound \(1 \ [\text{avg. } 2.0604 \ \text{Å}]\) than the longer formal nitrogen-to-Mg(0) interactions \([\text{avg. } 2.117 \ \text{Å}]\) displayed by compound \(4\). The closest \(\text{Na}--\text{Mg}\) separation in \(9 \ [\text{Mg}_3-\text{Na}_3 \ 3.6290(12) \ \text{Å}]\) is also elongated in comparison to even the longer of the \(\text{Na}--\text{Mg}\) contacts reported for compound \(4 \ [3.4529(7) \ \text{Å}]\), in which a modicum of Mg–Na bonding was supported by bond paths located in the QTAIM analysis. In contrast, the \(\text{Na}--\text{C}_{\text{centroid}}\) distances to the Dipp substituents \([\text{avg. } 2.414 \ \text{Å}]\) is also elongated in comparison to even the longer of the \(\text{Na}--\text{Mg}\) contacts reported for compound \(4\).

Figure 2. (a) QTAIM molecular graph of the BP86-optimized geometry of \(9\). The electron density contours are computed in the \([\text{Mg}--\text{N}]\) planes with bond critical points (BCPs) shown as small green spheres. (b) Natural Localized Molecular Orbital of the Mg–Mg bond in \(9\).

Further supported by NBO analysis through the identification of a natural localized molecular orbital of a Mg–Mg \(\sigma\)-bond with a roughly equal contribution from the 3s orbitals of each Mg center (Figure 2b). In contrast to comparable calculations performed on monomeric species such as \(1\) and \(5\), no persuasive evidence of a NNA could be identified. Rather, QTAIM analysis revealed two further weak bond critical points (where \(\rho = 0.0034\)) between the Na cations and the Mg–Mg bond critical point itself. Perturbation energy analysis of this unusual interaction with both Na\(^+\) cations estimates an overall \(\sigma\)-donation strength between the Mg–Mg bond and each Na\(^+\) cation of \(\Delta E(2) \approx 25 \ \text{kcal} \ \text{mol}^{-1}\).

Magnesium(I) complexes comprising an isolated Mg–Mg interaction have displayed broad applicability as soluble molecular reducing agents.\(^7\) The QTAIM and NBO results suggest, however, that the chemistry of \(9\) is better considered in terms of its \([\text{Na}_2\text{Mg}_2]^{4+}\) core rather than as an isolated \([\text{Mg}--\text{Mg}]^{2+}\) unit. This raises the possibility that new patterns of cooperative reactivity may arise between the dissimilar metal centers. Treatment of molten alkali metals or their solutions in liquid ammonia with gaseous CO have long been known to give rise to ill-defined and shock-sensitive mixtures of oxocarbon anions, \([\text{C}_3\text{O}_3]^{2-}\) \((n = 2-6)\).\(^{32,33}\) Although molecules such as \(1-3\) are unreactive toward CO, Jones, Maron and co-workers have shown that addition of monodentate bases yields unsymmetrical Mg–Mg bonded species, \([\{(\text{BDI})(\text{D})\text{Mg}--\text{Mg}(\text{BDI})\}]{\}}\ (\text{D} = \text{DMAP or N-heterocyclic carbene}), which do effect CO oligomerization.\(^{17,34}\) Although these reactions have provided derivatives of the deltan dianion, \([\text{C}_3\text{O}_3]^{2-}\), DFT calculations indicated a trimerization mechanism that proceeds through the initial generation of reactive intermediates containing \(\text{trans}\)-bent ethynediolate, \([\text{O}--\text{C}==\text{C}--\text{O}]^{2-}\), dianions. In support of this hypothesis, DMAP adducts of the less encumbered \(N\)-mesityl (2) and \(N\)-o-xylyl variants were found to react with only two molecules of CO. Although the structures of the resultant bimetallic compounds comprised an unusual bridging \(c\)-ethynediolate dianion, \([\mu-O(H)=\text{C}(\text{C}(_2\text{H}_5)\text{N}+\text{N}\text{Me}_2)\text{O}]^{2-}\), its formation was reasoned to be a result of intramolecular \(\text{C}--\text{H}\) activation of Mg-ligated DMAP by an initially formed \([\text{O}--\text{C}==\text{C}--\text{O}]^{2-}\) intermediate.\(^{34}\) In a very recent related advance, compound 2 and its \(N\)-o-xylyl substituted analogue have also been shown to mediate the cooperative hexamerization of CO in the presence of \([\text{Mo}(\text{CO})_6]_2\) with formation of magnesium benzenehexolate complexes, \([\{(\text{BDI})\text{Mg}_2(\text{C}_3\text{O}_3)\}]{\}}^{15}\)

