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Review

Bulky guanidinates for the stabilization of low oxidation state metallacycles

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Contents

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ABSTRACT

This article summarizes the development of a new class of very bulky guanidinate ligands. These have been used to prepare unprecedented examples of heterocycles containing groups 2, 13, 14 or 15 elements in the +1 oxidation state. The ligands have also been harnessed in the preparation of the only examples of guanidinato, and/or closely related amidinato, complexes of iron(I), cobalt(I) and planar four-coordinate lanthanide(II) metals. Preliminary studies of the further chemistry of these very reactive complexes are also reviewed. Throughout, the tendency of the bulky guanidinate ligands to exhibit ligating and stabilizing properties more akin to those of bulky β-diketiminate ligands than less bulky amidinates or guanidinates, will be discussed.

1. Introduction

The field of main group chemistry has been undergoing a rapid renaissance over the last two decades. Prior to this, it was a common (but not universal) belief that the molecular chemistry of the s- and p-block elements was a well-trodden path with no major discoveries to make, and no big surprises in store. The main group elements exhibited, by and large, one or two oxidation states in molecular compounds, and the coordination numbers in these compounds were very predictable. Indeed, “the double bond rule” assured us, for various reasons, that p-block elements of the second and subsequent rows would not form multiple bonds with themselves or other elements in their compounds [1]. In 1981, three breakthroughs definitively disproved this rule, namely the syntheses and structural characterizations of the first room temperature stable phosphaalkyne, $P{\equiv}CBu^t$ [2]; diphosphene, $Mes^*P{=}PMes^*$ ($Mes^* = C_6H_2Bu^t{}_3$-2,4,6) [3]; and disilene, $Mes_2Si{=}SiMes_2$ (Mes = mesityl) [4]. Since that time, the realization that sterically bulky ligands can kinetically stabilize compounds containing low coordinate heavier p-block elements in unusually low oxidation states has led to an explosion of interest in the area. The compound types that have resulted from this work are too numerous and varied to summarize here, but highlighted examples include monomeric and dimeric group 13 metal(I) complexes, e.g. RM: (diyls) [5] and RMMR (dimetallenes) [6] respectively (R = bulky alkyl, aryl, amide etc.; M = Al, Ga, In or Tl), and dimeric heavier group 14 element(I) alkyne analogues, REER (R = bulky alkyl, aryl etc.; E = Si, Ge, Sn or Pb) [7]. The further reactivity of compounds from this field of study has proven fascinating. In addition, new, and sometimes controversial, models have been required to be developed to describe the unusual bonding and structural features they often exhibit.

Central to the advancement of the chemistry of low oxidation state p-block compounds has been the development of a wide variety of bulky monodentate, bidentate and higher denticity ligands. These can provide steric and, in some cases, electronic protection from processes such as disproportionation, oxidation, hydrolysis

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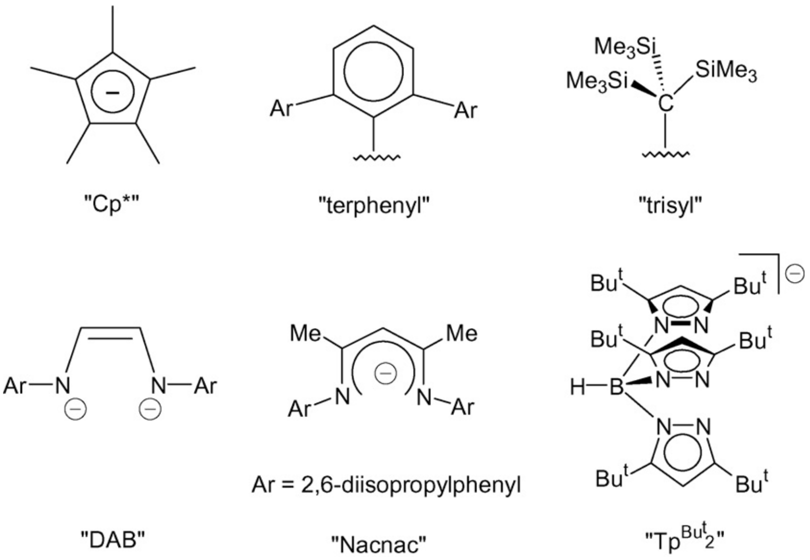


Fig. 1. Structures and colloquial names of some commonly used bulky ligands.

and oligomerization. Some of the more common ligand types that have been successfully employed include those shown in Fig. 1. Of most relevance to this review are the dianionic diazabutadiene (DAB), and anionic β-diketiminate (Nacnac$^-$), which incorporate the widely utilized 2,6-diisopropylphenyl substituent (Ar) at their N-centers. These have been used by many research groups to prepare stable five- and six-membered heterocycles respectively, that contain chelated p-block elements in low oxidation states. Perhaps the most important heterocycles have been those incorporating group 13 elements in the +1 oxidation state, *viz.* [:M(DAB)]$^-$ (M = B [8] or Ga [9]) and [:M(Nacnac)] (M = Al [10], Ga [11], In [12] or Tl [13]). These possess a singlet lone pair of electrons at the group 13 center and can, therefore, be thought of as analogues of the hugely important N-heterocyclic carbene (NHC) class of ligand. As a result, the reactivity and coordination chemistry of the metallacycles have been extensively investigated [14–16].

The importance of such group 13 metallacycles initially prompted us to consider the possibility of extending their ranks to presumably more strained four-membered examples, which we believed might display significantly different reactivity than their five- or six-membered counterparts. To achieve this goal we have developed a range of very bulky guanidinate (and related) ligands that have 2,6-diisopropylphenyl (Ar) substituents on at least two of their N-centers, *viz.* [ArNC(NR$_2$)NAr]$^-$ (R = alkyl, aryl etc.). In addition to group 13 metal(I) heterocycles, such bulky guanidinates have now been used to prepare heterocycles containing low oxidation state metal centers from every block of the periodic table. This rather personalized review details how the chemistry of these ligands has emerged in our group over the past 4 years. It will be shown that their stabilizing and ligating properties are perhaps more closely related to those of bulky β-diketiminates [17] than less bulky amidinates and guanidinates. The coordination and applications chemistry of the latter ligands is extensive and has been covered in a number of excellent and comprehensive reviews [18–22], the most recent by Edelmann from 2008 [18]. Therefore, here reference will only be made to guanidinate or amidinate coordination chemistry from other groups when comparisons are instructive.

2. Properties, preparation and group 1 complexes of bulky guanidinates

Guanidinate anions (Fig. 2) have the general formula, [(RN)$_2$CNR'$_2$]$^-$ (R, R' = alkyl, aryl, silyl etc.), and are closely related to both amidinates, [(RN)$_2$CR']$^-$, and carboxylates. Since the preparation of the first transition metal guanidinate complex by Lappert and co-workers in 1970 [23], numerous coordination complexes involving metals from across the periodic table have been described. In these, the guanidinates (or amidinates) have exhibited many coordination modes, but by far the two most common are when they act as delocalized N,N'-chelating or bridging ligands. Given that the N–M–N bite angles of chelating guanidinate ligands are generally acute, *ca.* 65° [18], the bridging coordination mode is often favored for their transition metal complexes, e.g. the intensively studied metal–metal multiply bonded "paddlewheel" or "lantern" compounds pioneered by the group of Cotton et al. [24]. The bridging mode can also occur for guanidinate complexes of the p-block elements [18], especially when the ligand N- and backbone C-substituents are not sterically demanding. The reason for this is the close to parallel alignment of the N-lone pairs in such ligands. In contrast, the use of bulky ligand substituents can cause the ligand N-lone pairs to converge, thereby enforcing N,N'-chelation of metal centers.

At the outset of our work with guanidinate ligands, it was clear that bulky substituents would be required at both the ligand N- and C-centers to compel the ligand to chelate low oxidation state metal fragments, but also to provide kinetic protection to the metal fragment from disproportionation and other decomposition processes. Considering the success that had been previously had in stabilizing low oxidation state metallacycles with DAB^{2-} and Nacnac$^-$ ligands having bulky 2,6-diisopropylphenyl N-substituents, similarly substituted guanidinates were targeted. Surprisingly, a survey of the literature revealed that there were no crystallographically characterized complexes incorporating such ligands and only one report

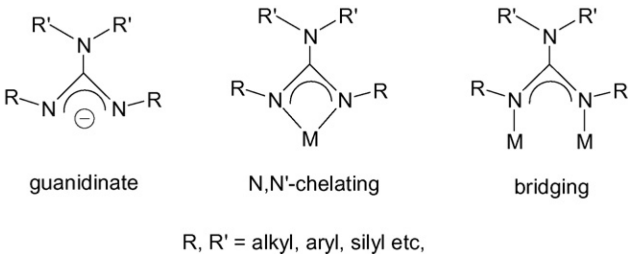


Fig. 2. General formula of guanidinate anions and two of their common bonding modes.

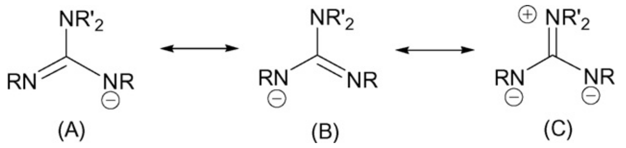
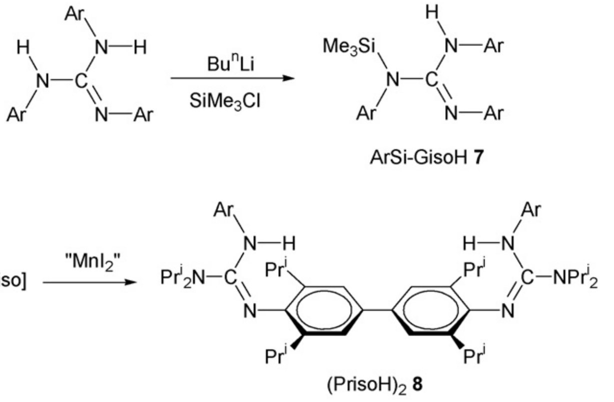


Fig. 3. Resonance forms of guanidinate anions.

[25] and two early patents [26,27] detailed the synthesis of neutral Ar-substituted guanidines, e.g. Ar(H)NC(NRR′)=NAr (Ar = $C_6H_3Pr^i_2$-2,6; NRR′ = NMe_2 or N(H)Ar).

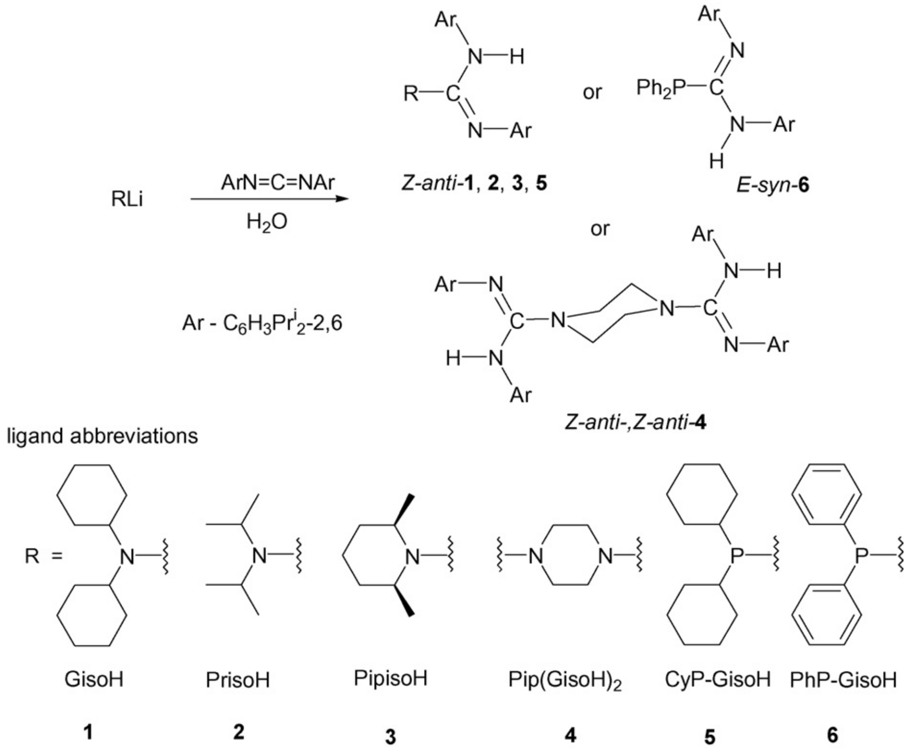
In contrast, numerous complexes incorporating related Ar-substituted amidinates, $[(ArN)_2CR]^-$ (R = H, alkyl, aryl etc.) had been described in the literature [18]. In several of these reports the ability of the amidinates to kinetically stabilize what would normally be thought to be thermally labile fragments was demonstrated. An excellent illustration of this is the indium hydride complex, $[HIn(Fiso)_2]$ (Fiso = $[(ArN)_2CH]^-$), which is stable until 160 °C in the solid state and can be heated at reflux in toluene for 3 h [28]. This can be compared to less hindered indium hydride complexes, for example $[InH_3(NMe_3)]$ which decomposes above −30 °C in solution and has not yet been isolated in the solid state. Accordingly, Ar-substituted amidinates have been used by us to access low oxidation state metallacycles (*vide infra*), but in general, related guanidinates appear to be more stabilizing. The reasons for this are two-fold. Firstly, bulkier amino substituents can be more readily incorporated at the backbone C-centers of guanidinates than the alkyl or aryl C-substituents of amidinates. This enhances the ability of guanidinates to chelate metal centers, relative to amidinates. Secondly, guanidinates have three possible resonance forms (Fig. 3), one of which, form C, does not occur for amidinates. The two coordinating N-centers of this iminium/diamido resonance structure have formal negative charges, which leads to guanidinates being more N-electron rich than amidinates. In several of the s- and p-block metal(I) complexes mentioned below, this is thought to aid stabilization of their electron deficient metal centers.



