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New horizons in low oxidation state group 2 metal chemistry

Bastian Rösch and Sjoerd Harder *

Since the seminal report on Mg in the +I oxidation state in 2007, low-valent complexes featuring a Mg^I–Mg^I bond developed from trophy molecules to state-of-the-art reducing agents. Despite increasing interest in low-valency of the other group 2 metals, this area was restricted for a long time to a rare example of a Ca^I(arene)Ca^I inverse sandwich. This feature article focuses on the most recent developments in the field, highlighting recent breakthroughs for Be, Mg and Ca. The more exotic metal Be was the first to be isolated as a zero-valent complex which could be oxidized to a Be^I species. There also has been interest in breaking the Mg^I–Mg^I bond with superbulky β-diketiminate ligands (BDI) that suppress (BDI)Mg–Mg(BDI) bond formation. This led to Mg–Mg bond elongation or Mg–N bond cleavage. Several reports on attempts to isolate (BDI)$Mg^\bullet$ radicals by combinations of ligand bulk, addition of neutral ligands or UV(vis) irradiation led to reduction of the aromatic solvents, underscoring the high reactivity of these open shell species. Only recently, zero-valent complexes of Mg were introduced. Double reduction of a (BDI)MgI complex with Na gave [(BDI)Mg^-]Na^+. This Mg^0 complex crystallized as a dimer in which the Na^+ cations bridge the two (BDI)Mg^- anions which react as Mg nucleophiles. Thermal decomposition led to spontaneous formation of Na^0 and a trinuclear (BDI)MgMgMg(BDI) complex. This mixed-valence Mg_3-complex is a prime example of the fleeting multinuclear Mg_n intermediates discussed on the way from Mg metal to Grignard reagent. Attempts to prepare low-valent Ca^I compounds by reduction of (BDI)CaI led to dearomatization of the arene solvents: (BDI)Ca(arene)Ca(BDI). Reduction in alkanes prevented this decomposition pathway but led to N_2 reduction and isolation of (BDI)Ca(N_2)Ca(BDI), representing the first example of molecular nitrogen fixation with an early main group metal. As the N_2^{2-} anion reacts in most cases as a very strong two-electron reductant, LCa(N_2)CaL could be seen as a synthon for hitherto elusive Ca^I–Ca^I complexes. Theoretical calculations suggest that participation of Ca d-orbitals is relevant for N_2 activation. These most recent developments in low-valent group 2 metal chemistry will revive this area and undoubtly lead to new reactivities and applications.

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Introduction

The development curves for the low oxidation state chemistry of the main group metals could not have been more different. While low-valent p-block elements have become well established over the past decades, the metals of the early main group metals were for a long time only accessible in their metallic state or in oxidation states that equal their group number. The electropositive s-block metals are known to lose their valence electrons easily, forming highly ionic salt-like compounds with most non-metals and it is therefore not surprising that their low oxidation state chemistry was late to arrive. Carmona's groundbreaking isolation of the first low-valent Zn^I complex[1] (**1**, Scheme 1a) inspired computational studies on low-valent alkaline-earth (Ae) metal compounds,[2,3] finally leading to the more challenging isolation of the first Mg^I complexes by Jones and coworkers in 2007 (**2** and **3**).[4] These dinuclear complexes were kinetically stabilized towards disproportionation by bulky guanidinate or β-diketiminate (BDI) ligands.

The last decade has seen enormous developments in Mg^I chemistry.[5–8] Apart from a better understanding of the highly flexible Mg–Mg bond, for which the bonding electron-pair should be formulated as a non-nuclear-attractor (a local maximum in the electron density that is not centered on an atom),[9,10] various bulky ligand systems were developed for stabilizing the Mg–Mg bond (Scheme 1b). This library of Mg^I complexes, now including more than 20 further examples, certainly contributed to numerous applications of these fascinating species as a ''new class of quasi-universal reducing agents'' with many advantages.[7] They are soluble in apolar solvents and can be easily added in exact stoichiometric quantities. They have also been shown to be safe and highly selective reducing agents and can be described as ''molecular

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bottles'' containing two electrons. Although no experimental measure of their reduction potential was feasible so far, it is likely that they are less reducing in comparison to alkali metals and hence prevent undesired over-reduction.[11] However, considering the reported potentials for the $Mg^{2+/0}$ (−2.61 V) and $Mg^{2+/1+}$ (−2.29 V) redox couples, Mg^I dimers should still be considered strongly reducing.[7,12] It can be fairly stated that many unusual novel complex types would not have been accessible without these state-of-the-art reducing agents.[8]

In addition to their rich metal reduction chemistry, the redox reactivity of Mg^I complexes has been thoroughly investigated. Amongst others, examples vary from reductive C–C[13–16] and N–N[13,17] bond coupling to C–H[18] and C–F bond cleavage[19–21] or CO_2[22] and SO_2[23] reduction. The insertion of alkenes in sterically less hindered Mg–Mg bonds can be reversible, highlighting the first reversible redox processes for s-block metals.[24,25] Furthermore, facile ethylene activation at asymmetrically NHC-coordinated Mg^I complexes has been described (NHC = N-heterocyclic carbene).[26] It was shown that the reactivity of these complexes can be conveniently controlled by the bulk of the β-diketiminate ligand.

While since 2007 low-valent Mg^I chemistry irresistibly continues its success story, the low oxidation state chemistry of the other group 2 metals remained largely unexplored. Computational studies highlight the difficulty of isolating low-valent complexes of the heavier Ae metals, especially when the group is descended.[2,5] Despite many attempts, the syntheses of Ae–Ae bonded complexes of Be or the Ca–Sr–Ba triad has so far never been achieved. Interestingly, Westerhausen and coworkers reported a paramagnetic Ca^I complex (**4**, Scheme 1a) which has been extensively studied by various spectroscopic and calculational methods.[27] Despite the many good arguments for a −2 charge on the bridging $Ph_3C_6H_3$ ring,[28] and consequently the assignment of a +I oxidation to the Ca centers, the electron distribution in **4** is unambiguous and a −4 charge on $Ph_3C_6H_3$ flanked by Ca^{II} centers has also been proposed.[29]

Apart from the many open questions in low-valent group 2 metal chemistry,[30] there is also still an enormous potential in this area. Recent developments involve breakthroughs in isolation of zero-valent and +I valent complexes for the lightest and most exotic metal in the group: Be. More recent reports on Mg^0 and Ca^I chemistry urged us to write a thought-provoking feature article on low-valent Ae metal chemistry which hopefully assists the further development of this exciting field.

Recent developments in low-valent Be chemistry

Although low-valent Mg chemistry made considerable progress in the recent years and newly prepared complexes of Mg have been established as valuable reducing agents, reports about the lighter congener Be remained scarce. Being the most toxic non-radioactive metal, strict safety requirements are needed to handle Be and its complexes.[31] Despite this claim to fame, rare examples of low oxidation state complexes of Be include the first neutral zero-valent s-block metal complexes isolated by Braunschweig in 2016: $Be^0(CAAC)_2$ (**5**, Scheme 2, CAAC = cyclic alkyl amino carbene).[32] As Be is by far the most electronegative early main group metal (χ = 1.57),[33] it is also relatively amenable to its isolation within Be(0) complexes. The key to the stability of the electron-rich Be^0 nucleus in $Be^0(CAAC)_2$ is the Be–CAAC bond which is a synergistic donor–acceptor bond of considerable covalency. Comprehensive analysis showed that these brightly colored complexes adopt a closed-shell singlet configuration and their surprising stability was attributed to an unusually strong three-center two-electron π-bond across the C–Be–C entity. Although computational studies predict that Be^I

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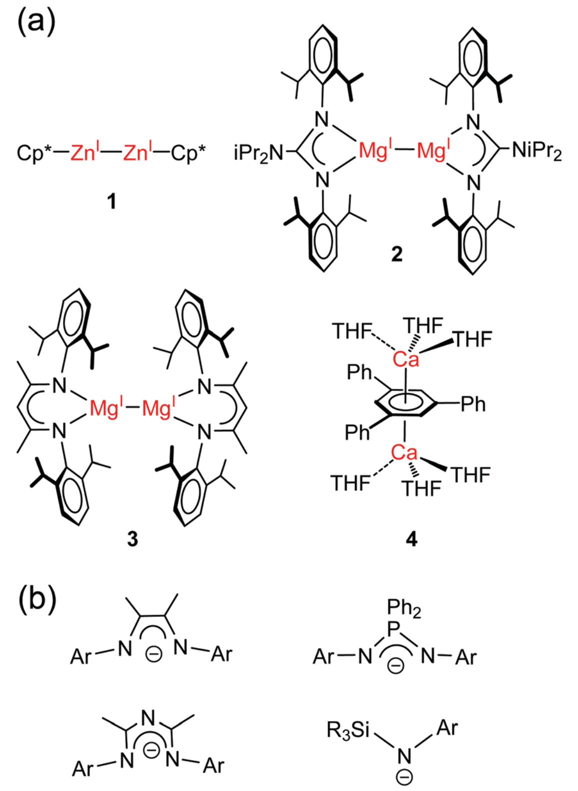
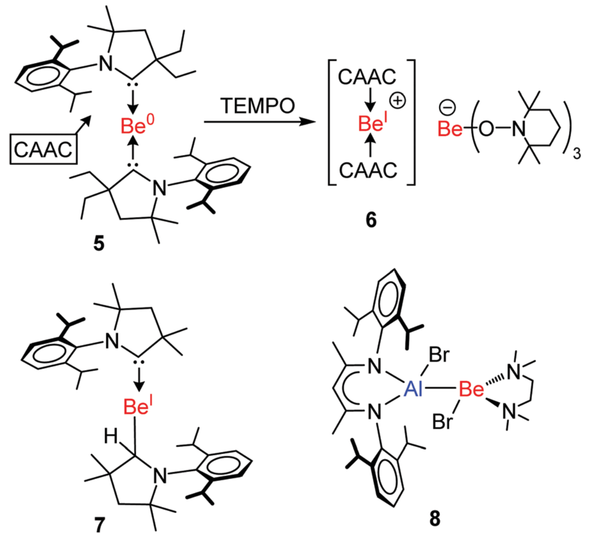
Sjoerd Harder

Dutchman Sjoerd Harder started out as an organolithium chemist (PhD 1990, Brandsma, Utrecht). After post-docs in theoretical chemistry (1991, von Ragué Schleyer, Erlangen) and heterobimetallic group 1 chemistry (1992, Streitwieser, Berkeley), a third post doc stay (1993, Brintzinger, Konstanz) was extended to a habilitation (1998) in which styrene polymerization catalysed by the heavier group 2 metals Ca, Sr and Ba was investigated. The catalytic potential of these metals was further exploited during professorships in Essen (2004), Groningen (2010) and Erlangen (2012-now). Awards include the H. J. Backer prize in organic chemistry (1990), the Schlenk Lecture Award (2017, Tübingen) and the RSC Main Group Chemistry Award (2020).