As an initial assay of its reactivity, therefore, a solution of compound 9 in benzene was treated with 2 atm of \(^{13}\text{CO}\) at room temperature. The conversion of 9 was complete after 3 days to provide the quantitative generation of a single new species (10). The formation of compound 10 was characterized by the loss of symmetry associated with the \([\text{SiN}^{\text{Dipp}}]\) ligand environments implied by NMR spectroscopy.

Insight into the electron densities and, in turn, the nature of the interatomic interactions within compound 9, was obtained with QTAIM topological analysis. The Mg–Mg bond critical point (\(\rho = 0.0194\)) has a negative energy density (\(\Delta E(2) = -0.00362\)) and Laplacian (\(\nabla^2 \rho(r) = -0.0136\)) which are indicative of a stabilizing covalent bond (Figure 2a). This is
ennediolates of magnesium have previously been obtained from reactions of β-diketiminato magnesium hydride and magnesium anthracene complexes with CO,4,11,14,43 and Aldridge and co-workers have inferred the intermediacy of an unperturbed ethynediolate dianion. The structure of compound 10 (Figure 3) is unique among molecular main group complexes in containing an unperturbed ethynediolate dianion, which supports a change in formal Mg oxidation state from +1 to +2.

This latter deduction was further supported by QTAIM and NBO analyses of the electronic structure and bonding interactions within 10. QTAIM analysis revealed strong BCPs between each Mg center and the O termini of the O–C≡C–O moiety (ρ_{Mg–O} = 0.0506, ρ_{Mg–O} = 0.05182) as well as two between the Na⁺ ions and the O termini (ρ_{Na–O} = 0.0232, ρ_{Na–O} = 0.0238). Donor-acceptor NBO energy analysis also afforded further support to the η²-C=C=O binding mode between the Na⁺ ions and the O–C≡C–O moiety.

The mechanism of formation of 10 was also interrogated by DFT calculations (Figure 4). In a manner reminiscent of that computed for the generation of Jones and Maron’s deltate ([C₆O₃]⁺) derivatives, the addition of CO occurs sequentially.17,34 The transformation of 9 to 10 is significantly exergonic (ΔG = −65.2 kcal mol⁻¹) and each stage of the reaction profile invokes cooperative interactions between CO and both dissimilar metals of the [Na₂Mg₉] unit. Consistent with the slow formation of 10, the kinetic barrier associated with the initial CO insertion [TS(9-A)], involving a single Mg and a single Na of 9 and the generation of a Mg−μ-C=O−μ-Na bridging interaction, is quite high and rate limiting (28.2 kcal mol⁻¹). Although the formation of the resultant species (A) is endergonic (ΔG = +15.0 kcal mol⁻¹), the overall exergonicity of CO insertion (ΔG = −10.0 kcal mol⁻¹) is ensured by its rapid isomerization to species B, in which a doubly reduced molecule of CO interacts with all four alkaline metal centers. Sequestration of a further molecule of CO by B to provide C and subsequent C−C coupling are then facile to provide 10, in which the (μ-OC≡CO) unit is encapsulated.
and protected toward further oligomerization by the [\text{Na}_2\text{Mg}]^{2-} unit.