Scheme 2.

A number of synthetic methods have been used to prepare guanidinate ligands, but the most common has been the insertion of carbodiimides into the metal–nitrogen bond of metal amide complexes [18,19]. This technique has been utilized to access a range of mono- and bifunctional Ar-substituted guanidines and related phosphaguanidines (Scheme 1) [29]. The synthesis of the precursor carbodiimide, ArN=C=NAr, has been described in a Japanese patent [30], and more recently by Cowley and co-workers [31]. In a general reaction, this is treated with the appropriate lithium amide (or phosphide) in THF, followed by aqueous work-up. Although versatile, the route has steric limitations. An illustration of these is the fact that lithiated 2,2,6,6-tetramethylpiperidine does not react with ArN=C=NAr, even under reflux conditions. In contrast, it is known to react with smaller carbodiimides [32].

Two other Ar-substituted guanidines have been prepared by modification of other guanidines (Scheme 2) [29]. The first of these, ArSi-GisoH **7**, was synthesized by deprotonating $\{Ar(H)N\}_2C{=}NAr$ and quenching with $SiMe_3Cl$, whereas the other, $(PrisoH)_2$ **8**,



Scheme 1.

resulted in moderate yield from the reaction of deprotonated PrisoH with MnI_2. The mechanism of the second reaction is not known, but it is believed that the commercially sourced MnI_2 used in the reaction was contaminated with higher oxidation state Mn species. This led to the oxidative coupling of two $Priso^-$ anions through aryl *para*-positions of each. In this respect, it is of note that $(PrisoH)_2$ was not obtained from the reaction of $Priso^-$ with pure MnI_2 in THF.

All the guanidines and phosphaguanidines, **1**–**8**, have been crystallographically characterized. In each of the guanidines, the backbone amino substituent is effectively planar, while the phosphino substituents of the phosphaguanidines are pyramidal. As a result, the P-lone pair cannot be involved within the π-system of their N_2CP cores, and thus the resonance form equivalent to C (Fig. 3) is not accessible. In the solid state, the compounds have been shown to exist in a number of isomeric and tautomeric forms (that were assigned by comparison with the equivalent forms reported for amidines [22]) as shown in Schemes 1 and 2. Saying this, the *Z-anti*-form is the most common for the guanidines, though the extremely bulky compound, **7**, crystallizes in the rarely observed *Z-syn*-form. Although less bulky guanidines and phosphaguanidines can exist as mixtures of isomers in solution [32,33], NMR spectroscopic studies on **1**–**6** have shown them each to occur as one, or predominantly one, isomer in solution. It is likely that the solution isomeric forms of these compounds are the same as those observed in the solid state. NMR spectroscopic studies on **7** and **8** were not as clear-cut and showed two or three isomers of each in solution.

Deprotonation of the guanidines and phosphaguanidines with alkali metal reagents, e.g. $LiBu^n$, $K[N(SiMe_3)_2]$ or KH, cleanly leads to alkali metal salts of the ligands. These are the reagents of choice for the preparation of low oxidation state metallacycles or their precursors (*vide infra*). In this respect, their reaction with p-, d- or f-block halides effects the facile elimination of an alkali metal halide and transfer of the ligand to the other metal center. Group 1 guanidinate or phosphaguaninate complexes can be prepared *in situ* prior to their use as transfer reagents, or they can be isolated and stored prior to reaction. The crystal structures of four such compounds have been reported and their variable structural motifs are depicted in Fig. 4 [29]. It is clear that the ligand, metal and reaction solvent all have an influence on the structure of the reaction product. The complexes can be monomeric, dimeric or polymeric, while the ligands can chelate the metal in either an N,N′- or N,arene-fashion. Although more crystallographic data on such complexes is required before definite structural trends emerge, the interested reader is directed to a review article [34] detailing exhaustive studies on closely related alkali metal complexes of bulky aryl substituted amidinates, for which structural trends are apparent.

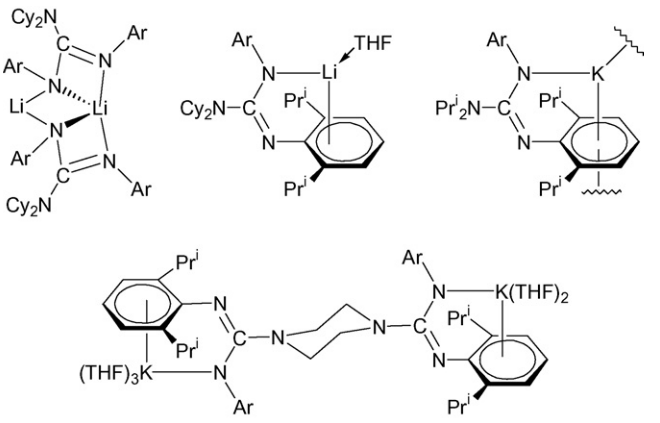
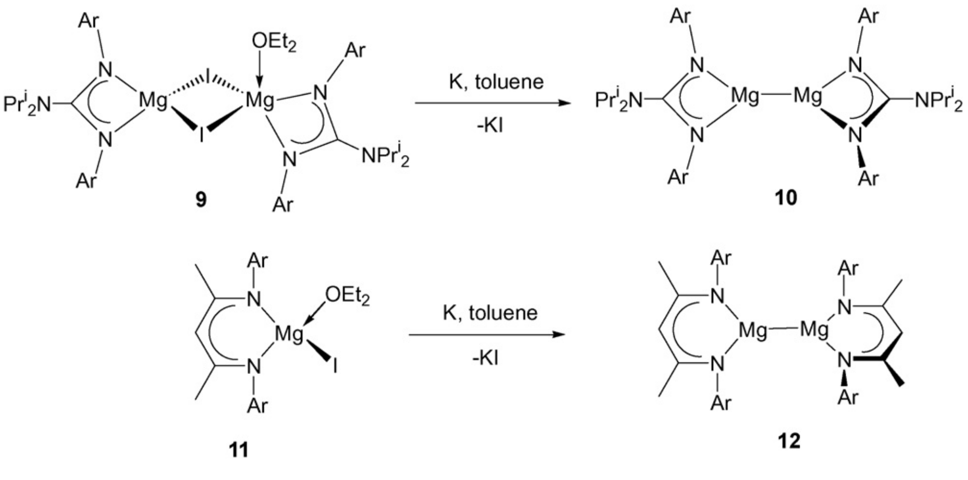


Fig. 4. Structural motifs displayed by crystallographically characterized bulky guanidinato alkali metal complexes.

3. Group 2 complexes

The chemistry of amidinato group 2 complexes is well developed and such compounds have found use in synthesis, catalysis and as materials precursors [18]. Guanidinato group 2 compounds are less common, though examples are known for all of the non-radioactive members, except beryllium [18,19]. In addition, prior to the development of the ligands described above, there were no examples of Ar-substituted guanidinato group 2 complexes, and no known heteroleptic compounds of the type, LMX (L = guanidinate, M = group 2 metal, X = halide). Bulky examples of the latter were seen as ideal precursors to metal(I) dimers, LMML, which could potentially be obtained *via* reduction methodologies. The possibility of preparing such exotic complexes seemed reasonable given that several related compounds, e.g. XMgMgX, X = H or Cl, had been prepared and spectroscopically studied in solid noble gas matrices [35,36]. Furthermore, theoretical studies on a variety of compounds of the type RMMR (R = alkyl, aryl etc.) suggested they might be viable synthetic targets [37]. Given the chemical similarities between zinc and magnesium, the possibility of accessing a magnesium–magnesium bonded compound seemed even more enticing after the landmark report of the first stable zinc(I) compound, Cp*ZnZnCp*, by Carmona et al. in 2004 [38,39]. A number



Scheme 3.

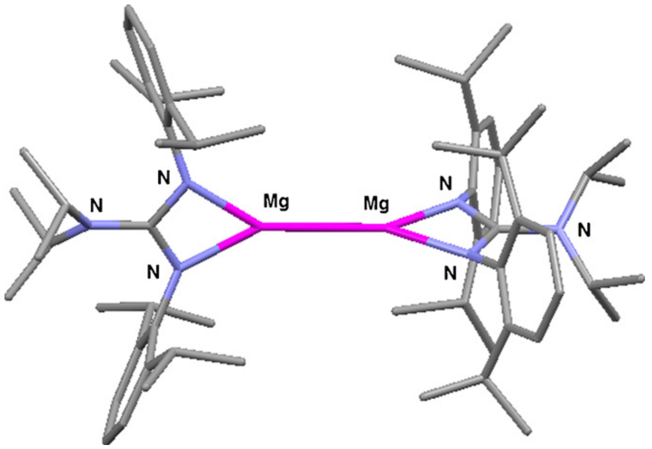


Fig. 5. The molecular structure of compound **10**.

of zinc(I) dimers, e.g. [(Nacnac)ZnZn(Nacnac)] [40], followed and the chemistry of these compounds is now rapidly emerging [41].

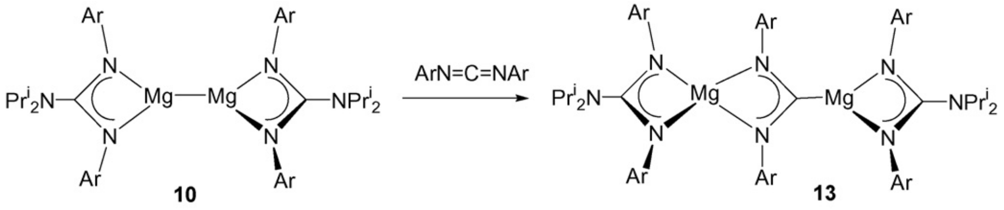
The guanidinato magnesium(II) iodide complex, **9** (Scheme 3), was prepared in good yield from the reaction of PrisoH and MeMgI. In the solid state the compound is dimeric and, unusually, has one four-coordinate and one five-coordinate magnesium center [42,43]. The reduction of this compound with potassium metal in toluene led to a low to moderate yield of the first stable magnesium(I) compound, **10**. The similar stabilizing properties of $Priso^-$ and the bulky β-diketiminate, $Nacnac^-$, were demonstrated by the fact that the known magnesium(II) complex, **11**, could also be reduced to give the closely related complex, **12**. As testament to the stabilizing abilities of their ligands, compounds **10** and **12** are remarkably thermally robust and do not decompose until they reach temperatures of greater than 170 °C and 300 °C respectively, with the deposition of Mg metal in the case of **10**. Both compounds are air and moisture sensitive but can be readily handled under an inert atmosphere.

