

N-Heterocyclic Carbene Analogues with Low-Valent Group 13 and Group 14 Elements: Syntheses, Structures, and Reactivities of a New Generation of Multitalented Ligands[†]

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Received July 12, 2010

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1. Introduction

The stabilization and isolation of highly reactive species has long been the subject of chemical research. This review will focus on a large and important class of reactive species that has only recently received considerable attention: low-valence element heterocycles of the group 13 and 14 elements. The unifying feature of these species is the bifunctionality at the element center, which has a lone pair of electrons and a formally vacant π -orbital. Therefore, these species can display not only the expected electrophilic reactivity of other low-valent species but also nucleophilic reactivity at the element center. It is, in fact, this unique reactivity that is the focal point of this review because, while these species are fundamentally important to a broader understanding of main group chemistry, their reactivity should also lead to applications in synthetic and materials chemistry, catalysis research, and perhaps beyond. The reactivity described in this review not only summarizes what has been done but also highlights the potential of these species.

While much of the research in this field is quite recent there has been an astonishing amount of work done, and therefore the focus will be limited to elements of groups 13 and 14 with two nitrogen functionalities in ring sizes from four to six. The four-membered ring systems will be limited to those based on amidinate and guanidinate backbones, while the six-membered rings all feature the well-known β -diketiminato ligand.

This review is organized in such a way as to group the elements and ring structures together. The intrinsic differences between the group 13 and 14 elements make it necessary to have slightly different parameters for each section, and these specifics are introduced at the beginning of their respective sections.

2. Group 13 Element(I) N-Heterocycles

It is the intention of the first section of this paper to review the synthesis, structure, bonding, properties, and function of monocyclic systems incorporating a group 13 element, formally in the +1 oxidation state and being N,N-chelated by ligands with unsaturated backbones. The chemistry of

[†] This paper is part of the Main Group Chemistry special issue.

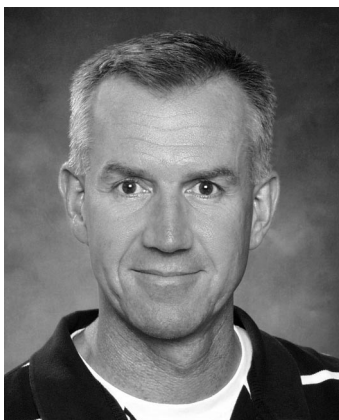
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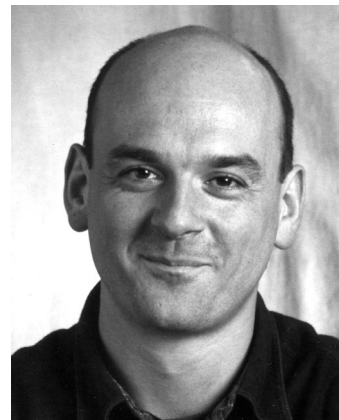


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Cameron Jones was born in Perth, Australia. He completed his B.Sc.(Hons.) degree at the University of Western Australia in 1984. From 1985 to 1987, he worked as a Research Officer at the University Department of Surgery, Royal Perth Hospital. His Ph.D. degree was gained from Griffith University, Brisbane, under the supervision of Professor Colin L. Raston in 1992. He then moved to a postdoctoral fellowship (1992–1994) at Sussex University under the supervision of Professor John F. Nixon FRS. From 1994, he held a lectureship at The University of Wales, Swansea, before moving to a Readership in Inorganic Chemistry at Cardiff University (1998). There, he was promoted to a Personal Chair in Inorganic Chemistry in 2002. In 2007, he moved to Monash University, Melbourne, where he is currently an ARC Professorial Research Fellow and Professor of Chemistry. He has been the recipient of several awards, including the Main Group Chemistry Prize of the Royal Society of Chemistry (2004) and the Senior Research Award of the Alexander von Humboldt Foundation (2008). His current research interests are wide ranging, with particular emphasis being placed on the fundamental and applied chemistry of low oxidation state/low coordination number s-, p-, and d-block metal complexes and unusual metal–metal bonded systems. In these and related areas, he has published more than 250 papers.

monomeric four-, five-, and six-membered heterocycles of the general form **A–C** (Figure 1) will be addressed. While only heterocycles of the type **B** are true valence isoelectronic analogues of the classical “Arduengo” N-heterocyclic carbenes, heterocycle types **A** and **C**, with their singlet lone pairs, can be thought of as isolobal with four- and six-membered N-heterocyclic carbenes. Because the chemistry