In summary, sodium reduction of a neutral diamidomagnesium provides a Mg(1) species in which the long Mg–Mg interaction is augmented by persistent Na–aryl interactions. Computational assessment indicates that the molecule is best considered to comprise a contiguous tetrametallic core, a viewpoint borne out by its reaction with CO, which results in ethynediolate formation mediated by the dissimilar metal centers. We are continuing to study this reactivity, particularly as a strategy to allow the isolation of low oxidation state derivatives of magnesium’s heavier group 2 congeners.

**REFERENCES**

1. Green, S. P.; Jones, C.; Stasch, A. Stable magnesium(1) compounds with Mg–Mg bonds. *Science* 2007, 318 (5857), 1754–1757.

(2) Stasch, A.; Jones, C. Stable dimeric magnesium(1) compounds: from chemical landmarks to versatile reagents. *Dalton Trans.* 2011, 40 (21), 5659–5672.

(3) Jones, C.; Stasch, A. Stable Molecular Magnesium(1) Dimers: A Fundamentally Appealing Yet Synthetically Versatile Compound Class. *Top. Organomet. Chem.* 2013, 45, 73–101.

(4) Jones, C. Dimeric magnesium(1) beta-diketimates: a new class of quasi-universal reducing agent. *Nat. Rev. Chem.* 2017, 1 (8), 0059.

(5) (a) Jones, C. Open questions in low oxidation state group 2 chemistry. *Commun. Chem.* 2020, 3 (1), 159. (b) Rösch, B.; Harder, S. New horizons in low oxidation state group 2 metal chemistry. *Chem. Commun.* 2021, 57 (74), 9354–9365.

(6) Wang, X. F.; Andrews, L. Infrared spectra of magnesium hydride molecules, complexes, and solid magnesium dihydride. *J. Phys. Chem. A* 2004, 108 (52), 11151–11152.

(7) Green, S. P.; Jones, C.; Stasch, A. Stable Adducts of a Dimeric Magnesium(1) Compound. *Angew. Chem., Int. Ed.* 2008, 47 (47), 9079–9083.

(8) Bonyhady, S. J.; Jones, C.; Nembenna, S.; Stasch, A.; Edwards, A. J.; McIntyre, G. J. Beta-Diketiminate-Stabilized Magnesium(1) Dimers and Magnesium(II) Hydride Complexes: Synthesis, Characterization, Adduct Formation, and Reactivity Studies. *Chem. – Eur. J.* 2010, 16 (3), 938–955.

(9) Overgaard, J.; Jones, C.; Stasch, A.; Iversen, B. B. Experimental Electron Density Study of the Mg-Mg Bonding Character in a Magnesium(1) Dimer. *J. Am. Chem. Soc.* 2009, 131 (12), 4208.

(10) Liu, Y.; Li, S.; Yang, X.-J.; Yang, P.; Wu, B. Magnesium Bond Stabilized by a Doubly Reduced alpha-Diimine: Synthesis and Structure of \( \text{K}([\text{TTFH}_2])_2\text{Mg}_2\text{Mgl}_2 \). *J. Am. Chem. Soc.* 2009, 131 (12), 4210–4211.

(11) Lalrempuia, R.; Kefalidis, C. E.; Bonyhady, S. J.; Schwarze, B.; Maron, L.; Stasch, A.; Jones, C. Activation of CO by Hydrogenated Magnesium(1) Dimers: Sterically Controlled Formation of Ethenediolate and Cyclopropanetriololate Complexes. *J. Am. Chem. Soc.* 2015, 137 (28), 8944–8947.

(12) Li, J.; Luo, M.; Sheng, X. C.; Hua, H. M.; Yao, W. W.; Pullarkat, S. A.; Xu, L.; Ma, M. T. Unsymmetrical beta-diketiminate magnesium(1) complexes: syntheses and application in catalytic hydroboration of alkene, nitrile and carbonyl compounds. *Org. Chem. Front.* 2018, 5 (24), 3538–3547.