The X-ray crystal structure of **10** (Fig. 5) is similar to that of **12** and the Mg–Mg distances in both (**10** 2.8508(12) Å, **12** 2.8457(8) Å) are only slightly longer than the reported sum of the covalent radii (2.82 Å) for two magnesium centers [44]. The fact that the two magnesium heterocycles in both compounds are effectively orthogonal to each other implies that there are no hydride ligands bridging their two magnesium centers. This possibility was carefully considered during the characterization of **10** and **12**, as solvent hydrogen abstraction during the reduction of **9** and **11** could have instead led to the magnesium(II) complexes, [(Priso)Mg(μ-H)$_2$Mg(Priso)] and [(Nacnac)Mg(μ-H)$_2$Mg(Nacnac)] respectively. These could potentially be difficult to differentiate from the magnesium(I) complexes. Other evidence found for the absence of hydride ligands in **10** and **12** includes minimal residual electron density about the Mg–Mg vectors in the final difference maps of the crystal structures of the two compounds, no observable hydride resonances in their NMR spectra, no obvious Mg–H stretching absorptions in their infrared spectra, and the presence of molecular ion peaks in their mass spectra. In addition, the reaction of **12** with D_2O led to the generation of a 98:2 mixture of D_2 and HD [45]. If **12** was actually [(Nacnac)Mg(μ-H)$_2$Mg(Nacnac)], its quenching with D_2O would be expected to generate predominantly HD. Final confirmation of the absence of hydride ligands in **12** (and by implication, **10**) came with the preparation of [(Nacnac)Mg(μ-H)$_2$Mg(Nacnac)], which was found to exhibit very different physical, spectroscopic and crystallographic properties than **12** [45]. The high yielding synthetic route to this compound is related to that used by Harder et al. to prepare calcium hydride complexes [46], and involved the reaction of [(Nacnac)MgBu^n] with $PhSiH_3$.

In order to ascertain the nature of the Mg–Mg bond in **10**, DFT calculations were carried out on the model complex, [{Mg[(Ar′N)$_2$CNMe$_2$]}$_2$] (Ar′ = $C_6H_3Me_2$-2,6) [42]. The geometry of the optimized structure was found to be in close agreement with that in the crystal structure of **10** but with a slightly underestimated Mg–Mg bond length. The HOMO of the model largely comprises a metal–metal σ-bonding interaction with high s-character (93.2%), while the LUMO and LUMO+1 are almost degenerate and predominantly encompass metal–metal π-bonding orbitals derived from metal p_x- and p_y-orbital overlaps respectively. The HOMO–LUMO gap is 93.0 kcal mol^{-1}, which compares well with calculations on other magnesium dimers, e.g. CpMgMgCp (89.5 kcal mol^{-1}) [37(a)]. Subsequent calculations on other models of **10** [35,47] and **12** [45] gave similar results and, in the case of **12**, pointed towards a not insignificant Mg–Mg bond dissociation energy of *ca.* 45 kcal mol^{-1}. The conclusion from all of these calculations were that **10** and **12** can be considered as possessing covalently bonded Mg_2^{2+} cores that have largely ionic interactions with bulky, chelating guanidinate or β-diketiminate anions that stabilize the compounds with respect to disproportionation. It is of note that high accuracy crystallographic data for **12** have been used to carry out an experimental charge density study on that compound [48]. This confirmed the covalent nature of its Mg–Mg interaction and the predominantly ionic interaction of the Mg_2^{2+} core with its β-diketiminate ligands. It did, however, highlight the fact that the electron density between the Mg centers of the compound is rather diffuse, and not dissimilar to the bonding in the Li_2 and Na_2 dimers. Indeed, this observation appeared consistent with the results of prior calculations on a model of **12** which showed that the potential energy surface about its equilibrium bond length is quite shallow [45]. As a result, the bond can be considered as “deformable” in that its lengthening by, for example, 0.2 Å costs only *ca.* 1.2 kcal mol^{-1}. It is noteworthy that one theoretical study has examined the metal–metal bonds of the group 2 metal(I) dimetallocenes, CpMMCp (M = Be, Mg, Ca, Sr or Ba), using an energy decomposition analysis technique [49]. This study indicated that in all compounds the electrostatic component of the metal–metal bond is greater than the covalent component, and in the case of CpMgMgCp the relative contributions are 58.8% and 41.2% respectively.

As the preparation of the magnesium(I) guanidinate dimer, **10**, is considerably lower in yield than that of **12**, the further chemistry of the latter has been more extensively studied to date. For example, it has been shown to form a variety of adducts, [(Nacnac)Mg(L)Mg(L)(Nacnac)] (L = THF, dioxane, 4-dimethylaminopyridine or 4-*tert*-butylpyridine), that are stable towards disproportionation [45]. The crystal structures of these reveal that their magnesium heterocycles had rotated from being orthogonal in the precursor, **12**, to close to parallel in the adducts. In addition, their Mg–Mg bonds were significantly elongated (by more than 0.2 Å) relative to **12**, which was taken as a manifestation of the diffuse and “deformable” nature of these bonds. No similar adducts have been reported for **10**, but it is noteworthy that its dissolution in THF leads to the deposition of magnesium metal over several hours, presumably *via* disproportionation [45].

A recent paper has highlighted the ability of **12** to act as a facile two-center/two-electron reductant towards a variety of unsaturated organic substrates [50]. These reactions lead either to double reduction of the substrate (in the case of CyN=C=NCy (Cy = cyclohexyl), PhN=NPh or cyclooctatetraene), reductive N–N coupling (for 1-adamantyl azide), or reductive C–C coupling (for Bu^{t}N=C=O). Compound **12** was said to hold potential as an alternative to more classical reducing agents, e.g. alkali metals and samarium(II) reagents, that are commonly used in organic and organometallic syntheses. As yet, the only observation of the related compound, **10**, acting as a reducing reagent has been in its reaction with the bulky carbodiimide, ArN=C=NAr. This gives the



Scheme 4.

magnesium magnesioamidinato complex, **13** (Scheme 4) in good yield [51]. Compound **13** is closely related to the product of the reaction of **12** with CyN=C=NCy and is likely formed *via* an initial adduct of the carbodiimide with the magnesium(I) compound, which subsequently inserts into the Mg–Mg bond of the compound.

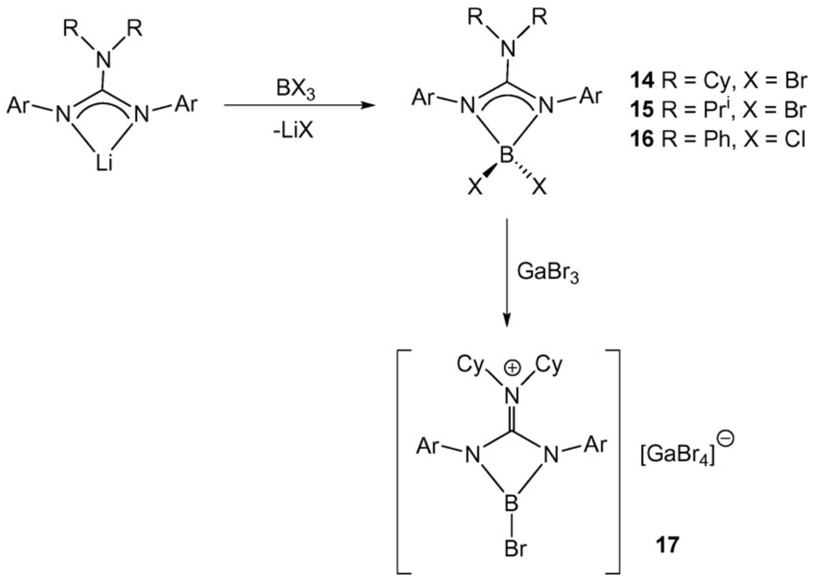
One unsuccessful reaction that has been attempted with **10** has been its treatment with H_2 in a benzene solution. Even when this mixture was heated to 80 °C for several hours, no reaction was observed [42]. This result contrasts with calculations on the reaction of several models of **10** with H_2 to form dimeric complexes of the type, [LMg(μ-H)$_2$MgL] (L = a guanidinate anion) [47]. These showed that hydrogenation of the Mg–Mg bonds of the complexes is exothermic by *ca.* 25 kcal mol^{-1}. Clearly, in the experimental situation there is a significant activation energy to overcome before the hydrogenations will take place. Indeed, this is reminiscent of the hydrogenation of magnesium metal itself (to give MgH_2), which although exothermic (by *ca.* 17.6 kcal mol^{-1}), requires temperatures in excess of 300 °C to occur [52]. Given the importance of the Mg/MgH_2 system as a hydrogen storage medium, compounds such as **10** and **12** hold much potential as soluble models to study the mechanisms and kinetics of the catalyzed or uncatalyzed hydrogenation of magnesium metal.

To date, the success had in using the bulky guanidinate, Priso$^-$, and the closely related β-diketiminate, in forming stable magnesium(I) compounds has not been extended to the other group 2 metals. It is, however, only a matter of time before the ranks of stable group 2 metal(I) complexes incorporating these or other ligands will expand. In fact, this has already begun with the recent reports of the remarkable calcium(I) inverse sandwich complex, [{(THF)$_3$Ca}$_2$(μ-C$_6$H$_3$Ph$_3$-2,4,6)] [53], and the dianionic diazabutadiene stabilized magnesium(I) dimer, [K(THF)$_3$]$_2$[{(MeCNAr)$_2$}MgMg{(ArNCMe)$_2$}] [54].

4. Group 13 complexes

The coordination and further chemistry of group 13 element(I) complexes is extensively developed. The most studied of these compounds are the diyls, :MR (M = group 13 element, R = bulky aryl, alkyl, C$_5$Me$_5$$^-$ etc.), which have been employed as boron or metal donor Lewis bases in the formation of complexes with elements from every block of the periodic table [5,14]. Although not as widely studied, the chemistry of related group 13 metal(I) heterocycles is rapidly emerging. As mentioned in Section 1, systems that have been examined in this field include the neutral six-membered heterocycles, [:M(Nacnac)] (M = Al [10], Ga [11], In [12] or Tl [13]) stabilized by a β-diketiminate ligand, and the five-membered anionic heterocycles [:M(DAB)]$^-$ (M = B [8] or Ga [9]) which are valence isoelectronic analogues of the typical N-heterocyclic carbene (NHC) class of ligand. The gallium heterocycle can be considered as a gallyl anion and its nucleophilicity is demonstrated by the fact that it has formed complexes with more than 40 s-, p-, d- and f-block elements [16,55]. It should be noted that its direct boron analogue, the boryl anion [:B(DAB)]$^-$, was reported more recently but its coordination chemistry is also developing [56].

With the preparation of the first four-membered NHC, :C{(ArN)$_2$PNPr^i$_2$}, by Despagnet-Ayoub and Grubbs in 2004 [57] came the challenge of preparing group 13 element analogues, [:M{(RN)$_2$CR′}], and investigating their chemistry. The obvious ligands to potentially achieve this goal were guanidinates or amidinates. However, given the likely instability of such heterocycles towards disproportionation and other decomposition pathways, very bulky examples of these ligands were thought necessary. It seemed that 2,6-diisopropylphenyl (Ar) substituted examples might be appropriate, and that guanidinate ligands would have a

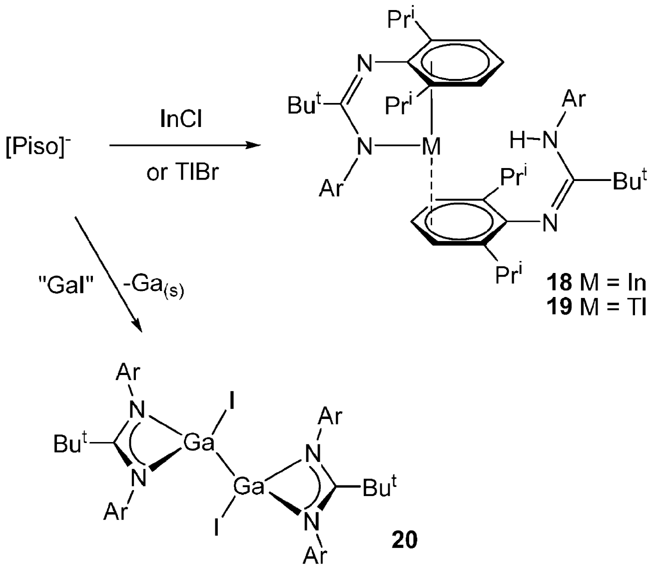


Scheme 5.

superior stabilizing ability over amidinates, given their aforementioned greater nucleophilicity. Although the group 13 coordination chemistry of guanidinates and amidinates is extensive and has been reviewed [18–20], that of Ar-substituted guanidinates was unknown prior to 2006.