Scheme 1 (a) Pioneering examples of low-valent Zn^{I}, Mg^{I}, and Ca^{I} complexes. (b) Anionic ligands for stabilization of Mg^{I} complexes.

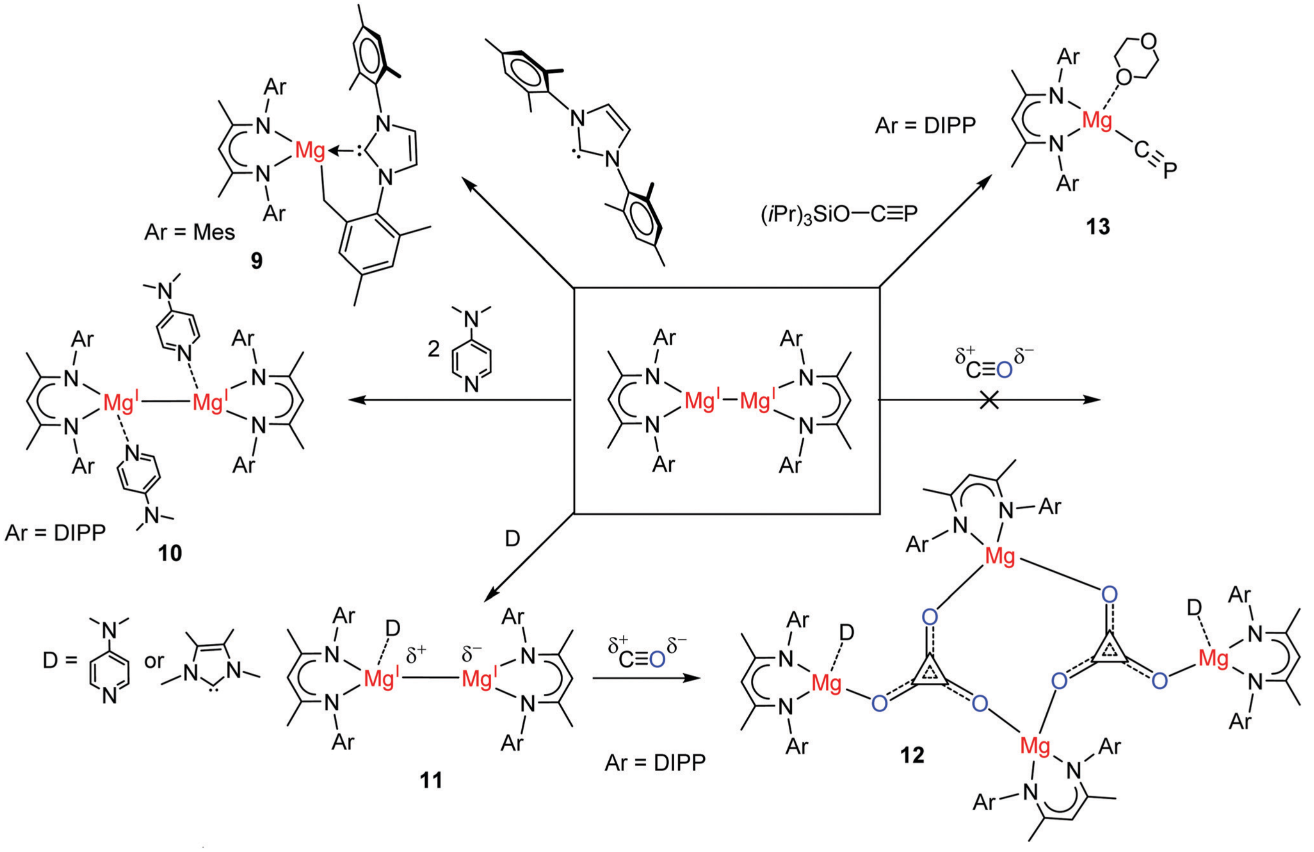


Scheme 2 Examples of low-valent Be^{0} and Be^{I} complexes.

complexes with a Be–Be bonding motive should be even more stable than complexes with Mg–Mg bonds,[2,5] the Be–Be bond is still unknown. However, selective oxidation of **5** with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) gave the first example of a paramagnetic Be^{I} complex featuring the radical cation Be^{I}(CAAC)$_2^{+}$ (**6**, Scheme 2).[34] Theoretical investigations of this unique Be^{I} radical cation indicate an unpaired electron with a considerable amount of the spin density localized on the Be atom. In this context, very recently Braunschweig and coworkers synthesized and characterized a neutral Be^{I} radical (**7**, Scheme 2).[35] This first example of a stable neutral s-block radical complex is NMR-silent and the calculated spin density at Be is significantly lower than that for radical cation **6**. In 2019, Jones and coworkers described the syntheses of first structurally characterized compounds with unsupported Be–Al bonds (**8**, Scheme 2).[36] Based on the very similar electronegativity of Be (χ = 1.57) and Al (χ = 1.61)[33] and analysis of the atomic charges by NPA, these compounds may also be considered as 'quasi'-Be(I) species.[37]

Recent developments in low-valent Mg chemistry

While the group of Mg^{I}–Mg^{I} bonded compounds is steadily growing, recent years have seen increased interest in the preparation of hitherto unknown stable monomeric Mg^{I} radicals.[30] Towards this end, addition of strong Lewis bases to Mg^{I}–Mg^{I} compounds has led to a considerable elongation of the Mg–Mg bond by more than 0.2 Å but cleavage was never observed.[6,38] Interestingly, it was calculated that the Mg–Mg bond distance is more affected by the sterics than by the electronics of the utilized Lewis base.[38] That said, while reaction of Mg^{I} complexes with moderately bulky NHCs gave the anticipated Mg bond elongation, addition of sterically hindered NHCs leads to C–H bond activation at the NHC (**9**, Scheme 3). This may be attributed to generation of a highly reactive transient intermediate (${}^{\mathrm{DIPP}}$BDI)Mg$^{\bullet}$ radical species (${}^{\mathrm{DIPP}}$BDI = HC{C(Me)N[2,6-(*i*Pr)-phenyl]}$_2$).[39] The longest Mg–Mg distance so far was reported for the strong donor complex [(${}^{\mathrm{DIPP}}$BDI)Mg(DMAP)]$_2$ (**10**, 3.196(1) Å; DMAP = 4-dimethylaminopyridine, Scheme 3), but no Mg bond cleavage to yield a Mg radical species was observed.[38] Although Mg–Mg bond lengthening is expected to increase the reactivity of these low-valent Mg^{I} compounds, the coordinative saturation of the Mg centers in the adducts causes the opposite.[40] To get around this problem, Jones and coworkers prepared related 1 : 1 Lewis base adducts (${}^{\mathrm{Ar}}$BDI)Mg(D)-(${}^{\mathrm{Ar}}$BDI)Mg (D = Donor). These asymmetric complexes show similarly elongated Mg–Mg bonds but feature four- and three-coordinated Mg centers, the latter enabling coordination of reducible substrates (**11**, Scheme 3).[40,41] The one-sided donor in these so-called "activated" Mg^{I} compounds polarizes the Mg–Mg bond electron density towards the three coordinated Mg center, increasing its nucleophilicity. Although rapid "hopping" of the Lewis base between the two magnesium centers was observed, the reactivity of the polarized Mg–Mg was significantly increased. While symmetric [(${}^{\mathrm{Ar}}$BDI)Mg]$_2$ or [(${}^{\mathrm{Ar}}$BDI)Mg(D)]$_2$ are inert toward a reaction with carbon monoxide (CO), unsymmetrical "activated" adducts can reductively dimerize or trimerize CO to yield magnesium–ethenediolate or –deltate complexes (**12**, Scheme 3), respectively. This is in agreement with theoretical calculations which corroborate a nucleophilic attack of the