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of heterocycles of the type **A–C** is not nearly as developed as that of heavier group 14 NHC analogues, a fairly comprehensive treatment of the field can be given here. This includes information in several prior reviews, which have detailed certain isolated aspects of the area.^{1–10} Special attention is paid to the applications and further chemistry directly derived from heterocycles **A–C**, while comparisons with the chemistry of NHCs is made where appropriate. It should be noted that it is outside the scope of this review to systematically draw comparisons between the chemistry of heterocycles of type **A–C** and that of related group 13 element(I) systems, for example, metal and boron diyls, $E-R$ ($E = B-Tl$; $R = \text{alkyl, aryl, amino, etc.}$), polycyclic systems, for example, $:E(Tp)$ ($Tp = \text{a tris(pyrazolyl)borate}$), etc. The known chemistry of such compounds is considerably more extensive than that of **A–C** and has been the subject of numerous reviews.¹¹

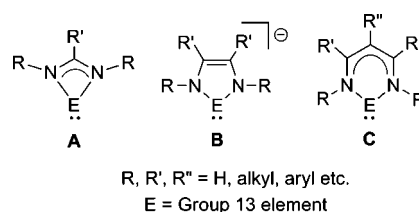


Figure 1. General structures of group 13 metal(I) N-heterocycles.

2.1. Boron(I) Heterocycles

2.1.1. Four-Membered Rings

The preparation of the first four-membered NHC, $\text{:C}\{\text{(DipN)}_2\text{PNPr}'_2\}$ (Dip = 2,6-diisopropylphenyl), was reported by Grubbs and Despagne-Ayoub in 2004.¹² It was not until 2008 that the first efforts to form boron(I) analogues of such systems were described. Cowley et al. carried out DFT (B3LYP) and MP2 calculations on the model boron(I) guanidinate complex, $\text{:B}\{(\text{PhN})_2\text{CNMe}_2\}$, which yielded singlet–triplet energy gaps for the heterocycle of 6.0 and 10.1 kcal mol^{−1} respectively.¹³ These values are significantly smaller than those calculated for heavier group 13 analogues (*vide infra*), but they suggested that singlet boron(I) guanidinate complexes may be stable at ambient temperature if sufficiently sterically protected. The boron lone pair of the singlet state of the model was found to be associated with the HOMO of the complex, implying that such heterocycles should be nucleophilic. Potential neutral or cationic guanidinato boron(III) halide precursors to boron(I) heterocycles have been described, namely, $[\text{X}_2\text{B}\{(\text{ArN})_2\text{CNR}_2\}]$ (X = Cl or Br, Ar = mesityl (Mes) or Dip, R = cyclohexyl (Cy), Prⁱ or Ph) and $[\text{BrB}\{(\text{DipN})_2\text{CNCy}_2\}][\text{GaBr}_4]$,^{13,14} though attempts to reduce these with Na, K, or Na/K alloy in various solvents led to no reaction or intractable product mixtures. Stable four-membered boron(I) heterocycles remain unknown to date.

2.1.2. Five-Membered Rings

Prior to their eventual isolation, two theoretical studies examined the geometry and electronic structure of the model N-heterocyclic boryl anion, $[\text{:B}\{\text{N}(\text{H})\text{C}(\text{H})\}_2]^-$, with similar results. DFT calculations at several levels of theory suggested that although its singlet–triplet gap (20.2–23.1 kcal/mol) is significantly less than those of heavier group 13 analogues (*vide infra*), N-heterocyclic boryl anions should be experimentally achievable targets.¹⁵ The results of this study, and those from *ab initio* calculations of the heterocycle,¹⁶ showed that the singlet lone pair at the boron center is associated with the HOMO, and that, although polarized, the B–N bonds of the heterocycle are essentially covalent. Moreover, an NBO analysis of the heterocycle pointed toward a build up of negative charge at its B-center, all of which implied that such systems should be very nucleophilic entities. A number of theoretical techniques were employed in both studies to determine the degree of π -delocalization over the heterocycle. These indicated that although the delocalization is significant and the p-orbital at boron (orthogonal to the heterocycle plane) is partially occupied, there is considerably less aromatic stabilization than in the isoelectronic parent N-heterocyclic carbene, $\text{:C}\{\text{N}(\text{H})\text{C}(\text{H})\}_2$. In a closely related study, quantum chemical calculations at the density functional level have been applied to examine the P-heterocyclic boryl anion, $[\text{:B}\{\text{P}(\text{H})\text{C}(\text{H})\}_2]^-$, which incorporates the parent diphosphabutadiene in the heterocycle backbone.¹⁷ It was found that the P–B bonds in the anion are more covalent than the N–B bonds in $[\text{:B}\{\text{N}(\text{H})\text{C}(\text{H})\}_2]^-$ due to the lower electronegativity of phosphorus relative to nitrogen. Despite this, the singlet–triplet energy gap for the boron center of the P-heterocycle was calculated at several levels of theory to be significantly lower (11.5–12.7 kcal/mol) than that of $[\text{:B}\{\text{N}(\text{H})\text{C}(\text{H})\}_2]^-$.