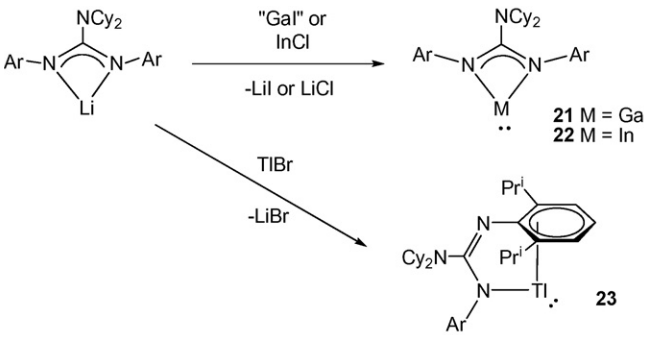
DFT and MP2 calculations on the model boron(I) guanidinate complex, [:B{(PhN)$_2$CNMe$_2$}], were carried out by Cowley and co-workers and these gave singlet–triplet gaps for the heterocycle of 6.0 and 10.1 kcal mol^{-1} respectively [31]. While these values are considerably smaller than those calculated for heavier group 13 analogues (*vide infra*), they suggested that singlet boron(I) guanidinate complexes may be stable at ambient temperature if sufficiently sterically protected. Potential guanidinato boron dihalide precursors, **14**–**16**, to these targets have been prepared by our group [58] and that of Cowley and co-workers [31], using salt elimination routes (Scheme 5). However, attempts to reduce these complexes with Na, K or Na/K alloy in various solvents led to no reaction, even when the mixtures were heated at reflux for extended periods. This is presumably because there is no facile pathway for reduction of the four-coordinate boron centers of the complexes. Accordingly, the cationic three coordinate boron complex, **17**, was prepared by halide abstraction in the expectation that the enhanced electrophilicity of its boron center would facilitate its reduction with alkali metals [58]. Unfortunately, all efforts in this direction led to intractable product mixtures. It is of note that the X-ray crystal structure of **17** revealed the guanidinate ligand to exist predominantly as its iminium/diamido resonance form.

Early attempts to prepare four-membered group 13 metal(I) NHC analogues involved the bulky amidinate ligand, [ArNC(Bu^t)NAr]$^-$ (Piso$^-$), developed by the group of Jordan [59]. Reactions of alkali metal salts of Piso$^-$ with group 13 metal(I) halides led to differing outcomes. Indium(I) and thallium(I) amidinate complexes, **18** and **19** (Scheme 6), were accessible, but instead of N,N′-chelating the metal centers, the Piso$^-$ ligand acts as a localized N,Ar-donor, giving rise to "five-membered" isomeric forms of the target complexes [60]. X-ray crystallography showed the metal centers of **18** and **19** to be additionally weakly coordinated by a molecule of PisoH, which presumably originates from partial decomposition of [M(Piso)] generated in the reaction. Theoretical studies on a model of **18** indicated that the strength of the interaction between the In(Piso) and PisoH fragments is less than 2 kcal mol^{-1}. In contrast, reaction of Li[Piso] with Green's "GaI" led to partial disproportionation and the formation of the gallium(II) dimer, **20**, in low yield [61].



18 M = In
19 M = Tl
20

Scheme 6.



21 M = Ga
22 M = In
23

Scheme 7.

At this stage it was reasoned that the use of bulkier, more N-electron rich guanidinate ligands, e.g. Giso$^-$, might enforce N,N′-chelation of the group 13 metal(I) centers and prevent disproportionation from occurring. This proved to be the case for Ga and In, the monomeric complexes of which, **21** and **22**, were prepared in moderate to good yields (Scheme 7) [62]. In contrast, N,Ar-chelation by the ligand occurred in the Tl complex, **23**, presumably because the ionic radius of Tl$^+$ is too large to accommodate N,N′-chelation, even from a ligand as bulky as Giso$^-$. Although **21**–**23** are air and moisture sensitive, they are remarkably thermally stable and do not decompose below 150 °C. In the solid state, each was shown by X-ray crystallography to be monomeric, while **21** (Fig. 6) and **22** are isomorphous and possess two-coordinate metal centers that have no close inter- or intramolecular interactions. The structures of **21** and **22** are obviously related to those of their β-diketiminate counterparts, [:M(Nacnac)] (M = Ga [11] or In [12]), and this again highlights similarities between the coordination and stabilizing properties of bulky guanidinates, e.g. Giso$^-$, and β-diketiminates, e.g. Nacnac$^-$. However, due to the fact that the Ar groups are bent away from the metal center in **21** and **22**, the Giso$^-$ ligand does not provide as much steric shielding to the metal centers of these complexes as does the Nacnac$^-$ ligand in [:M(Nacnac)] (M = Ga or In). This can be quantified to some extent for the gallium heterocycles by determining their (*p*-Ar–C)–Ga–(*p*-Ar–C) angles from their crystal structures. These are *ca.* 131° and 187° respectively which indicates that the metal centers of complexes of Giso$^-$ may be more open to reactivity than those of Nacnac$^-$ complexes. It is of note that the reactivity of **22** towards oxidation processes has been

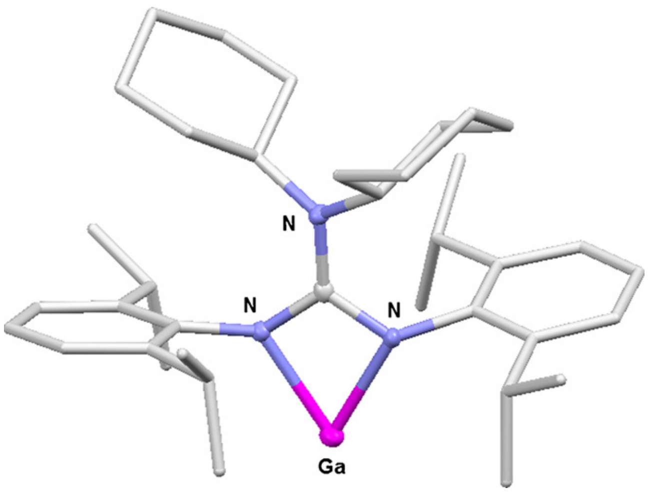
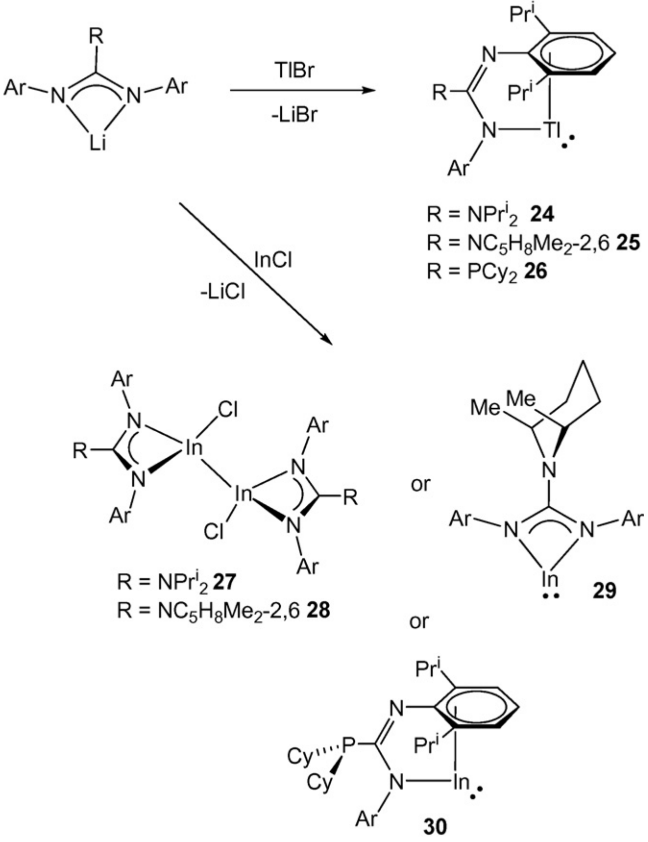


Fig. 6. The molecular structure of compound **21**.

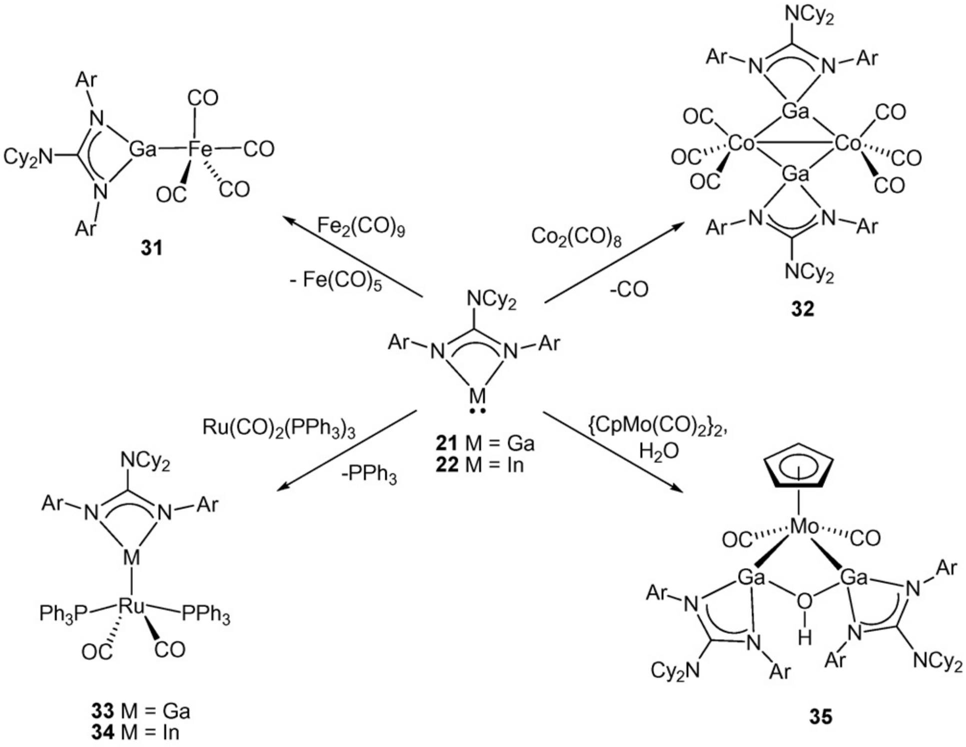
demonstrated with its treatment by either I_2 or $SiMe_3I$ which yield $[I_2Ga(Giso)]$ and $[(Me_3Si)(I)Ga(Giso)]$ respectively [63].

In order to shed light on the effect that the backbone substituent of bulky guanidinates and phosphaguanidinates has on their ability to stabilize group 13 metal(I) heterocycles, the lithium salts of Priso⁻, Pipiso⁻ and CyP-Giso⁻ have been reacted with InCl and TlBr (Scheme 8) [63]. All reactions with TlBr led to monomeric N,Ar-chelated complexes, **24**–**26**, that are structurally equivalent to **23**. The reactions with InCl were more variable in their outcome. For example, the reaction with Li[Priso] led to disproportionation and the formation of the indium(II) species, **27**. When the bulkier Pipiso⁻ ligand was employed, a mixture of an indium(II) complex, **28**, and the N,N′-chelated indium(I) compound, **29**, resulted. The reaction with the phosphaguanidinate gave the N,Ar-chelated complex, **30**. In contrast, the reactions of salts of the three ligands with "GaI" led to disproportionation and the formation of mixtures of Ga^{II} and/or Ga^{III} products. The results of this study showed that the guanidinate backbone substituent has a marked effect on the stabilizing properties of the ligand and that bulkier Giso⁻ appears to have a superior steric profile.

Considering their potential use as metal donor ligands, theoretical calculations were carried out on models of **21** and **22** (and their as yet unknown Al analogue) to determine the nature of their frontier orbitals [62]. In all $[:M\{(PhN)_2CNMe_2\}]$ (M = Al, Ga or In), the singlet lone pair of the metal is largely associated with the HOMO, while the metal p-orbital, orthogonal to the heterocycle plane, is associated with the LUMO. The metal lone pairs have high s-character, e.g. M = Ga $4s^{1.90}4p^{0.37}$, but do exhibit sufficient directionality to suggest they may behave as σ-donor ligands. Unlike the significant delocalization over the NCN fragment of NHCs, there is effectively no overlap of the N-p-orbital lone pairs with the empty p-orbital at the metal center. An examination of the HOMO–LUMO gaps in the series (M = Al 61.8, Ga 67.4, In 63.5 kcal mol^{-1}) showed them to be much greater than the singlet–triplet gap of their aforementioned B analogue [31], but significantly less than the HOMO–LUMO gaps of models of the related six-membered het-



Scheme 8.