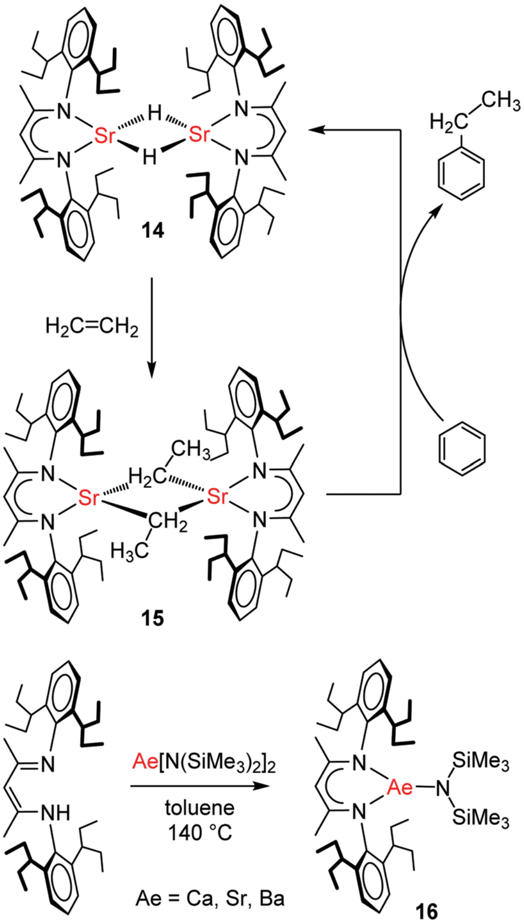


Scheme 3 Reactivity of Mg^I compounds with different Lewis bases, CO and $iPr_3SiOC{\equiv}P$ (DIPP = 2,6-(*i*Pr)-phenyl; Mes = 1,3,5 trimethylphenyl).

three-coordinate magnesium center at one of the π*-orbitals of CO at the beginning of the reaction. Recently, even a reductive hexamerization of CO to benzenehexolate Mg complexes has been reported using $[(^{Ar}BDI)Mg]_2$ (Ar = Xyl, Mes) in cooperation with $Mo(CO)_6$ under a CO atmosphere.[42] Noteworthy, reduction of $iPr_3SiOC{\equiv}P$ with $[(^{DIPP}BDI)Mg]_2$ gave access to a Mg–cyaphido complex, containing a cyaphide anion at the Mg center (**13**). This is the first example for a cyaphide transfer reagent that exhibits Grignard-like reactivity, enabling the introduction of the cyaphide anion to different metals by a simple salt-metathesis route.[43]

While previous attempts to obtain a stable Mg^I radical have aimed to cleave the Mg–Mg bond by addition of strong donor molecules, we and others have tried to suppress Mg–Mg bond formation by reduction of superbulky Mg^{II} halides of the form LMgX (L = superbulky spectator ligand; X = halide).[30] In 2019, we developed a superbulky version of the ubiquitously used β-diketiminate ligand ^{DIPP}BDI by replacing the *i*Pr groups for 3-pentyl groups and abbreviated the ligand as $^{DIPeP}BDI$ (HC{C(Me)N[2,6-(3-pentyl)-phenyl]}₂).[44] This BDI ligand was found to be unsurpassed in its ability to control Schlenk equilibria for $(^{DIPeP}BDI)AeR$ complexes of the larger Ae metals Sr and Ba (**14**, **15** and **16**, Scheme 4).[45,46]

This property is directly related to the large $Et_2(H)C$-substituents in which the Et groups not only act as arms that saturate the Ae metal coordination sphere by anagostic Ae···Et interactions but also greatly improve the solubility of its complexes (in most cases good solubility in pentane is observed). The $^{DIPeP}BDI$ ligand was successfully used in the synthesis of highly nucleophilic Sr hydride and alkyl complexes, that mediate the nucleophilic aromatic substitution at benzene under ambient conditions (Scheme 4).[45] The big advantages of the β-diketiminate ligand with bulky DIPeP substituents are not only increased steric protection and solubility but also its inertness towards highly reactive groups like Sr–Et. The $^{DIPeP}BDI$ ligand is therefore a potential candidate for stabilization of the open-shell Mg radical: $(^{DIPeP}BDI)Mg^{\bullet}$. However, reduction of the magnesium iodide precursor $(^{DIPeP}BDI)MgI{\cdot}(Et_2O)_n$ (*n* = 0 or 1, **17**, Scheme 5a) with sodium gave the dinuclear complex $[(^{DIPeP}BDI)Mg]_2$ (**18**, Scheme 5a), featuring an exceptionally long Mg–Mg bond of 3.0513(8) Å (*cf.* Mg–Mg in $[(^{DIPP}BDI)Mg]_2$: 2.8457(8) Å, Bragg's metal radii[47] of Mg: 1.42 Å).[44] Attempts to break this bond by addition of Lewis bases to a benzene solution of **18** were unsuccessful (several species were observed in ^1H NMR) but color change from yellow to deep red seemed indicative for bond elongation. In an attempt to trap a potential radical species by addition of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) prior to reduction of **17** with Na, deep red colored crystals of $[(^{DIPeP}BDI)Mg(C_6H_6)Mg(^{DIPeP}BDI)]$ (**19**, Scheme 5a) were isolated. The crystal structure shows an anti-aromatic $(C_6H_6)^{2-}$ anion sandwiched between two Mg^{2+} cations and is best described as a $(^{DIPeP}BDI)Mg$–norbornadiene

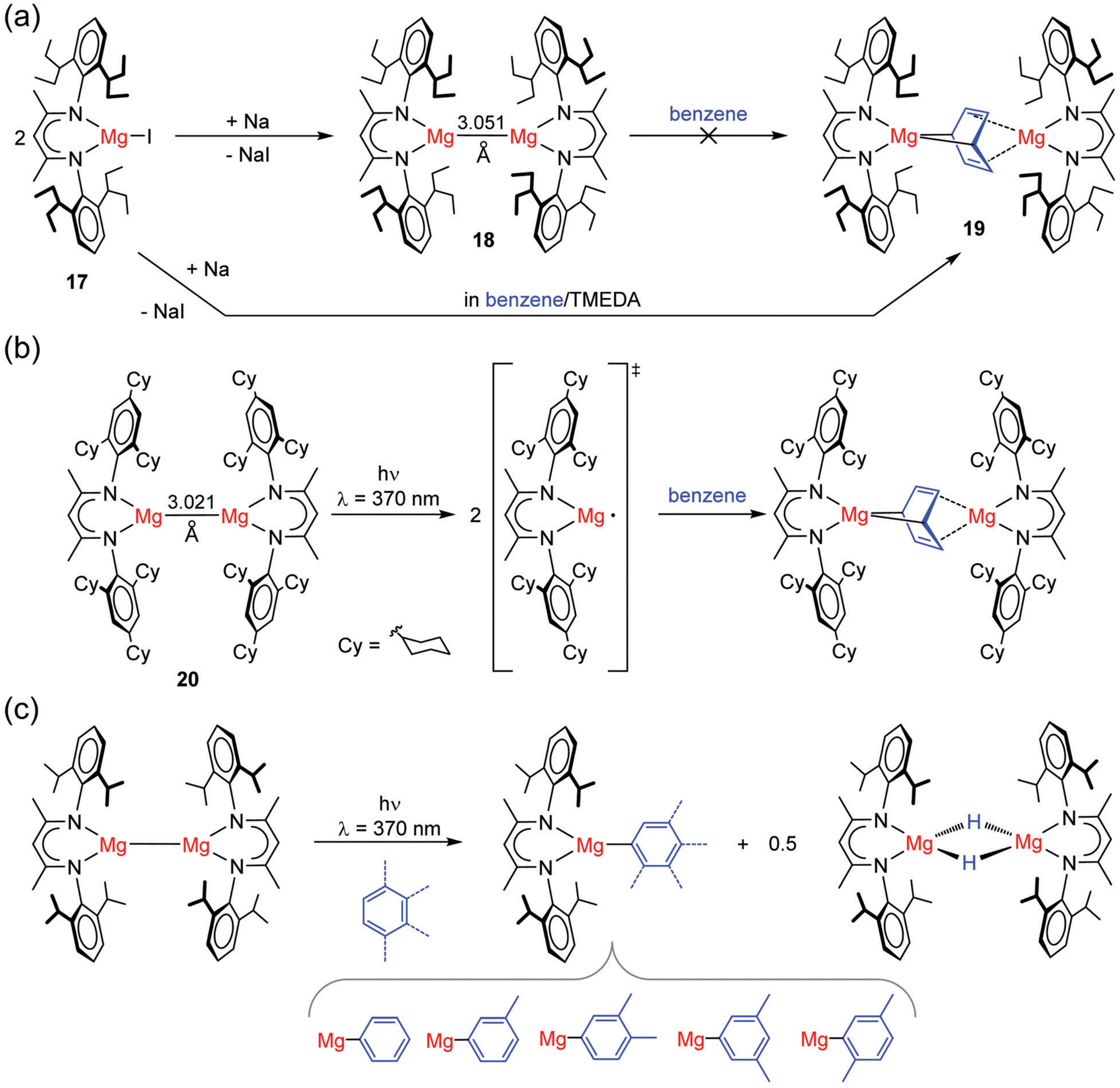


Scheme 4 Examples of reactive heavier Ae metal complexes stabilized by ^{DIPeP}BDI.