(13) Pernik, I.; Maitland, B. J.; Stasch, A.; Jones, C. Synthesis and attempted reductions of bulky 1,3,5-triazapentadienyl groups 2 and 13 halide complexes. *Can. J. Chem.* 2018, 96 (6), 513–521.

(14) Ma, M. M.; Wang, H. H.; Wang, J. J.; Shen, L. Y.; Zhao, Y. X.; Xu, W. H.; Wu, B.; Yang, X. J. Mg-Mg-bonded compounds with \( \text{N}_3 \)dip-substituted phenanthrene-diamido and o-phenylene-diamino ligands. *Dalton Trans.* 2019, 48 (7), 2295–2299.

(15) Gntner, T. X.; Rösch, B.; Ballmann, G.; Langer, J.; Eisen; H.; Harder, S. Low Valent Magnesium Chemistry with a Super Bulky beta-Diketiminate Ligand. *Angew. Chem., Int. Ed.* 2019, 58 (2), 607–611.

(16) Boutland, A. J.; Dange, D.; Stasch, A.; Maron, L.; Jones, C. Two-Coordinate Magnesium(1) Dimers Stabilized by Super Bulky Amido Ligands. *Angew. Chem., Int. Ed.* 2016, 55 (32), 9239–9243.

(17) Yuvaraj, K.; Douair, I.; Paparo, A.; Maron, L.; Jones, C. Reductive Trimerization of CO to the Deltane Dianion Using Activated Magnesium(1) Compounds. *J. Am. Chem. Soc.* 2019, 141 (22), 8764–8768.

(18) Rösch, B.; Gentner, T. X.; Eyselien, J.; Friedrich, A.; Langer, J.; Harder, S. Mg-Mg bond polarization induced by a superbulky beta-diketiminate ligand. *Chem. Commun.* 2020, 56 (77), 11402–11405.

(19) Platts, J. A.; Overgaard, J.; Jones, C.; Iversen, B. V.; Stasch, A. First Experimental Characterization of a Non-nuclear Attractor in a Dimeric Magnesium(1) Compound. *J. Phys. Chem. A* 2011, 115 (2), 194–200.

(20) Wu, L. C.; Jones, C.; Stasch, A.; Platts, J. A.; Overgaard, J. Non-Nuclear Attractor in a Molecular Compound under External Pressure. *Eur. J. Inorg. Chem.* 2014, 2014 (32), 5536–5540.
(21) Stasch, A. Synthesis of a Dimeric Magnesium(I) Compound by an Mg(I)/Mg(II) Redox Reaction. Angew. Chem., Int. Ed. 2014, 53 (38), 10200–10203.

(22) Bakewell, C.; White, A. J. P.; Crimin, M. R. Addition of Carbon-Fluorine Bonds to a Mg(I)/Mg(I) Bond: An Equivalent of Grignard Formation in Solution. J. Am. Chem. Soc. 2016, 138 (39), 12763–12766.

(23) Rosch, B.; Gentner, T. X.; Eyselein, J.; Langer, J.; Olsen, H.; Harder, S. Strongly reducing magnesium(0) complexes. Nature 2021, 592 (7856), 717–719.

(24) Shannon, R. D. Revisited effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. 1976, 32 (SEP1), 751–767.

(25) (a) Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. Synthesis, reaction and structure chemistry of a nucleophilic aluminium anion. Nature 2018, 557 (7703), 92–95. (b) Roy, M. M. D.; Hicks, J.; Vasko, P.; Heilmann, A.; Baston, A.-M.; Goicoechea, J. M.; Aldridge, S. Probing the Extremes of Covalency in M–Al bonds: Lithium and Zinc Aluminyl Compounds. Angew. Chem., Int. Ed. 2021, 60 (41), 22301–22306.