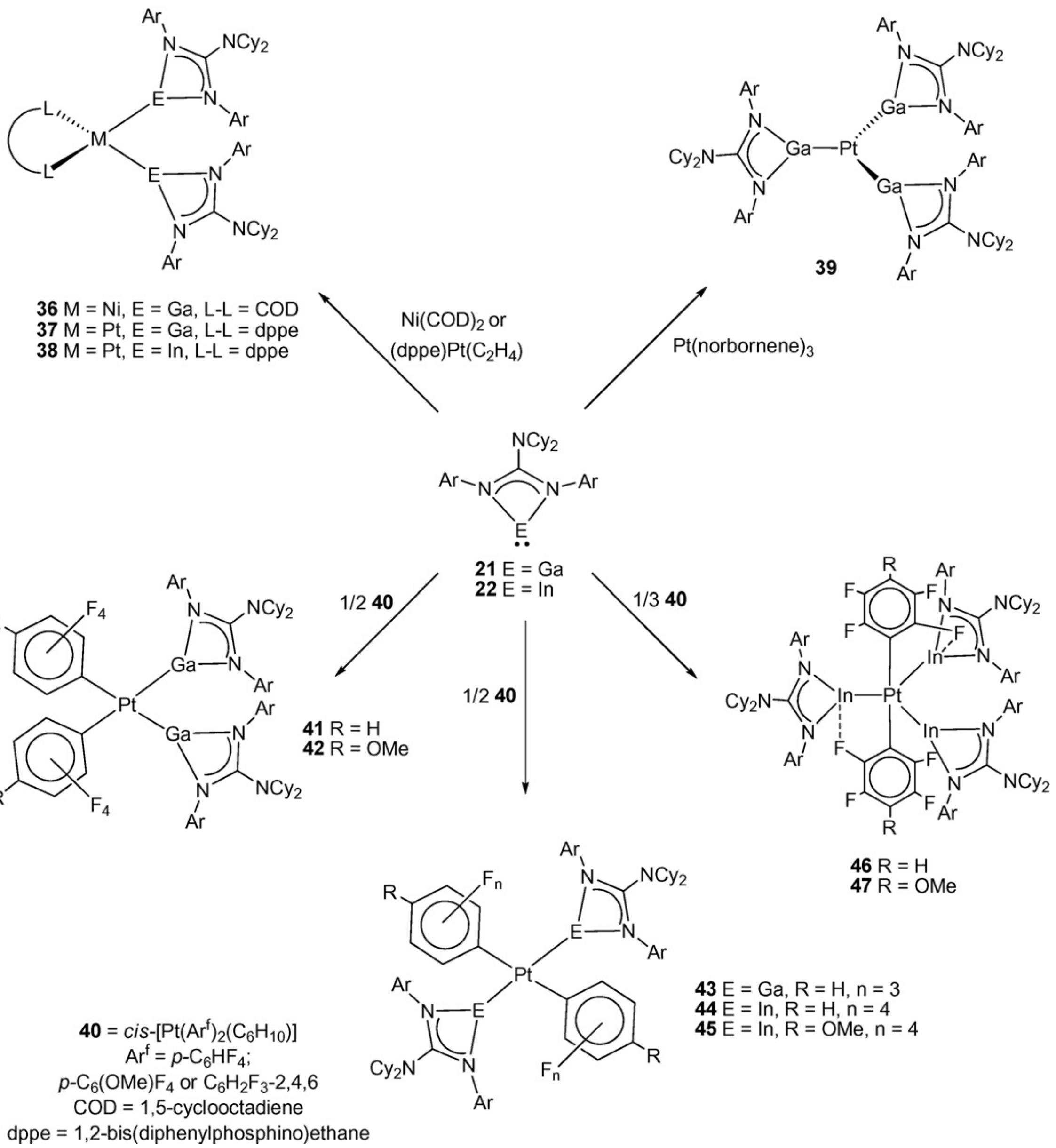


Scheme 9.

erocycles, [:M(Nacnac)], i.e. >90 kcal mol^{-1} [16]. Therefore, it was concluded that **21** and **22** held the promise of acting as both σ-donor and weak π-acceptor ligands.

The coordination chemistry of **21** and **22** has begun to be examined and a summary of the complexes derived from these ligands is shown in Schemes 9 and 10. In general, the coordination chemistry of these heterocycles reflects that of metal diyls, :MR (M = Ga or In), and the six-membered heterocycle, [:Ga(Nacnac)], in that they can act as both terminal and bridging ligands. However, **21** and **22** appear to be less nucleophilic than the previously examined ligands. Evidence for this proposal includes the fact that **21** does not displace CO from Fe(CO)$_5$ [64], whereas [:Ga(Nacnac)] and gallium diyls do. In addition, several of the group 10 complexes of the heterocycles are unstable to heterocycle ligand loss in solution at room temperature [65,66]. Moreover, the results of these synthetic studies, not surprisingly, highlight a lower nucleophilicity of the indium heterocycle, **22**, relative to its gallium counterpart, **21**.

The relatively poor σ-donor properties of the two heterocycles are likely related to the calculated high s-character of their metal lone pairs. From a comparison of the structural properties and infrared spectra of **31** with those of other gallium complexes and [Fe(CO)$_4$(PPh$_3$)], the conclusion was drawn that the four-membered heterocycle is, at best, acting as a very weak π-acid in this complex [64]. This is not surprising given the considerable π-acidity of the carbonyl co-ligands in **31**. It might be expected that late transition metal, carbonyl free complexes of **21** might display more π-backbonding to the Ga center of the heterocycle. At first glance this appears to be the case in the homoleptic platinum(0) complex, **39** (Scheme 10) [65]. Despite the bulk of its ligands, the crystal structure of this compound (Fig. 7) exhibited, what were at the time, the shortest reported Pt–Ga bonds. This was said to be a possible indication of Pt–Ga π-bonding. Further evidence for this proposal came from the results of DFT calculations on a model of the complex. A Charge Decomposition Analysis (CDA) of the geometry optimized model indicated a mean 39.8% π-contribution to the covalent component of the Pt–Ga bonds. Similar π-contributions to Ga–M bonds of homoleptic gallium diyl complexes of group 10 metals had been previously calculated and were said to be



Scheme 10.

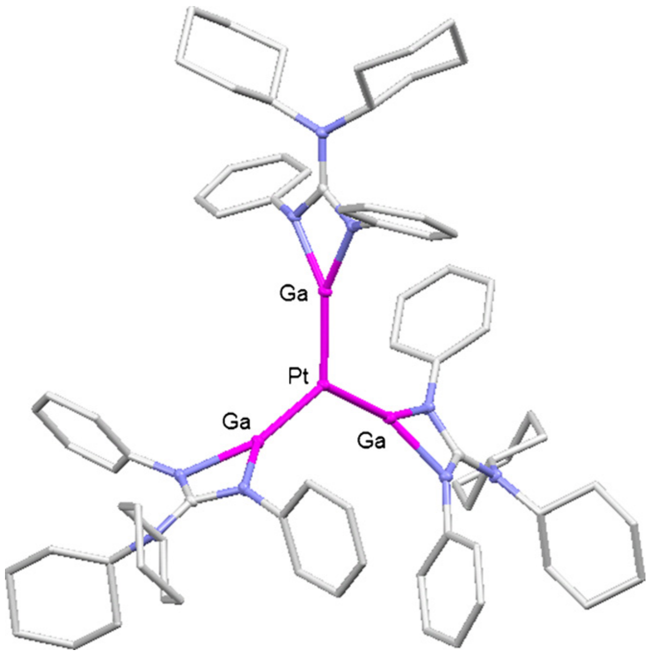


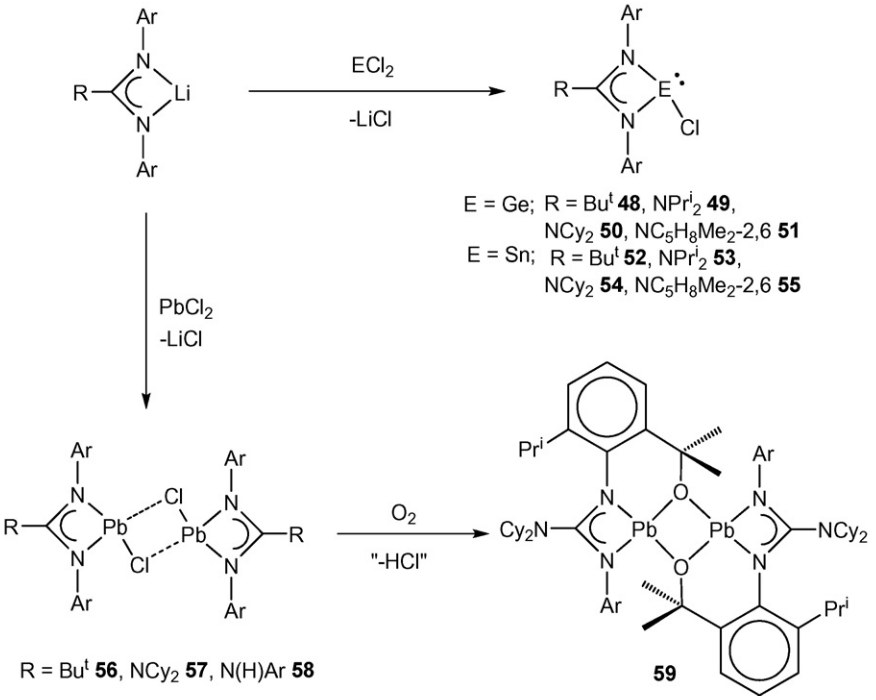
Fig. 7. The molecular structure of compound **39** (isopropyl groups omitted).

significant [67]. However, in the case of the model of **39**, it was calculated that the mean electrostatic component of the polarized Ga–Pt bonds is greater than the covalent component and, therefore, the Pt–Ga π-bonding in the complex is not substantial. As with other gallium(I) transition metal complexes [5], this arises in part from an energy mismatch between the empty p-orbital at gallium and filled d-orbitals of appropriate symmetry at the transition metal center. It is of interest to note that an attempt to form the In analogue of **39** was not successful and instead a low yield of the indium bridged cluster, [{Pt(norbornene)}$_3${μ_3-In{[N(Ar)]$_2$CNCy$_2$}}$_2$], resulted from the 3:1 reaction of **22** with [Pt(norbornene)$_3$] [66].

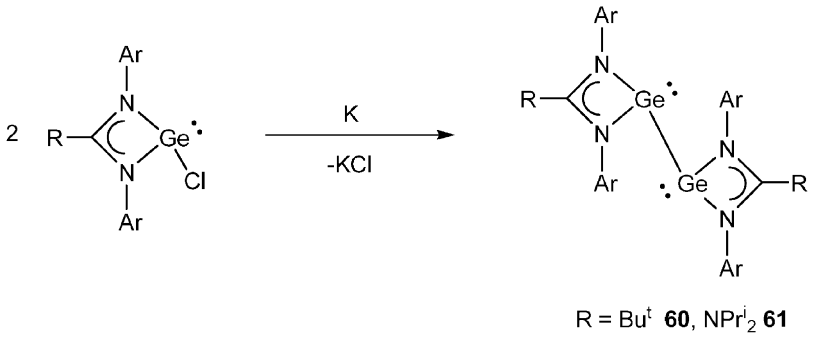
Although the indium heterocycle, **22**, is a weaker nucleophile than the gallacycle, **21**, the X-ray crystal structures of two complexes, **46** and **47**, show that it is electrophilic and probably more so than **21** [66]. The compounds were prepared in the 3:1 reactions of **22** with the reactive platinum(II) bis(aryl) complexes, *cis*-[Pt(Ar^f)$_2$(1,5-C$_6$H$_{10}$)] **40** (Ar^f = *p*-C$_6$HF$_4$ or *p*-C$_6$(OMe)F$_4$). In the solid state, two indium heterocycles in each are acting as Lewis bases, but at the same time are accepting electron density from *ortho*-fluoro substituents of the aryl ligands. The resulting In···F interactions are strong enough to persist in solution, as determined by ^{19}F NMR studies. Accordingly, the heterocycles were said to display “Lewis amphoteric” behavior. It was proposed that the In···F interactions helped to stabilize the complexes towards ligand loss and the formation of the 2:1 complexes, **44** and **45**. The fact that similar 3:1 complexes of the gallium heterocycle cannot be formed (but the 2:1 complexes, **41** and **42**, can) perhaps indicates that the gallium center of **21** is less electrophilic than the indium center of **22**. It is noteworthy that similar Lewis amphoteric behavior, in the form of an intramolecular Al···F$_{ortho}$ contact, has been demonstrated by a related aluminum(I) heterocycle in the complex, [(C$_6$F$_5$)$_3$BAl(Nacnac)] [68]. The complex was said to be “Janus faced” after the two faced god of Roman mythology.