anion interacting with a (^{DIPeP}BDI)Mg cation.[44] Addition of THF gave the THF-adduct of **19** in which the $(C_6H_6)^{2-}$ anion is nearly flat. The considerable steric demand of the ^{DIPeP}BDI ligand proved to be beneficial for the formation of the benzene dianion. While for the latter ligand the $(C_6H_6)^{2-}$ complex **19** was the major product, the somewhat smaller ^{DIPP}BDI ligand gave only product mixtures containing [(^{DIPP}BDI)Mg(C_6H_6)Mg(^{DIPP}BDI)]. Using an even less sterically hindered ^{Mes}BDI ligand, the $(C_6H_6)^{2-}$ complex could not be observed at all (Mes = 2,4,6-$Me_3C_6H_2$). It was concluded that bulky ligands, such as ^{DIPeP}BDI, prevent the dimerisation of the Mg^{I} radical. This highly reactive intermediate then reduces the benzene solvent and subsequent coupling with a second Mg^{I} radical gave the $(C_6H_6)^{2-}$ complex. In support of this theory is the most recent observation that similar reduction of benzene solvent is observed when $[(^{TCHP}BDI)Mg]_2$ (**20**, Scheme 5b), with the superbulky ^{TCHP}BDI ligand (TCHP =2,4,6-tricyclohexylphenyl), was irradiated with blue or UV-light.[48] In addition, irradiation of toluene or xylene solutions of $[(^{DIPP}BDI)Mg]_2$ gave completely regio- and chemo-selective C–H bond activations (Scheme 5c). Accordingly, heating a toluene solution of **19** gave a clean C–H bond activation at the benzene ring.[44] Computational studies suggest the reaction to proceed *via* photochemically generated Mg^{I} radicals.[48] Due to the high reduction potential of benzene, **19** is strongly reducing and reductively cleaves H_2 or the C–F bond in C_6H_5F at elevated temperatures. However, with *t*BuOH it did not react as a two-electron supply but as a classical Brønsted base, producing a mixture of 1,4- and 1,3-cyclohexadiene. Since the ^{DIPeP}BDI ligand was not bulky enough to stabilize the (^{DIPeP}BDI)Mg$^{\bullet}$ species and prevent Mg–Mg bond formation, the even bulkier ligand ^{DIPeP}BDI* (HC{C(*t*Bu)N[2,6-(3-pentyl)-phenyl]}$_2$) was introduced. This ligand carries bulky *t*Bu groups in the ligands backbone. Although ^{DIPeP}BDI* is considerably bulkier than ^{DIPeP}BDI, reduction of (^{DIPeP}BDI*)MgI (**21**, Scheme 6) with potassium gave again a dinuclear Mg^{I} complex (**22**, Scheme 6).[49] Formation of the Mg–Mg bond is enabled by cleavage of one of the Mg–N bonds which implies that the Mg–Mg bond is stronger than the Mg–N bond. It is therefore questionable whether open-shell (BDI)Mg$^{\bullet}$ radicals can be isolated using superbulky BDI ligands. Theoretical calculations on the asymmetric complex **22**, which contains one two- and one three-coordinate Mg^{I} center, confirm a strongly polarized Mg–Mg bond. Despite polarization of the Mg–Mg bond, preliminary studies so far have not confirmed higher reactivity.

While reduction of **21** with potassium gave **22**, reduction with Na/NaCl (a readily dispersible reducing agent recently introduced by the Jones group)[50] led to overreduction and formation of the formally Mg^{0} species: [(^{DIPeP}BDI*)Mg^{-}]Na^{+} (**23**, Scheme 6).[51] Formation of this complex, which crystallizes as dimer, demonstrates that the open-shell (BDI)Mg$^{\bullet}$ easily picks up a second electron to form a closed shell (BDI)Mg^{-} anion (Fig. 1). Since the electronegativity of Na is lower than that of Mg, the Mg center in **23** has formally a negative charge and resides in the formal oxidation state zero. Indeed, DFT calculations on **23** support an unusually high electron density on Mg which is partially transferred to Na: calculated NPA charges for Mg (+0.57) and Na (+0.50) are both positive but abnormally low. The Mg center in **23** reacts either as a nucleophile (*e.g.* in reaction with PhF) or as a strong base (*e.g.* in reaction with H_2) and can also be used as an anion in salt metathesis (*e.g.* the reaction with **21** gave **22** and NaI). Complex **23** could be seen as the Mg analogue of the recently discovered aluminyl potassium complexes, $R_2Al^{-}K^{+}$,[52,53] which show remarkable reactivities[54,55] and generally also crystallize dimeric with bridging alkali metal cations.

In analogy, **23** could be described as a magnesyl sodium complex. The formally negatively charged Mg center in **23** is also a very strong reducing agent. Room temperature decomposition of **23** led to reduction of Na^{+} to metallic Na^{0} and crystals of a complex with a Mg_3 core could be isolated (**24**, Scheme 6). DFT calculations are conform with the oxidation state assignment Mg^{I}–Mg^{0}–Mg^{I}. This Mg_3 cluster reacts like atomic Mg^{0} and could be seen as the smallest possible piece of magnesium metal that is soluble in organic solvents. Although mixed-valence Mg^{0}/Mg^{I} complexes have been detected by mass spectrometry,[56–58] complex **24** is the first well-defined multimetallic low-valent Mg complex. In reactions with *n*BuI, the Grignard reagent *n*BuMgI was formed,



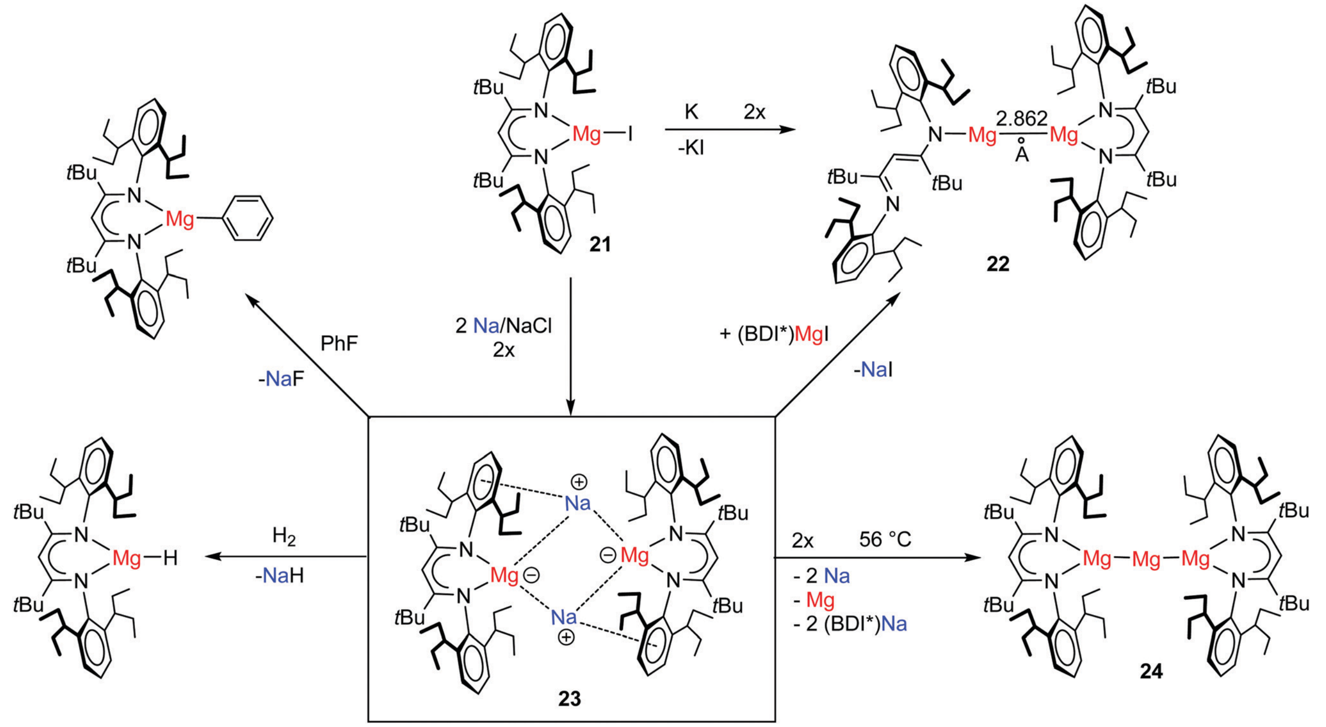
Scheme 5 Reduction of arene substrates at transient Mg^I radicals and UV-light enabled selective C–H bond activation.

indicating that low-valent magnesium clusters like **24** may be transient intermediates during Grignard formation. The structure of **24** may be representative for so-called ''Cluster-Grignard's'' (RMg_nX) which have been proposed to be early intermediates in the Grignard synthesis.[56,57]

Recent developments in low-valent heavier alkaline-earth metal chemistry

Whereas low-valent Mg^I chemistry has developed rapidly, low-valent Ca chemistry is only slowly emerging. Theoretical calculations highlight the difficulty of isolating molecular Ca^I complexes[2,5] and it is not surprising that so far only one low-valent example of Ca has been reported (Scheme 1a, **4**).[27] Despite many attempts, Ca–Ca bonding was never achieved and it has been demonstrated that common spectator ligands, like ^{DIPP}BDI, are not able to kinetically stabilize an intermediate $[(^{DIPP}BDI)Ca]_2$ complex against the thermodynamically favored disproportionation to Ca^0 and $Ca^{II}(^{DIPP}BDI)_2$.[14]

Considering its increased steric protection, solubility and inertness towards highly reactive groups, we wondered whether our ^{DIPeP}BDI ligand would be able to stabilize a Ca^I compound. Attempts to access first Ca^I complexes of type $[(^{DIPeP}BDI)Ca]_2$ led to fast reduction of the benzene solvent (Scheme 7) to give a dinuclear complex with an anti-aromatic, non-planar, $C_6H_6^{2-}$ anion that bridges the Ca^{II} centers (**25-C_6H_6**, Fig. 2a).[59] Changing the solvent to toluene or *p*-xylene, both electron-rich alkylated arenes which are much harder to reduce, similarly led to reduction of the solvent and formation of



Scheme 6 Synthesis of polarized Mg^I and Mg^0 complexes with the superbulky $^{DIPeP}BDI*$. Reactivity of the anionic Mg^0 and trinuclear Mg^0 complexes.