(26) (a) Schwamm, R. J.; Anker, M. D.; Lein, M.; Coles, M. P. Reduction vs. Addition: The Reaction of an Aluminyl Anion with 1,3,5,7-Cyclooctatetraene. Angew. Chem., Int. Ed. 2019, 58 (5), 1489–1493. (b) Evans, M. J.; Anker, M. D.; McMullin, C. I.; Neale, S. E.; Coles, M. P. Dihydrogen Activation by Lithium- and Sodium-Aluminyls. Angew. Chem., Int. Ed. 2021, 60 (41), 22289–22292.

(27) Grams, S.; Eyselein, J.; Langer, J.; Faber, C.; Harder, S. Boosting Low-Valent Aluminium(1) Reactivity with a Potassium Reagent. Angew. Chem., Int. Ed. 2020, 59 (37), 15982–15986.

(28) Schwamm, R. J.; Coles, M. P.; Hill, M. S.; Mahon, M. F.; McMullin, C. I.; Rajabi, N. A.; Wilson, A. S. S. A Stable Calcium Alumanyl. Angew. Chem., Int. Ed. 2020, 59 (10), 3928–3932.

(29) Gentner, T. X.; Mulvey, R. E. Alkali-Metal Mediation: Diversification of Applications in Main-Group Organometallic Chemistry. Angew. Chem., Int. Ed. 2021, 60 (17), 9247–9262.

(30) Pardue, D. B.; Gustafson, S. J.; Periana, R. A.; Ess, D. H.; Cundari, T. R. Computational study of carbon-hydrogen bond deprotonation by alkali metal superbases. Comput. Theor. Chem. 2013, 1019, 85–93.

(31) Hicks, J.; Juckel, M.; Paparo, A.; Dange, D.; Jones, C. Multigram Syntheses of Magnesium(1) Compounds Using Alkali Metal Halide Supported Alkali Metals as Dispersible Reducing Agents. Organometallics 2018, 37 (24), 4810–4813.

(32) Buchner, W.; Weiss, E. Zur kenntnis sogenannter alcalinalkalocarbonyl n-ubcr reaction von geschmolzenem kalium mit kohlenmonoxid. Helv. Chim. Acta 1964, 47, 1415.

(33) Weiss, E.; Buchner, W. Zur kenntnis sogenannter alcalinalkalocarbonyle V. Die Kristallstruktur des natriumacetylendiolats. Chem. Ber. 1965, 98, 126.

(34) Yuvaraj, K.; Douair, I.; Jones, D. D. L.; Maron, L.; Jones, C. Sterically controlled reductive oligomerisations of CO by activated magnesium(1) compounds: delta vs. ethenediolate formation. Chem. Sci. 2020, 11 (13), 3516–3522.

(35) Paparo, A.; Yuvaraj, K.; Matthews, A. J. R.; Douair, I.; Maron, L.; Jones, C. Reductive Hexameration of CO Involving Cooperativity Between Magnesium(I) Reductants and Mo(CO)6: Synthesis of Well-Defined Magnesium Benzenehexolate Complexes. Angew. Chem., Int. Ed. 2021, 60 (2), 630–634.

(36) Fang, M.; Farnaby, J. H.; Ziller, J. W.; Bates, J. E.; Furche, F.; Evans, W. J. Isolation of (CO)3 and (CO)4 Radical Complexes of Rare Earths via Ln(NR2)3/K Reduction and K2(18-crown-6)2 Oligomerization. J. Am. Chem. Soc. 2012, 134 (14), 6064–6067.

(37) Ryan, A. J. J.; Ziller, J. W.; Evans, W. J. The importance of the counter-cation in reductive rare-earth metal chemistry: 18-crown-6 instead of 2,2,2-cryptand allows isolation of Y-II(NR2)3 and ynediolate and enediolate complexes from CO reactions. Chemical Science 2020, 11 (7), 2006–2014.