5. Group 14 complexes

The chemistry of amidinate complexes of the group 14 elements in both the +2 and +4 oxidation states is well developed and has been reviewed [18]. Surprisingly, only a handful of group 14 complexes incorporating guanidinate ligands not mentioned in Section 2 of this review have been structurally characterized. Moreover, no examples of amidinato or guanidinato group 14 element(I) complexes had been reported. The previously demonstrated stabilizing properties of bulky Ar-substituted guanidinates suggested that such complexes might be accessible *via* the reduction of compounds of the type, [(guanidinate)M^{II}X] (M = group 14 element; X = halide). Although such complexes were previously unknown, the similarities between the ligating properties of bulky guanidinates and β-diketiminates, and the prior preparations of



Scheme 11.



Scheme 12.

the complexes, [(Nacnac)$M^{II}X$] (M = Ge, Sn or Pb; X = halide) [69], implied they may be accessible. It is noteworthy, however, that all attempts to reduce [(Nacnac)$M^{II}X$] have not given +1 oxidation state complexes, but instead generally lead to Nacnac$^-$ modification reactions [70].

A series of guanidinato group 14 halides have been prepared by salt elimination reactions (Scheme 11) [71–74]. The results of these reactions are similar to those involving the related bulky amidinate ligand, Piso$^-$. In the solid state all the Ge and Sn complexes are monomeric, whereas the lead(II) species are associated into dimeric units through weak chloride bridges [74]. In contrast, the more sterically hindered lead β-diketiminate complexes, [(Nacnac)$Pb^{II}X$], are monomeric [69(b)]. It is of interest that a crystalline sample of the lead compound, [(Giso)PbCl] **57**, was found to undergo a ligand modification reaction with atmospheric oxygen to give a low yield of the lead alkoxide species, **59** [74]. It is not known what the mechanism of this unusual reaction is, but it was suggested that it involved elimination of HCl *via* a radical process. To date, no examples of silicon(II) complexes of the form, [(guanidinate)SiX] or [(Nacnac)SiX] have been reported, but one related monomeric chlorosilylene, [$\{PhC(NBu^t)_2\}SiCl$] [75], has been obtained from the potassium reduction of [$\{PhC(NBu^t)_2\}SiCl_3$]. The further chemistry of this silylene has begun to be examined [15].

Reductions of all the Giso$^-$, Priso$^-$ and Piso$^-$ substituted complexes shown in Scheme 11 with potassium metal have been attempted. To date, success has only been had with **48** and **49**. Their reductions with excess potassium in toluene afforded the diamagnetic germanium(I) complexes, **60** and **61**, in low yields as lime green or dichroic green-red crystals respectively (Scheme 12) [71]. They are thermally very stable materials but are extremely air and moisture sensitive. The X-ray crystal structures of the compounds (e.g. Fig. 8) reveal them to have Ge–Ge distances (**60**: 2.6380(8) Å; **61**: 2.6721(13) Å) consistent with single bonded interactions, while their "trans-bent" geometries ($C_{backbone}$–Ge–Ge angles *ca.* 101°) suggest a stereochemically active lone pair of electrons at each germanium center. The compounds are closely related to the terphenyl stabilized digermynes, e.g. Ar*GeGeAr* (Ar* = $C_6H_3Ar_2$-2,6), developed by Power et al. [6,7]. These are germanium analogues of alkynes, but they are not linear and instead adopt "trans-bent" structures (C–Ge–Ge = *ca.* 129°) in the solid state. Their Ge–Ge interactions (*ca.* 2.28 Å) are considerably shorter than those of **60** and **61**, and theoretical studies on models of digermynes point towards Ge-Ge bond orders of close to 2 with the compounds exhibiting significant singlet diradicaloid character. Compounds **60** and **61** can be viewed as base stabilized amido-digermynes. In this respect, it is interesting to note that in one adduct of a digermyne, [Ar*Ge(CNMes)Ge(CNMes)Ar*] (Mes = mesityl), the Ge–Ge distance (2.6626(8) Å) is close to those in **60** and **61** [76]. Also of note is the recent preparation of a related digermylene, [$\{Ge[(Bu^tN)_2CPh]\}_2$], by the potassium reduction of [$ClGe\{(Bu^tN)_2CPh\}$] [77]. In contrast to "trans-bent" **60** and **61**, its crystal structure reveals a "gauche-bent" geometry which was confirmed as the thermodynamically favored conformation by DFT calculations.

DFT theoretical calculations on a model of **60**, *viz.* [$Ge\{(Ar'N)_2CMe\}]_2$ (Ar′ = $C_6H_3Me_2$-2,6), have also been performed and these led to an optimized geometry close to that of the experimental molecule [71]. The HOMO of the molecule largely comprises the high p-character Ge–Ge σ-bond, while the Ge lone pairs (HOMO-4) have high s-character but some directionality. Interestingly, the LUMO resembles a Ge–Ge π-bonding orbital, similar to that calculated for terphenyl substituted distannynes [6,7]. This observation highlighted the possibility of populating the LUMOs of **60** and **61** by their reduction with alkali metals, thus giving dianions with double bond character. In practice, the reactions of **60** and **61** with potassium led to their decomposition.

Although [(Nacnac)GeCl] has not been reduced to a germanium(I) species, it has proved a versatile reagent for the preparation of Nacnac$^-$ substituted Ge^{II} and Ge^{IV} complexes [15]. The synthetic potential of the related guanidinato germanium(II) and tin(II) complexes, **48**–**55**, has also been realized to some extent. The reported reactions of these compounds are depicted in Scheme 13. Firstly, the guanidinato germanium(II) cation, **62** [72], was prepared by a halide extraction reaction, *cf.* the preparation of [Ge(Nacnac)]$^+$ [78].

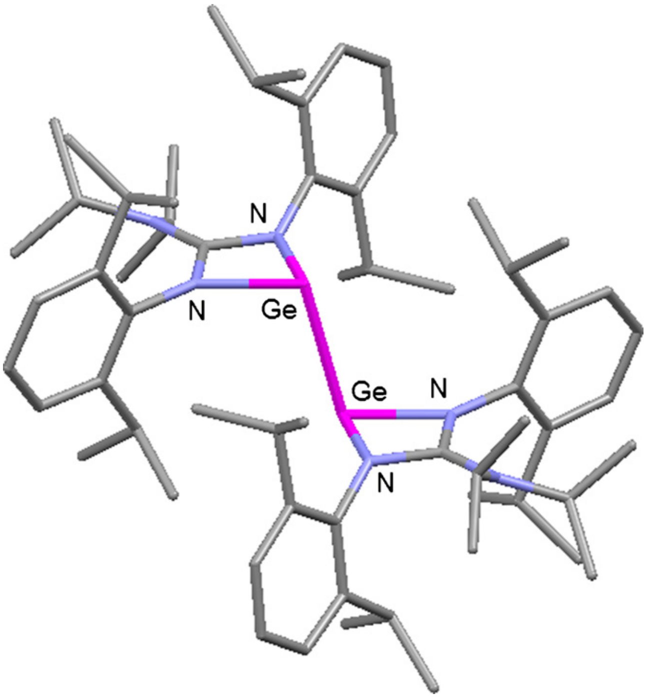
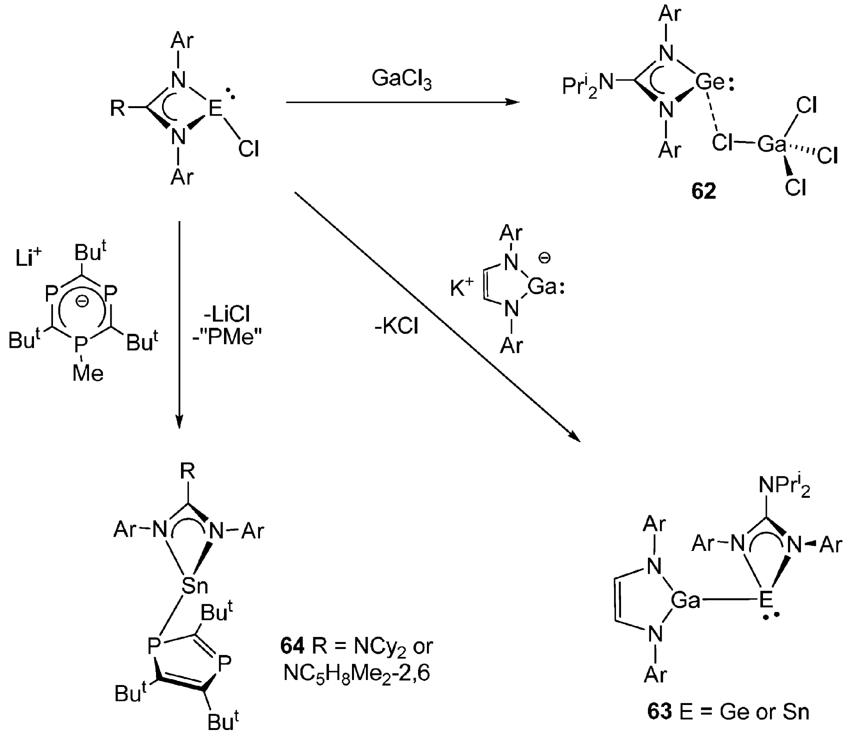


Fig. 8. The molecular structure of compound **61**.



Scheme 13.

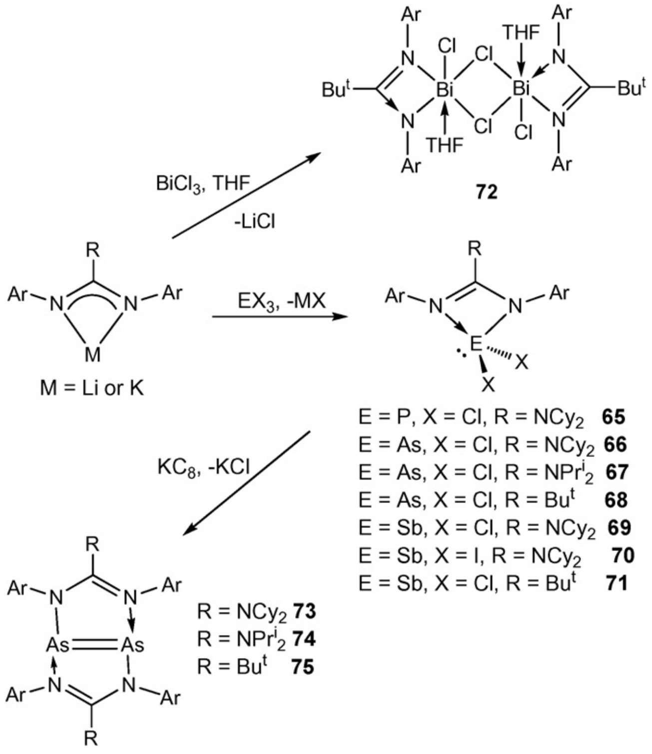
This cation is isoelectronic to the gallium(I) species, [:Ga(Giso)] **21**, and has a close contact with the $GaCl_4$ anion in the solid state. Salt metathesis reactions have given the germanium and tin gallyl complexes, **63** [79], and the tin diphospholyl species, **64** [73]. The latter are formed *via* elimination of the phosphinidene fragment, PMe, from the triphosphacyclohexadienyl reagent after the initial salt elimination. In the solid state, the diphospholyl ring is η^1-coordinated to the tin centers of the compounds, but in solution, NMR studies indicate fluxional coordination behavior for this ligand.

6. Group 15 complexes

The guanidinato and amidinato coordination chemistry of the group 15 elements is not as developed as those of groups 13 and 14 [18,19]. In addition, prior to the development of bulky Ar-substituted guanidinate ligands, there were no examples of such complexes with the group 15 element in the +1 oxidation state. In contrast, the chemistry of the dipnictenes, RE = ER (R = bulky alkyl, aryl, amide etc.; E = P, As, Sb or Bi), kinetically stabilized by sterically bulky monodentate ligands, is now extensive [80]. Given the obvious stabilizing credentials of bulky guanidinates, they have been employed in attempts to prepare base stabilized dipnictenes.

A variety of +3 oxidation state precursors to guanidinato dipnictenes have been prepared, as summarized in Scheme 14 [81,82]. Closely related complexes involving the bulky amidinate, Piso⁻, have been included for comparison, as in previous sections. In the solid state all the P, As and Sb complexes, **65**–**71**, are monomeric with distorted "saw-horse" geometries. The four-coordinate group 15 elements have stereochemically active lone pairs and the geometries of the chelating guanidinate or amidinate ligands imply they have predominantly localized backbones. In contrast, the recently reported Bi complex, **72**, is dimeric, and each six-coordinate Bi center is coordinated by a molecule of THF [82].