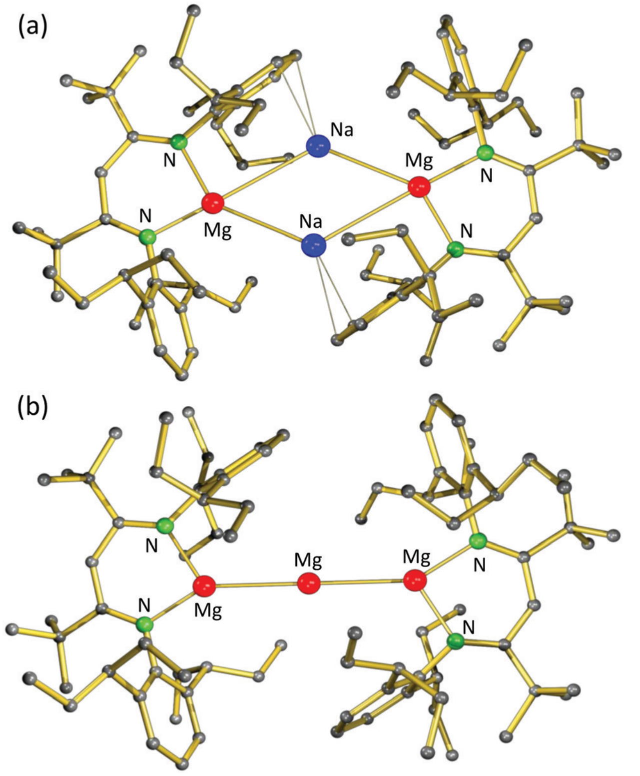
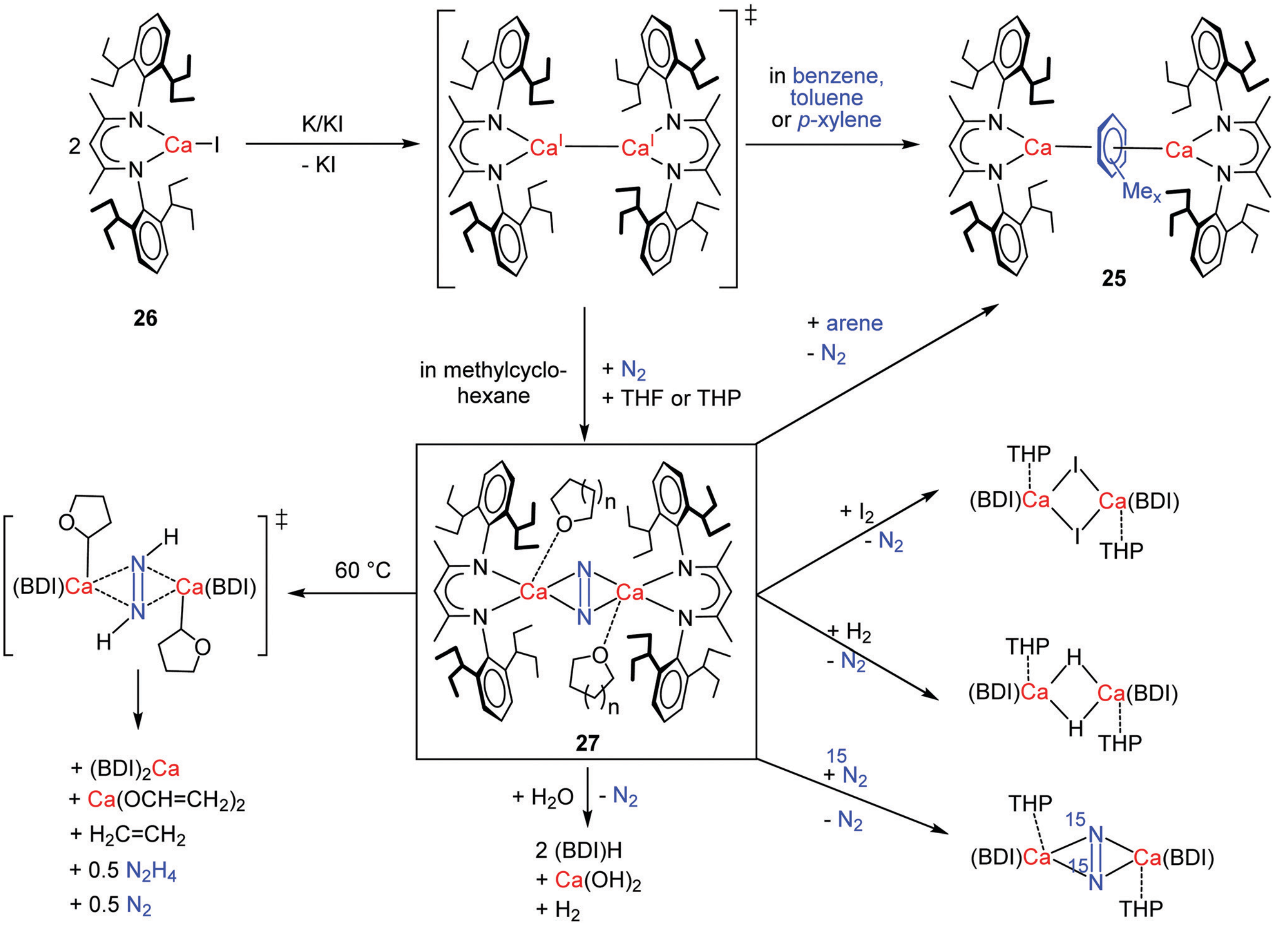


Fig. 1 Crystal structures of (a) $[(^{DIPeP}BDI*)Mg^-]Na^+$ (**23**) and (b) $(^{DIPeP}BDI*)MgMgMg(^{DIPeP}BDI*)$ (**24**).

$C_6(Me)H_5^{2-}$ and $C_6Me_2H_4^{2-}$ anions. Like Westerhausen's inverse sandwich complex **4**, these compounds form intensely black-colored crystals. Whereas **25-C_6H_6** is NMR silent and paramagnetic (probably due to unpaired electrons in the $C_6H_6^{2-}$ anion), complexes with reduced toluene or *p*-xylene are diamagnetic. Comprehensive future studies will certainly reveal further fascinating aspects of these inverse sandwiches. The facile reduction of stable, electron-rich, aromatic solvents is a forebode of the extreme reducing properties of *in situ* generated Ca^I complexes. Isolation of low-valent Ca complexes therefore requires inert alkane solvents. The highly flexible 3-pentyl groups in the $^{DIPeP}BDI$ ligand increase the solubilities of its complexes and are in this respect highly advantageous. The Ca iodide precursor $(^{DIPeP}BDI)CaI$ (**26**, Scheme 7) is very well soluble in various alkanes. Performing its reduction in methylcyclohexane instead of aromatic solvents gave complex **27** (Scheme 7) which could be characterized as a dinuclear Ca^{II} complex with a side-on bridging N_2^{2-} anion. This demonstrates that intermediate Ca^I complexes are even able to reduce N_2 which ironically was used during synthesis as a protective gas. The formation of **27** represents the first example for molecular nitrogen fixation with an early main group metal. Due to poor crystallization of the Lewis base-free complex, **27** was structurally characterized as its THF and THP (tetrahydropyran) adduct, the latter being more thermally stable and suitable for reactivity studies. Both, the THF and THP adducts, crystallize as centrosymmetric dimers with side-on bridging N_2^{2-} moieties (Fig. 2b). The N–N bond distances (average: 1.265(3) Å) are considerably longer than that in N_2 (1.098 Å) and consistent with a typical N=N double bond, indicating strong activation of N_2.

Although the bridging N_2 moiety in **27** should be regarded as an electron-rich N_2^{2-} anion, it was hard to functionalize this fragment. Addition of H_2, I_2 or protic reagents like H_2O or ROH



Scheme 7 Attempts to isolate a $Ca^I–Ca^I$ complex led to reduction of the aromatic solvent or N_2. Initial reactivity studies of CaN_2 complexes are shown.

led in all cases to release of gaseous N_2. This means that N_2^{2-} did not react as a nucleophile or base but rather acts as an electron reservoir that delivers 2e for reduction. The N_2-bridged Ca complexes could therefore be seen as a synthon for our target Ca^I complex: $[(^{DIPeP}BDI)Ca]_2$. Noteworthy is the fact that the N_2 fragment in **27** exchanges with isotope-labeled $^{15}N_2$, indicating that there may be an equilibrium between **27** and $[(^{DIPeP}BDI)Ca]_2$. As an exception to the redox reactivity of **27**, the THF-solvated complex decomposed at 60 °C by deprotonation of the THF α-CH_2 group, a reaction typical for s-block metal complexes. This gave N_2H_2 which disproportionated to N_2H_4 and N_2. The THP complex is more stable but at elevated temperatures unselective decomposition was observed.

Comprehensive theoretical studies demonstrated that partially filled d-orbitals on electron-rich Ca^I could be responsible for the fast and smooth N_2 reduction which proceeds even at temperatures as low as −60 °C. Energy decomposition with natural orbitals for chemical valence analysis (EDA-NOCV) showed that the interaction between the hypothetical Ca^I complex $[(^{DIPeP}BDI)Ca]_2$ and N_2 consists of strong π-backdonation from populated Ca^I d-orbitals to N_2 π* orbitals. This observation fuels the current discussion on the relevance of d-orbitals for the Ca–Sr–Ba triad.