Examples of the P, As and Sb complexes have been treated with KC_8. In the case of the phosphorus complexes, intractable mixtures of many P-containing products were obtained. Reduction of the Sb complexes resulted in deposition of antimony metal, whereas reduction of the As-complexes led to the first examples of base stabilized amidodiarsenes, **73**–**75**, in low to moderate yields [81]. It is of note that the only related β-diketiminato complex to contain a group 15 element center in the +1 oxidation state, *viz.* $[(\eta^1\text{-N-L})_2\text{As–As}{=}\text{As}(\eta^2\text{-N,N}'\text{-L})]$ ($L = [(ArNCH)_2CPh]^-$), was subsequently prepared *via* the KC_8 reduction of $[LAsI_2]$ [83].



Scheme 14.

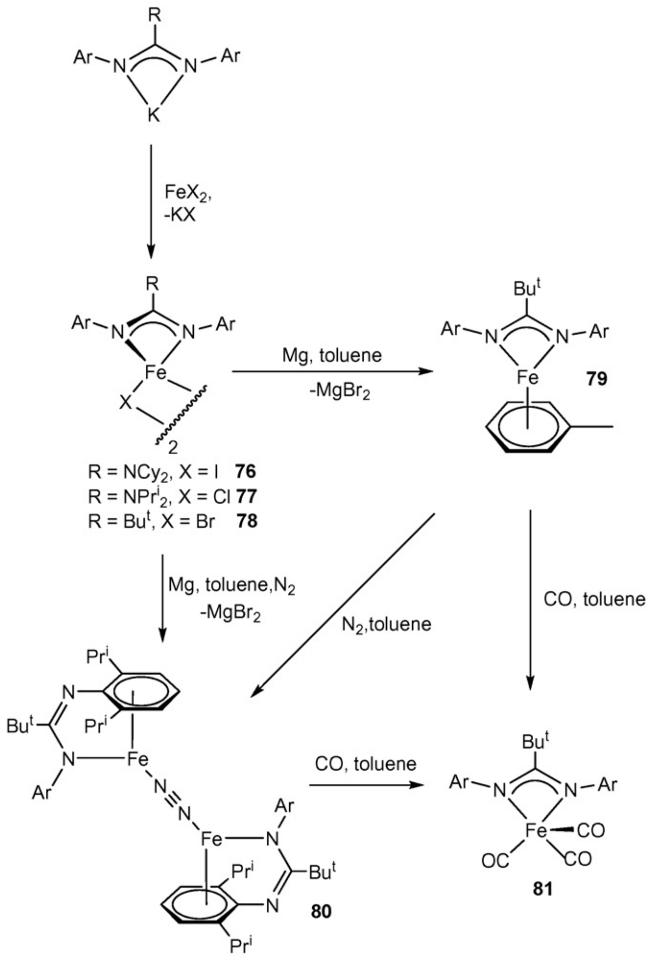
The X-ray crystal structures of **73**–**75** revealed that their ligands possess localized backbones, but also that they had changed their coordination mode from N,N′-chelating in the precursors to bridging in the reduced products. This, again, highlighted the coordinative versatility of the guanidinate ligands (and Piso$^-$). The As–As distance in the complexes, e.g. **73** 2.2560(5) Å, are short and in the normal range for As=As double bonds. Theoretical studies on a model complex, $[As_2\{\mu\text{-}(Ar'N)_2CNMe_2\}_2]$ ($Ar' = C_6H_3Me_2\text{-}2,6$) confirmed that the As–As interaction comprises a σ- and a π-bond, each of which is high in p-character, as is generally accepted for diarsenes [80]. The As–As π*-orbital is associated with the LUMO of the model.

7. Transition metal complexes

Structurally characterized guanidinato and amidinato complexes of the transition metals number more than 1000 [18–20]. The ligands in these compounds have exhibited a variety of coordination modes, though the two most common are N,N′-chelating and bridging. The latter mode is adopted in the ubiquitous multiply bonded dinuclear “paddle wheel” or “lantern” complexes, e.g. $[M_2(\mu\text{-guanidinate})_{3\text{ or }4}]$, originally developed by Cotton et al. [24]. Despite the plethora of such compounds, and the multitude of applications they have found, until recently there were no examples of guanidinato or amidinato first row transition metal complexes with a group 3–9 metal in the +1 oxidation state. Moreover, only one nickel(I) complex, $[Ni_2\{\mu\text{-}(NSiMe_3)_2CPh\}_2]$, has been reported [84], though this readily decomposes *via* disproportionation at room temperature. Copper(I) amidinates and guanidinates are, not surprisingly, relatively common [18–20].

It was proposed that the similarities between the stabilizing properties of bulky β-diketiminates and bulky guanidinates (and the related amidinate, Piso$^-$), might lend the latter to the synthesis of first row transition metal(I) complexes. This seemed an attainable goal as β-diketiminates had already been utilized in the preparation of metal(I) complexes from groups 5–12 [85]. These highly reactive species have already found a variety of applications as, for example, reagents for small molecule activations, catalysts and as enzyme mimics.

The first success in this area was had with iron(I). The potential iron(II) precursor molecules, **76**–**78**, were prepared by salt metathesis reactions (Scheme 15) [86]. All the complexes are stable towards redistribution reactions and their structural characterizations showed them to be halide bridged dimers. Unusually, reduction reactions of the amidinato complex, **78**, proceeded cleanly, whereas those of the bulkier guanidinate complexes yielded only intractable mixtures of products [86]. Reduction of **78** with magnesium in toluene under an argon atmosphere gave a good yield of the toluene capped, low spin complex, **79**. This represented the first amidinato iron(I) complex and is closely related to the low spin β-diketiminate complex, $[(Nacnac)Fe(\eta^6\text{-}C_6H_6)]$, developed by Holland and co-workers [85(d)]. When the reduction was carried out under an atmosphere of dinitrogen, the low spin, nitrogen bridged complex, **80**, resulted. This could also be prepared by bubbling N_2 gas through toluene solutions of **79**, which leads to displacement of the toluene ligand and a change in the coordination mode of the Piso$^-$ ligand from N,N′- to N,Ar-chelating. Compound **80** is related to the high spin, N,N′-chelated, dinitrogen bridged β-diketiminate complex, [(Nacnac)Fe=N=N=Fe(Nacnac)] [87], though in this compound the X-ray crystallographic and Raman spectroscopic data (N–N distances *ca.* 1.18 Å; $\nu(N_2)$: 1810 cm^{-1}) indicated significant activation of the N_2 ligand. In **80**, the same data (1.124(6) Å; $\nu(N_2)$: 2005 cm^{-1}) are consistent with only weak N_2 activation. Treating either **79** or **80** with CO gave high yields of the iron(I) carbonyl complex, **81**.



Scheme 15.

Soon after this report appeared, Tsai et al. published two papers on the remarkable amidinate bridged chromium(I) complexes, **82**–**84** (Fig. 9) [88]. These were prepared *via* KC_8 reductions of chromium(II) or chromium(III) precursors. All three compounds are diamagnetic and have extremely short Cr–Cr bonds (*ca.* 1.74 Å). Theoretical studies on models of each showed that they possess Cr–Cr quintuple bonds, and as such they are closely related to the landmark quintuply bonded complex, Ar′CrCrAr′ ($Ar = C_6H_3Ar_2\text{-}2,6$), reported by Power and co-workers [89]. Very recently, a guanidinate bridged, quintuply bonded system closely related to **83** and **84**, *viz.* $[Cr_2\{\mu\text{-}(ArN)_2CNMe_2\}_2]$, was reported to be obtained from the reduction of a chromium(II) chloride precursor, $[\{Cr(\mu\text{-}Cl)[(ArN)_2CNMe_2]\}_2]$ [90]. X-ray crystallography showed this diamagnetic material to have the shortest metal–metal distance, 1.7293(12) Å, yet reported.

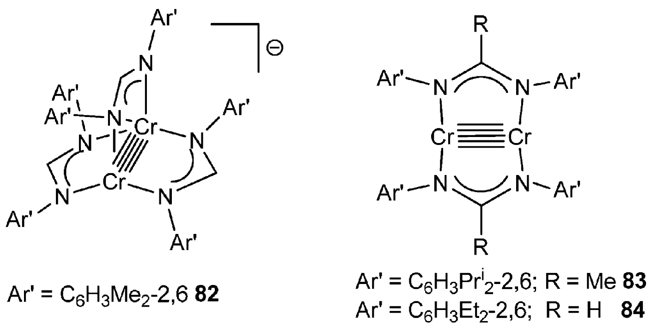
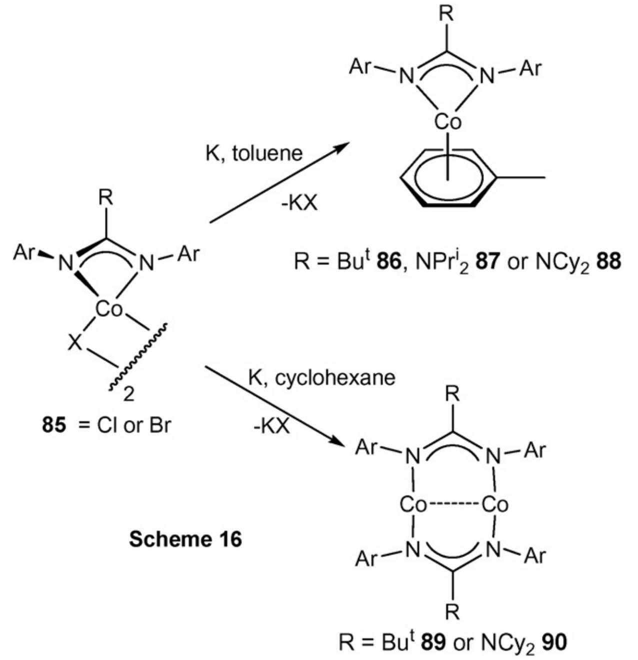
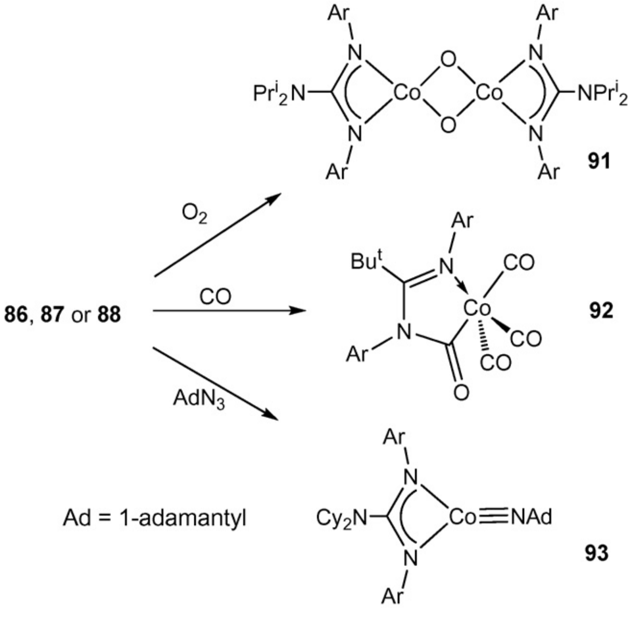


Fig. 9. Amidinate bridged, quintuply bonded chromium(I) dimers, **82**–**84**.



Scheme 16.



Scheme 17.

The earlier studies by Tsai prompted an extension of the use of bulky guanidinates and amidinates to the preparation of cobalt(I) species. The heteroleptic cobalt(II) precursor complexes, **85**, were prepared by salt metathesis reactions [91]. Their reduction with potassium metal in toluene under a nitrogen atmosphere did not lead to dinitrogen complexes, but instead gave the very reactive toluene capped complexes, **86**–**88** (Scheme 16). These are reminiscent of the β-diketiminate complex, [(Nacnac)Co(η^6-toluene)] [85(e)], which has been shown to be effective in small molecule activation reactions. SQUID studies on **87** revealed it to be a high spin d^8-complex with an $S = 1$ ground state. Reduction of **86** and **88** in cyclohexane led to a very different result, namely the formation of the ligand bridged cobalt(I) dimers, **89** and **90**. The X-ray crystal structures of these dimers (e.g. Fig. 10) showed them to have the shortest Co–Co interactions (**89** 2.1404(10) Å; **90** 2.1345(7) Å) of the more than 5600 examples collected on the Cambridge Crystallographic Database. Unlike the related chromium dimers, **83** and **84**, they are paramagnetic and display what approximates as Curie behavior (**89**: $\theta = -3.07$ K, $C = 3.49$ cm^3 mol^{-1} K) in the temperature range of 300–2 K. These data are consistent with **89** and **90** possessing either two high spin d^8 metal centers (each $S = 1$) that have little magnetic communication, or the compounds have isolated $S = 2$ ground states. From a qualitative point of view, the latter can potentially be explained when comparisons are drawn with the related diamagnetic chromium(I) dimers, **83** and **84**. DFT calculations on a model of these suggested their quintuple bonds arise from the filling of five molecular orbitals having predominantly metal–metal bonding character (1 σ, 2 π and 2 δ). The unoccupied frontier molecular orbitals of that model system are largely metal–metal antibonding in character. If a similar ordering of molecular orbitals occurs for compounds **89** and **90**, then the extra six electrons that originate from the two cobalt centers (*cf.* chromium) could doubly occupy one and singly occupy four molecular orbitals having metal–metal antibonding character. This would give rise to compounds having quintet ground states and relatively strong Co–Co interactions (B.O.s of *ca.* 2). However, extensive theoretical calculations (CASPT2) on models of both the amidinate and guanidinate bridged dimers indicated highly multiconfigurational character to the wave functions of each, and an accurate quantification of their metal–metal bond orders was not possible.