Relevance of d-orbital participation for the heavier alkaline-earth metals

From a historical point of view, the unusually low-lying d-orbitals on Ca have been mentioned already at a very early stage. In 1937 Manning and Krutter ascribed the conductivity in metallic Ca *"to be due to an overlap between the lowest "s" band and the "d" band"*.[60] Wright and Weller studied the activity of Ca and Ba metal in the catalytic hydrogenation of ethylene and came to the conclusion that there is an interplay between Ca hydride species and ethylene activated on the surface of metallic Ca or Ba. This *"dual site"* mechanism was explained with *"some overlap of s-, p- and d-bands"*.[61] Also Pyykkö has been advocating considerable d-orbital character in the bonding to the heavier Ae metals and noticed that this increases from Ca to Sr and is especially relevant for Ba but decreases again from Ba to Ra due to relativistic effects.[62] The importance of d-orbitals in the chemistry of Ba led to its promotion to an honorary d-block metal.[63] Also Kaupp and Schleyer made early contributions to the field. In 1992, the unusually bent geometries of the metallocenes Cp^*_2Ae and the gas phase halogenides AeX_2 (Ae = Ca, Sr, Ba) were explained in part by d-orbital participation.[64–66]

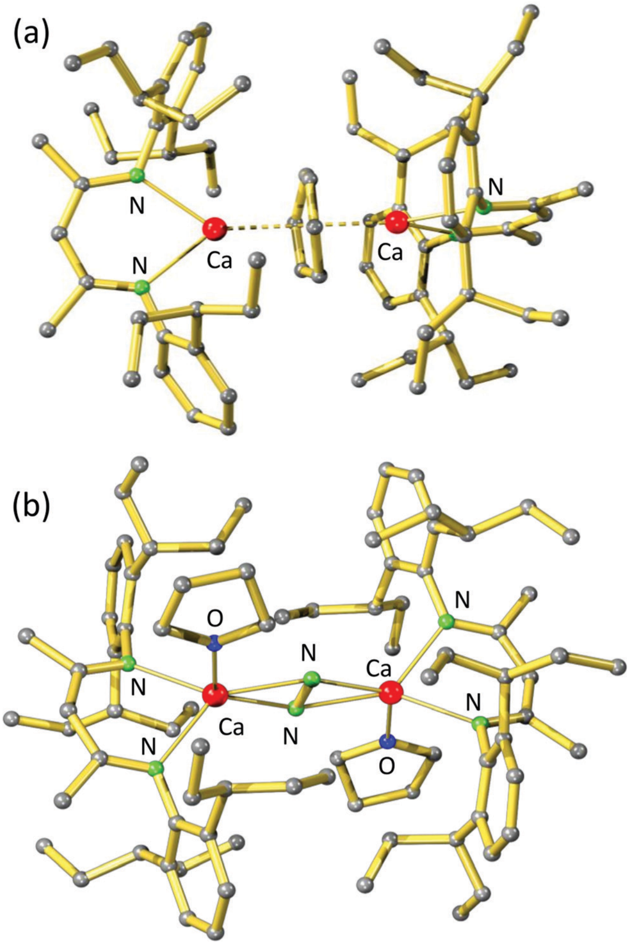


Fig. 2 Crystal structures of (a) [(^{DIPeP}BDI)Ca]$_2$(C$_6$H$_6$) (**25**) and (b) [(^{DIPeP}BDI)CaTHF]$_2$(N$_2$) (**27**).

The recent isolation of transition metal-like Ae^0 complexes such as Ae(CO)$_8$,[67] Ae(N$_2$)$_8$[68] and Ae(C$_6$H$_6$)$_3$[69] (Ae = Ca, Sr and Ba) in a matrix at 4 K refueled the controversial discussion about d-orbital contribution for s-block metals.[70–75] It is generally accepted that valence electrons for Ca, Sr and Ba reside in the corresponding s-orbitals. However, for Ae metals in the low oxidation state +I or 0, the penalty for promotion of electrons in d-orbitals is not that high and can be compensated by strong bonding interactions that are enabled by the presence of partially filled d-orbitals. This is especially true for the heavier metal Ba. The observed strong red shift of the CO vibrations in Ba(CO)$_8$, embedded in a Ne/CO-matrix, supports backbonding interactions between the Ba 5d-orbitals and the strong π-acceptor ligand CO. On a similar note, a large red shift in N$_2$ stretching frequencies was also observed in octa-coordinated Ae(N$_2$)$_8$ complexes, which is assigned to Ae(d$_\pi$) → N$_2$(π*) backdonation. Comparable backdonation in Ae(C$_6$H$_6$)$_3$ complexes indicate electron transfer from the occupied (n − 1)d-orbitals of Ae into vacant π* molecular orbitals (MO's) of the benzene ligands (n = principal quantum number: Ca 4, Sr 5, Ba 6). These interactions are supplemented by weak donation from filled π-orbitals of the arene into empty (n − 1)d-orbitals. Comprehensive computational analyses provide further insight in the role of d-orbitals in heavier Ae metal chemistry.[76–78] While the lighter atoms Be and Mg draw on (n)s and (n)p valence-orbitals, their heavier congeners Ca, Sr and Ba comprise (n)s and (n − 1)d valence-orbitals, as they are lower in energy than the (n)p-orbitals. In addition, mixing of (n)s- with (n − 1)d-orbitals leads to hybrid orbitals for covalent σ-bonding, while π-bonds of the heavier Ae use (n − 1)d(π)-orbitals. In this context it was claimed that Ca, Sr, Ba may exhibit "*the full bonding scenario of transition metals*" with reactivities closely related to those for the electropositive group 3 and 4 metals.[69] This awareness led most recently to the proposal to extend the d-block in the periodic table with the metals Ca, Sr, Ba and Ra.[78,79]

At this point it should be noticed that most of the experimentally verified Ae metal complexes are based on fully oxidized Ae^{2+} cations in which all valence orbitals are empty. In this case orbital interactions between Ae^{2+} and ligands are limited to weak donations into vacant Ae^{2+} orbitals which, considering the highly electropositive nature of Ae metals and the high ionicity of the ligand–Ae^{2+} bond, is only a small contribution. Examples for such ligand–Ae^{2+}(d) interactions can be found in calculational studies on (^{DIPP}BDI)Ca$^+$·(C$_6$H$_6$),[80] cationic Ca and Sr hydride clusters,[81,82] or larger neutral Ca hydride clusters.[77,83] Although there is some theoretical evidence for Ae d-orbital participation, it is not straightforward to find experimental proof. We contributed to this discussion by the experimental verification of ferrocenyl-bridged Ae metal amide complexes (Fig. 3).[84] Crystal structures obtained for the series Ae = Mg, Ca, Sr and Ba show that although Ca^{2+}, Sr^{2+} and Ba^{2+} are much larger ions than Mg^{2+}, Fe–Ca and Fe–Sr contacts are much shorter and the Fe–Ba distance is comparable to the non-bonding Fe–Mg distance.

Intramolecular Fe···Ae bonding for Ca, Sr and Ba was further supported by a characteristic tilting of the Cp rings, which increases with metal size, and causes ferrocene frontier orbitals of considerable d-character to protrude outwards. Atoms-In-Molecules (AIM) and EDA-NOCV methods confirm genuine Fe···Ae bonds for Ca, Sr and Ba which involve vacant d-orbitals on the Ae atoms and partially filled d-orbitals on Fe. Such d–d dative bonding between Fe and Ae metals is supported by most recent mass spectrometry evidence for hetero-bimetallic CaFe(CO)$_n{}^+$ cations (n = 5–12) in the gas phase.[85] The cation CaFe(CO)$_{10}{}^+$ can be best described as a Fe(CO)$_4{}^-$

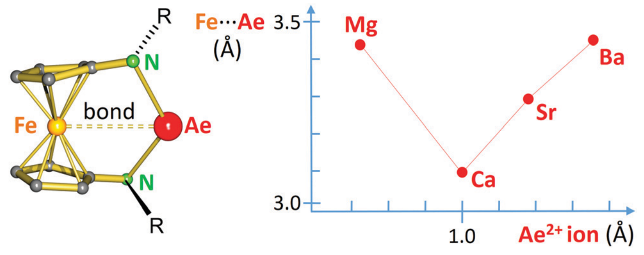


Fig. 3 Short Fe···Ae^{2+} contacts in ferrocenyl-bridged Ae metal amide complexes.[84]

fragment interacting with a $Ca(CO)_6^{2+}$ fragment and is held together by a Fe → Ca d–d dative bond.

Whereas the mainly empty d-orbitals on heavier Ae^{2+} cations only have minor influences on ligand bonding and activation, the much higher electron density on Ae^{I} or Ae^{0} nuclei can lead to considerable substrate activation by (Ae)d → (substrate)π* donation according to the Dewar–Chatt–Duncanson backbonding model. The very low electronegativities of the heavier Ae metals result in much more pronounced backbonding as typically observed for the nobler transition metals. Complexes like $Ba^0(C_6H_6)_3$ should be considered as Ba^{2+} nuclei interacting with partially negatively charged $C_6H_6^{\delta-}$ ions in which the C–C bond distances are considerably elongated.[69] Similarly, attempts to isolate a Ca^{I} complex led to N_2 activation and formation of **27** which should be described as N_2^{2-} sandwiched between Ca^{2+} cations.[59] EDA-NOCV studies show that the interaction between two $(^{DIPeP}BDI)Ca^+$ and a N_2^{2-} fragment, which is the best description for **27**, is mainly electrostatic and features only minor covalent contributions (*circa* 30%) with some d-orbital involvement. Interactions between two neutral $(^{DIPeP}BDI)Ca^{I}$ and a N_2 fragment are representative for the process of formation of **27** and display major covalency (*circa* 80%) and d-orbital occupation. The superb electron-donating characteristics of a highly electropositive nucleus like Ca^{I} may explain why N_2 can be reduced instantaneously at very low temperatures. The very high reactivity of heavier Ae^{I} or Ae^{0} nuclei makes their isolation a challenging tour-de-force.