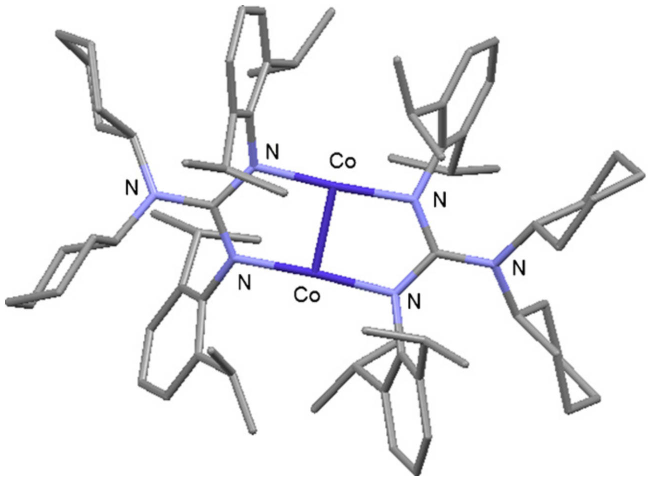
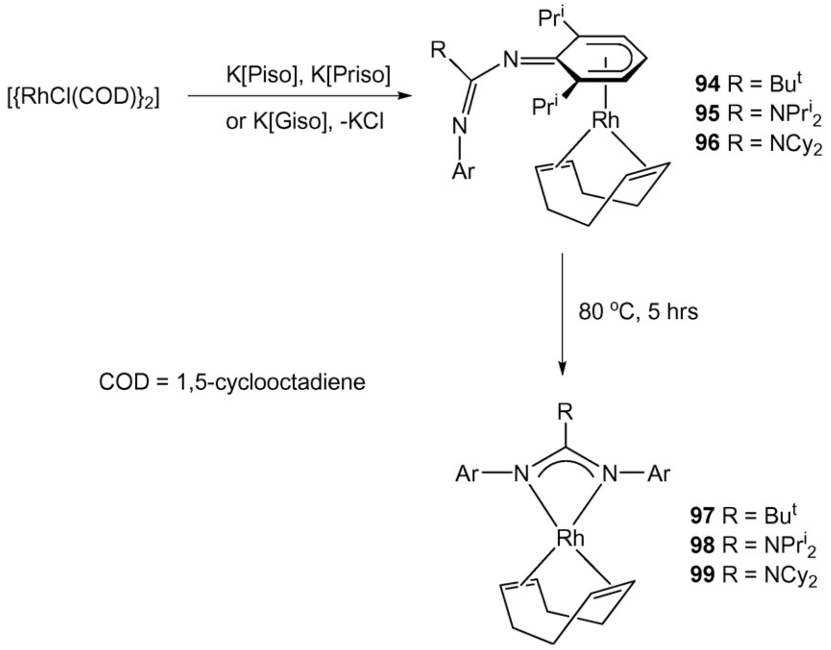


Fig. 10. The molecular structure of compound **90**.

Preliminary reactivity studies have been carried out on the cobalt(I) compounds, **86**–**88** [91]. Although they do not react with dihydrogen, **87** is readily oxidized to give the square planar cobalt(III) species, **91** (Scheme 17). Treatment of **86** with CO led to the unusual diamagnetic iminocarbamoyl complex, **92**, *via* insertion of CO into its N–Co bond. Perhaps of most interest is the reaction of **88** with 1-adamantyl azide (AdN$_3$) which gave a good yield of the diamagnetic, linear cobalt imide compound, **93** (*cf.* the formation of [(Nacnac)Co≡NAd] from [(Nacnac)Co(η^6-toluene)] and AdN$_3$ [85(e)]). Of note is the Co≡N distance in this compound (1.621(3) Å), which is identical to that in [(Nacnac)Co≡NAd], and both are shorter than in other four-coordinate imido cobalt complexes.

In a related study, salts of the same bulky ligands were allowed to react with the [{RhCl(COD)}$_2$] dimer in the expectation that monomeric N,N′-chelated products would be formed. This proved not to be the case and instead the unusual 18-electron iminocyclohexadienyl rhodium(I) complexes, **94**–**96**, resulted (Scheme 18) [92]. It seemed possible that these compounds could be isomerized to the expected 16-electron species, **97**–**99**. Indeed, this occurred



Scheme 18.

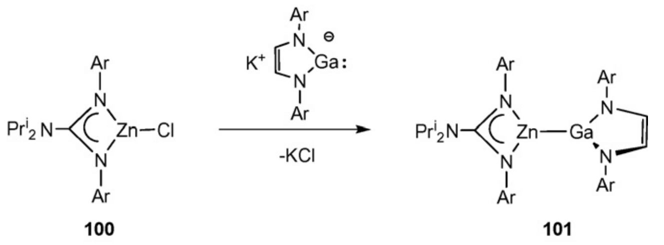
quantitatively by heating toluene solutions of the compounds at 80 °C for up to 5 h, thus indicating that **94**–**96** are the kinetic products of the original reaction and **97**–**99** are their thermodynamic isomers. Kinetic studies on these isomerizations were carried out and it was determined that they are unimolecular processes following first order kinetics. Not surprisingly, there was an inverse correlation between the rates of the isomerizations and the bulk of the ligand backbone substituent.

The only other transition metal compounds incorporating one of the bulky guanidinate ligands that are the focus of this review, have come from a study aimed at synthesizing compounds exhibiting the first Zn–Ga bonds in molecular compounds. In this respect [(Priso)ZnCl] **100** was prepared in the reaction of Li[Priso] and $ZnCl_2$. Its reaction with an anionic gallium(I) heterocycle (Scheme 19) yielded the sterically encumbered zinc gallyl complex, **101**, which was crystallographically characterized and shown to have a Zn–Ga bond length of 2.3230(7) Å [93].

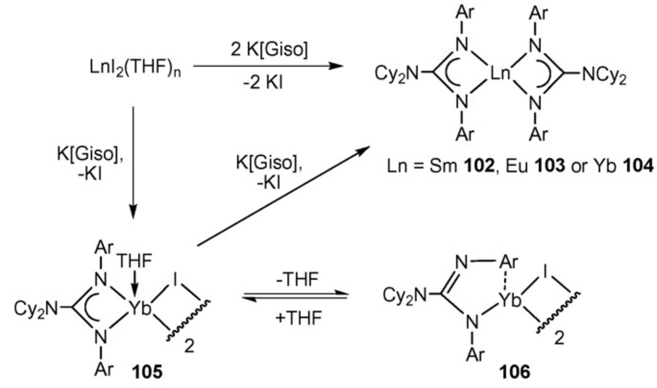
8. Lanthanide metal complexes

Although no lanthanide(I) complexes have been stabilized by bulky guanidinate ligands, one report has detailed the syntheses of the first structurally characterized homoleptic lanthanide(II) guanidinate complexes, **102**–**104**, by simple salt metathesis reactions (Scheme 20) [94]. It is of interest that these four-coordinate complexes were obtained even when the reactions were carried out in THF. In contrast, in the related reaction between SmI_2 and the less bulky amidinate anion, $[(ArN)_2CH]^-$ ($Fiso^-$), the six-coordinate complex, $[Sm(Fiso)_2(THF)_2]$ was formed [95]. These differences arise from the superior steric bulk of $Giso^-$. Analogies between ligands such as $Giso^-$ and β-diketiminates are again evident, considering that related homoleptic complexes such as $[Yb(Nacnac)_2]$ have been prepared [96]. In these complexes the ytterbium center has a distorted tetrahedral geometry, just as is the case with the ytterbium guanidinate species, **104**. In contrast, the solid state structures of the Sm and Eu analogues (e.g. Fig. 11) show their metal centers to have planar four-coordinate geometries, which were unprecedented for lanthanide chemistry. This geometry does not seem to be sterically enforced when it is taken into account that Yb^{2+} has a smaller ionic radius than Sm^{2+} and Eu^{2+}, and compound **104** is tetrahedral. It was proposed that the “vacant” coordination sites in **102** and **103** might allow access of linear unsaturated substrates, e.g. CO_2 or alkynes, to their metal centers, potentially giving rise to selective reductive coupling reactions, though this is yet to be realized.

Attempts were also made to form heteroleptic lanthanide complexes incorporating the $Giso^-$ ligand. The only success was had with Yb^{2+} in the formation of the five-coordinate dimeric complex, **105** [94]. When solid samples of this yellow compound were placed under vacuum, they lost their coordinated THF molecule to



Scheme 19.



Scheme 20.

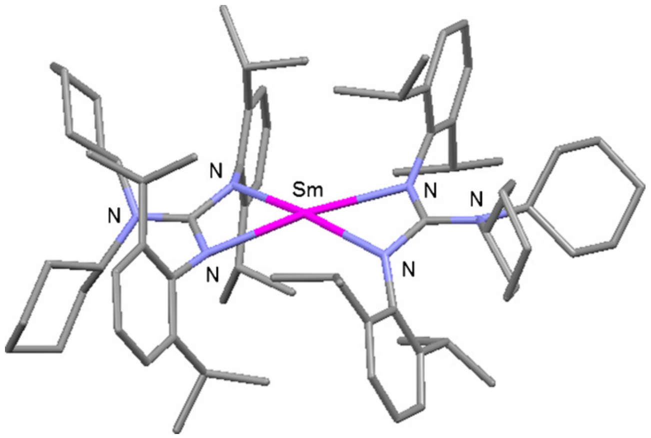


Fig. 11. The molecular structure of compound **102**.

give the red compound, **106**. Remarkably, this solid state process involved a change in the guanidinate ligand coordination from N,N′-chelating to N,Ar-chelating. Dissolution of **106** in THF quantitatively regenerated **105**. It is noteworthy that the only other example of an Ar-substituted guanidinato complex of a lanthanide metal is the Y(III) species, $[Y\{(ArN)_2CNMe_2\}(CH_2SiMe_3)_2(THF)]$, which is a highly active alkene hydrosilylation catalyst [97].

9. Conclusions

The rapid development of low oxidation state main group chemistry over the past two decades has generated some of the most interesting advances in the history of the field. These advances have been allowed by the emergence of an ever increasing variety of sterically and/or electronically stabilizing ligands. We have added to the discipline with the development of a new class of extremely bulky guanidinate ligand. These have been used to prepare unprecedented examples of heterocycles containing groups 2, 13, 14 or 15 elements in the +1 oxidation state. The ligands have also been harnessed in the preparation of the only examples of guanidinato, and/or closely related amidinato, complexes of iron(I), cobalt(I) and planar four-coordinate lanthanide(II) metals. Preliminary studies of the further chemistry of these very reactive complexes have highlighted their worth as unusual metal donor ligands, as novel reducing agents in organic synthesis, and in the activation of small molecules. Throughout all of these studies, the bulky guanidinate ligands have exhibited ligating and stabilizing properties more akin to those of bulky β-diketiminate ligands than less bulky amidinates or guanidinates. Saying this, the bulky guanidinates have certainly exhibited a much greater coordinative flexibility than β-diketiminates, which is demonstrated by the several coordination modes they have been shown to adopt. These coordination modes appear to be readily interchangeable in many of the guanidinate complexes described herein, which augers well for their future use in, for example, catalysis. Although the study of very low oxidation state complexes of bulky guanidinate ligands is only 4 years old, many exciting results have already been generated. There is no doubt that the future is bright for these ligands, and later generations of related ligands that will inevitably follow.

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