Since substrate activation according to Dewar–Chatt–Duncanson needs at least partially filled d-orbitals, this type of reactivity is only relevant for low-valent Ca, Sr or Ba complexes. This being said, also regular Ae^{II} complexes possess some degree of covalency. Covalent contributions in the Ae–Me bonds in $AeMe_2$ have been calculated as: Ca 11%, Sr 9%, Ba 6%.[86] Although small, this may allow for some extent of activation and could explain why the heavier Ae metal are privileged in alkene hydrogenation catalysis.[86–93]

Conclusions and outlook

Starting in 2007, low oxidation state group 2 metal chemistry has come a long way. After more than a decade, dinuclear Mg^{I}–Mg^{I} complexes moved from being trophy-molecules to well-established reducing agents for specialty applications. The current challenge to isolate stable mononuclear Mg^{I} radicals has already delivered fascinating reactivity, *e.g.* facile C–F bond cleavage and selective C–H bond activation in challenging substrates. Attempted cleavage of the Mg^{I}–Mg^{I} bond by addition of Lewis bases gave access to highly polarized, activated Mg^{I} compounds that proved to be successful in small molecule activation, *e.g.* reductive trimerization of CO.

Further reduction of a transient Mg^{I} radical led to isolation of first formal Mg^{0} complexes. The key to their isolation is the design of a superbulky β-diketiminate ligand that is inert to the high reactivity of low-valent Mg and at the same allows complex solubility in the more inert alkane solvents. Zero-valent dimers of the type $[(BDI)MgNa]_2$ are formally regarded to consist of $(BDI)Mg^-$ anions (magnesyl anions) which are bridged by Na^+ cations. The high electron density on these formally anionic Mg nuclei renders these metal centers nucleophilic, completely overturning the general principles of organomagnesium chemistry. While Mg generally occurs in complexes as Mg^{2+} cation, which is a Lewis acidic electrophile accepting electrons, the magnesyl anion reacts as a nucleophile or strong 2e donor. This development opens the field of group 2 metal chemistry with formally negatively charged metal centers which may be exploited in similar fashion as the recently introduced aluminyl anions. Access to the $(BDI)Mg^-$ anion will certainly give impetus to the field of heteronuclear Mg–metal bonding, a theme we actively pursue.

The chemistry of low-valent heavier Ae metals is still limited to one example for a Ca^{I} species (**4**). Although the metal oxidation state in **4** is ambiguous, it is clear that the molecule is strongly reducing. The question is merely where the electrons are located, on the metal or the ligand? Recent attempts to prepare $(BDI)Ca^{I}$–$Ca^{I}(BDI)$ species, stabilized by an extremely bulky β-diketiminate ligand, led to immediate reduction of either the aromatic solvent or the protective N_2 gas. The surprisingly facile activation of N_2 by a Ca^{I} intermediate at low temperature, demonstrates the high reactivity of low-valent heavier Ae metal species. Calculational studies suggest that the origin of N_2 activation lies in d-orbital participation. Although highly controversial, the relevance of d-orbitals in organocalcium complexes with Ca^{2+} metal centers has been discussed previously. In contrast to Ca^{II} centers in common organocalcium compounds, the partially filled d-orbitals in electron-rich low-valent Ca^{I} should be considered much more important for molecule activation. Their ability to donate electrons in antibonding π* orbitals, combined with Ca's strongly electropositive nature, makes Ca^{I} a very attractive nucleus for molecule activation. Although highly reductive Ca^{I}–Ca^{I} dimers are so far elusive, the recently isolated $(BDI)Ca(N_2)Ca(BDI)$ complex generally reacts like $(BDI)Ca^{I}$–$Ca^{I}(BDI)$. In the vast majority of reactions it acts as 2e donor and could therefore be considered a Ca^{I} synthon. Future research embraces the discovery of the complete potential of this powerful reductant in specialty applications as well as syntheses of similar complexes with the even more reducing Sr^{I} and Ba^{I} metals. Also the synthesis of complexes with heavier Ae^{0} nuclei is a highly challenging, but likely also highly rewarding, target.

Thinking along these lines, the role of CaO as additive for the iron catalyst used in the large-scale Haber–Bosch process may be more than just that of a structural modifier.[94] It is maybe also not coincidence that an earlier method for nitrogen fixation, the Frank–Caro process which converts acetylide and nitrogen in cyanamide, is also based on Ca: $CaC_2 + N_2 \rightarrow CaCN_2 + C$. Further research on the heavier Ae metals, especially in low-valent states, will shine light on the future of these metals in molecule activation.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 I. Resa, E. Carmona, E. Gutierrez-Puebla and A. Monge, *Science*, 2004, **305**, 1136–1138.
2 Y. Xie, H. F. Schaefer and E. D. Jemmis, *Chem. Phys. Lett.*, 2005, **402**, 414–421.
3 A. Velazquez, I. Ferna, G. Frenking and G. Merino, *Organometallics*, 2007, **26**, 4731–4736.
4 S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754–1758.
5 S. Krieck, L. Yu, M. Reiher and M. Westerhausen, *Eur. J. Inorg. Chem.*, 2010, 197–216.
6 A. Stasch and C. Jones, *Dalton Trans.*, 2011, **40**, 5659–5672.
7 C. Jones, *Nat. Rev. Chem.*, 2017, **1**, 0059.
8 S. Schulz, *Beryllium and Magnesium—Synthesis, Structure, Reactivity and Application*, Elsevier Inc., 2019.
9 J. A. Platts, J. Overgaard, C. Jones, B. B. Iversen and A. Stasch, *J. Phys. Chem. A*, 2011, **115**, 194–200.
10 L. C. Wu, C. Jones, A. Stasch, J. A. Platts and J. Overgaard, *Eur. J. Inorg. Chem.*, 2014, 5536–5540.
11 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.
12 J. Emsley, *The Elements*, Clarendon, Oxford, 1991.
13 S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna and A. Stasch, *Angew. Chem., Int. Ed.*, 2009, **48**, 2973–2977.
14 S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards and G. J. McIntyre, *Chem. – Eur. J.*, 2010, **16**, 938–955.
15 M. Ma, A. Stasch and C. Jones, *Chem. – Eur. J.*, 2012, **18**, 10669–10676.
16 A. Stasch, *Angew. Chem., Int. Ed.*, 2014, **53**, 10200–10203.
17 J. Zhou, L. L. Liu, L. L. Cao and D. W. Stephan, *Chem. – Eur. J.*, 2018, **24**, 8589–8595.
18 M. Garçon, A. J. P. White and M. R. Crimmin, *Chem. Commun.*, 2018, **54**, 12326–12328.
19 C. Bakewell, A. J. P. White and M. R. Crimmin, *J. Am. Chem. Soc.*, 2016, **138**, 12763–12766.
20 G. Coates, B. J. Ward, C. Bakewell, A. J. P. White and M. R. Crimmin, *Chem. – Eur. J.*, 2018, **24**, 16282–16286.
21 C. Bakewell, B. J. Ward, A. J. P. White and M. R. Crimmin, *Chem. Sci.*, 2018, **9**, 2348–2356.
22 R. Lalrempuia, A. Stasch and C. Jones, *Chem. Sci.*, 2013, **4**, 4383–4388.
23 A. J. Boutland, I. Pernik, A. Stasch and C. Jones, *Chem. – Eur. J.*, 2015, **21**, 15749–15758.
24 A. J. Boutland, A. Carroll, C. Alvarez Lamsfus, A. Stasch, L. Maron and C. Jones, *J. Am. Chem. Soc.*, 2017, **139**, 18190–18193.
25 D. Dange, A. R. Gair, D. D. L. Jones, M. Juckel, S. Aldridge and C. Jones, *Chem. Sci.*, 2019, **10**, 3208–3216.
26 K. Yuvaraj, I. Douair, L. Maron and C. Jones, *Chem. – Eur. J.*, 2020, **26**, 14665–14670.
27 S. Krieck, H. Görls, L. Yu, M. Reiher and M. Westerhausen, *J. Am. Chem. Soc.*, 2009, **131**, 2977–2985.
28 S. Krieck, H. Görls and M. Westerhausen, *J. Am. Chem. Soc.*, 2010, **132**, 12492–12501.
29 W. Huang and P. L. Diaconescu, *Dalton Trans.*, 2015, **44**, 15360–15371.
30 C. Jones, *Commun. Chem.*, 2020, **3**, 8–11.
31 D. Naglav, M. R. Buchner, G. Bendt, F. Kraus and S. Schulz, *Angew. Chem., Int. Ed.*, 2016, **55**, 10562–10576.
32 M. Arrowsmith, H. Braunschweig, M. A. Celik, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, T. Kramer, I. Krummenacher, J. Mies, K. Radacki and J. K. Schuster, *Nat. Chem.*, 2016, **8**, 890–894.
33 L. R. Murphy, T. L. Meek, A. Louis Allred and L. C. Alien, *J. Phys. Chem. A*, 2000, **104**, 5867–5871.
34 G. Wang, J. E. Walley, D. A. Dickie, S. Pan, G. Frenking and R. J. Gilliard, *J. Am. Chem. Soc.*, 2020, **142**, 4560–4564.
35 C. Czernetzki, M. Arrowsmith, F. Fantuzzi, A. Gärtner, T. Tröster and I. Krummenacher, *Angew. Chem., Int. Ed.*, 2021, DOI: 10.1002/anie.202108405.
36 A. Paparo, C. D. Smith and C. Jones, *Angew. Chem., Int. Ed.*, 2019, **58**, 11459–11463.
37 A. Paparo, A. J. R. Matthews, C. D. Smith, A. J. Edwards, K. Yuvaraj and C. Jones, *Dalton Trans.*, 2021, **50**, 7604–7609.
38 S. P. Green, C. Jones and A. Stasch, *Angew. Chem., Int. Ed.*, 2008, **47**, 9079–9083.
39 K. Yuvaraj, A. Carpentier, C. D. Smith, L. Maron and C. Jones, *Inorg. Chem.*, 2021, **60**, 6065–6072.
40 K. Yuvaraj, I. Douair, A. Paparo, L. Maron and C. Jones, *J. Am. Chem. Soc.*, 2019, **141**, 8764–8768.
41 K. Yuvaraj, I. Douair, D. D. L. Jones, L. Maron and C. Jones, *Chem. Sci.*, 2020, **11**, 3516–3522.
42 A. Paparo, K. Yuvaraj, A. J. R. Matthews, I. Douair, L. Maron and C. Jones, *Angew. Chem., Int. Ed.*, 2021, **60**, 630–634.
43 D. W. N. Wilson, S. J. Urwin, E. S. Yang and J. M. Goicoechea, *J. Am. Chem. Soc.*, 2021, **143**, 10367–10373.
44 T. X. Gentner, B. Rösch, G. Ballmann, J. Langer, H. Elsen and S. Harder, *Angew. Chem., Int. Ed.*, 2019, **58**, 607–611.
45 B. Rösch, T. X. Gentner, H. Elsen, C. A. Fischer, J. Langer, M. Wiesinger and S. Harder, *Angew. Chem., Int. Ed.*, 2019, **58**, 5396–5401.
46 T. X. Gentner, B. Rösch, K. Thum, J. Langer, G. Ballmann, J. Pahl, W. A. Donaubauer, F. Hampel and S. Harder, *Organometallics*, 2019, **38**, 2485–2493.
47 J. C. Slater, *J. Chem. Phys.*, 1964, **2**, 3199–3204.
48 D. D. L. Jones, I. Douair, L. Maron and C. Jones, *Angew. Chem., Int. Ed.*, 2021, **60**, 7087–7092.
49 B. Rösch, T. X. Gentner, J. Eyselein, A. Friedrich, J. Langer and S. Harder, *Chem. Commun.*, 2020, **56**, 11402–11405.
50 J. Hicks, M. Juckel, A. Paparo, D. Dange and C. Jones, *Organometallics*, 2018, **37**, 4810–4813.
51 B. Rösch, T. X. Gentner, J. Eyselein, J. Langer, H. Elsen and S. Harder, *Nature*, 2021, **592**, 717–721.
52 J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, *Nature*, 2018, **557**, 92–95.
53 R. J. Schwamm, M. D. Anker, M. Lein and M. P. Coles, *Angew. Chem., Int. Ed.*, 2019, **58**, 1489–1493.
54 K. Hobson, C. J. Carmalt and C. Bakewell, *Chem. Sci.*, 2020, **11**, 6942–6956.
55 J. Hicks, P. Vasko, J. M. Goicoechea and S. Aldridge, *Angew. Chem., Int. Ed.*, 2021, **60**, 1702–1713.
56 Y. Imizu and K. J. Klabunde, *Inorg. Chem.*, 1984, **23**, 3602–3605.
57 L. A. Tjurina, V. V. Smirnov, D. A. Potapov, S. A. Nikolaev, S. E. Esipov and I. P. Beletskaya, *Organometallics*, 2004, **23**, 1349–1351.
58 T. Kruczyński, F. Henke, M. Neumaier, K. H. Bowen and H. Schnöckel, *Chem. Sci.*, 2016, **7**, 1543–1547.
59 B. Rösch, T. X. Gentner, J. Langer, C. Färber, J. Eyselein, L. Zhao, C. Ding, G. Frenking and S. Harder, *Science*, 2021, **371**, 1125–1128.
60 M. F. Manning and H. M. Krutter, *Phys. Rev.*, 1937, **51**, 761–764.
61 L. Wright and S. Weller, *J. Am. Chem. Soc.*, 1954, **76**, 5948–5950.
62 P. Pyykkö, *J. Chem. Soc., Faraday Trans.*, 1978, 1256–1276.
63 L. Gagliardi and P. Pyykkö, *Theor. Chem. Acc.*, 2003, **110**, 205–210.
64 M. Kaupp, P. v. R. Schleyer, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1991, **94**, 1360–1366.
65 M. Kaupp, P. V. R. Schleyer, M. Dolg and H. Stoll, *J. Am. Chem. Soc.*, 1992, **114**, 8202–8208.
66 M. Kaupp, *Angew. Chem.*, 2001, **113**, 3642–3677.
67 X. Wu, L. Zhao, J. Jin, S. Pan, W. Li, X. Jin, G. Wang, M. Zhou and G. Frenking, *Science*, 2019, **365**, 912–916.
68 Q. Wang, S. Pan, S. Lei, J. Jin, G. Deng, G. Wang, L. Zhao, M. Zhou and G. Frenking, *Nat. Commun.*, 2019, **10**, 1–8.
69 Q. Wang, S. Pan, Y. B. Wu, G. Deng, J. H. Bian, G. Wang, L. Zhao, M. Zhou and G. Frenking, *Angew. Chem., Int. Ed.*, 2019, **58**, 17365–17374.
70 D. Koch, Y. Chen, P. Golub and S. Manzhos, *Phys. Chem. Chem. Phys.*, 2019, **21**, 20814–20821.
71 C. R. Landis, R. P. Hughes and F. Weinhold, *Science*, 2019, DOI: 10.1126/science.aay2355.
72 L. Zhao, S. Pan, M. Zhou and G. Frenking, *Science*, 2019, DOI: 10.1126/science.aay5021.
73 S. Pan and G. Frenking, *Phys. Chem. Chem. Phys.*, 2020, **22**, 5377–5379.
74 D. Koch, Y. Chen, P. Golub and S. Manzhos, *Phys. Chem. Chem. Phys.*, 2020, **22**, 5380–5382.

75 B. Huo, R. Sun, B. Jin, L. Hu, J. H. Bian, X. L. Guan, C. Yuan, G. Lu and Y. B. Wu, *Chem. Commun.*, 2021, **57**, 5806–5809.

76 T. Bettens, S. Pan, F. De Proft, G. Frenking and P. Geerlings, *Chem. – Eur. J.*, 2020, **26**, 12785–12793.

77 I. Fernández, N. Holzmann and G. Frenking, *Chem. – Eur. J.*, 2020, **26**, 14194–14210.

78 M. Zhou and G. Frenking, *Acc. Chem. Res.*, 2021, DOI: 10.1021/acs.accounts.1c00277.

79 G. Frenking, I. Fernández, N. Holzmann, S. Pan, I. Krossing and M. Zhou, *JACS Au*, 2021, **1**, 623–645.

80 L. Garcia, M. D. Anker, M. F. Mahon, L. Maron and M. S. Hill, *Dalton Trans.*, 2018, **47**, 12684–12693.

81 D. Mukherjee, T. Höllerhage, V. Leich, T. P. Spaniol, U. Englert, L. Maron and J. Okuda, *J. Am. Chem. Soc.*, 2018, **140**, 3403–3411.

82 D. Schuhknecht, T. P. Spaniol, I. Douair, L. Maron and J. Okuda, *Chem. Commun.*, 2019, **55**, 14837–14839.

83 B. Maitland, M. Wiesinger, J. Langer, G. Ballmann, J. Pahl, H. Elsen, C. Färber and S. Harder, *Angew. Chem., Int. Ed.*, 2017, **56**, 11880–11884.

84 P. Stegner, C. Färber, J. Oetzel, U. Siemeling, M. Wiesinger, J. Langer, S. Pan, N. Holzmann, G. Frenking, U. Albold, B. Sarkar and S. Harder, *Angew. Chem., Int. Ed.*, 2020, **59**, 14615–14620.

85 X. Jin, Y. Bai, Y. Zhou, G. Wang, L. Zhao, M. Zhou and G. Frenking, *Angew. Chem., Int. Ed.*, 2021, **60**, 13865–13870.

86 C. Lambert and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1129–1140.

87 J. Spielmann, F. Buch and S. Harder, *Angew. Chem., Int. Ed.*, 2008, **47**, 9434–9438.

88 D. Schuhknecht, C. Lhotzky, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem., Int. Ed.*, 2017, **56**, 12367–12371.

89 H. Bauer, M. Alonso, C. Fischer, B. Rösch, H. Elsen and S. Harder, *Angew. Chem., Int. Ed.*, 2018, **57**, 15177–15182.

90 A. S. S. Wilson, C. Dinoi, M. S. Hill, M. F. Mahon and L. Maron, *Angew. Chem., Int. Ed.*, 2018, **57**, 15500–15504.

91 J. Martin, C. Knüpfer, J. Eyselein, C. Färber, S. Grams, J. Langer, K. Thum, M. Wiesinger and S. Harder, *Angew. Chem., Int. Ed.*, 2020, **59**, 9102–9112.

92 X. Shi, C. Hou, L. Zhao, P. Deng and J. Cheng, *Chem. Commun.*, 2020, **56**, 5162–5165.

93 P. Stegner, C. Färber, U. Zenneck, C. Knüpfer, J. Eyselein, M. Wiesinger and S. Harder, *Angew. Chem., Int. Ed.*, 2021, **60**, 4252–4258.

94 M. C. Tsai, U. Ship, I. C. Bassignana, J. Küppers and G. Ertl, *Surf. Sci.*, 1985, **155**, 387–399.