A number of theoretical studies have examined various aspects of heterocyclic boryl anions since the early reports

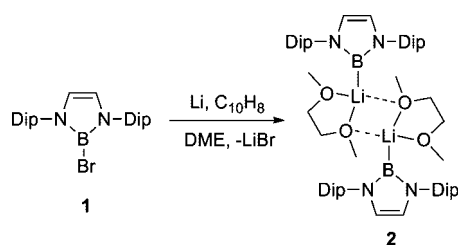
mentioned above. In one very thorough study, a variety of electronic properties of $[\text{:B}\{\text{N}(\text{H})\text{C}(\text{H})\}_2]^-$ were calculated and compared with 15 isovalent group 13–16 heterocycles.¹⁸ Although the conclusions drawn from this study were essentially the same as from those above, the π -accepting capabilities of the boryl anion in its late transition metal complexes were predicted to be weak, while again it was suggested that cyclic boryl anions would be very strong nucleophiles. This has been quantified to some extent in a recent study, which utilized DFT and *ab initio* methods to investigate the nucleophilicity of a series of model N-, O- and N/O-heterocyclic boryl anions as their lithium complexes, $[\text{LiB}\{\text{E}(\text{R})\text{C}(\text{H})\}_2]^-$ (E = N, O, or both; R = nothing (for E = O) or H, Me, Ph etc. (for E = N)).¹⁹ The proton affinities (and by implication, the nucleophilicity) of all were found to be very high, which based on the polarity of the $\text{B}^{\delta-}-\text{Li}^{\delta+}$ bond is not surprising. In fact, calculations on the experimentally observed lithium boryl complex, $[(\text{THF})_2\text{LiB}\{\text{N}(\text{Dip})\text{C}(\text{H})\}_2]$ (*vide infra*), have indicated that its B–Li interaction is largely ionic with a polarity not dissimilar to that of the C–Li bonds of alkyl lithium reagents.^{20,21} The kinetic stabilities of cyclic boryl anions have also been calculated to increase with increasing steric bulk of the heterocycle substituents.²²

Based on the relatively small calculated singlet–triplet energy gaps of N-heterocyclic boron(I) heterocycles, it is not surprising that analogues incorporating each of the heavier group 13 metals in the +1 oxidation state were experimentally realized before their boron counterparts. Saying this, five-membered boron(I) heterocycles, $[\text{:B}\{\text{N}(\text{R})\text{C}(\text{R}')\}_2]^-$ (R, R' = H, alkyl, aryl, etc.) were seen as particularly attractive targets because they could be regarded as examples of boryl anions, BR_2^- . Prior to 2006, no s-block metal boryl complexes had been crystallographically characterized, though their reactivity as nucleophilic boryl anions had been implied by the products of trapping reactions with various electrophiles.^{1,23} These were important steps forward in boryl chemistry because in almost all of the numerous organic synthetic transformations involving boron reagents, the boron species acts as an electrophile. Furthermore, the few examples of reactions in which boron does act as a nucleophile are generally metal-catalyzed. Given the vast importance of carbanions in organic synthesis, the availability of a well-defined source of boryl anions would open up many synthetic possibilities to the organic and inorganic chemist.

A number of early attempts were made to prepare five-membered boryl anions. Most notable is the work of Weber et al. who investigated the reductions of several 1,3,2-diazaboroles, for example, $[\text{XB}\{\text{N}(\text{Bu}')\text{C}(\text{H})\}_2]$ (X = Br, SMe, SBu') with alkali metals under a number of conditions.^{24,25} In all cases, boron(I) products were not isolated, but instead boron(III) and boron(II) products were, for example, $[\text{HB}\{\text{N}(\text{Bu}')\text{C}(\text{H})\}_2]$ or $[\{\text{B}\{\text{N}(\text{Bu}')\text{C}(\text{H})\}_2\}_2]$. It was suggested that intermediates in these reactions could be the target boryl anion, $[\text{B}\{\text{N}(\text{Bu}')\text{C}(\text{H})\}_2]^-$, or the boron radical, $[\text{B}\{\text{N}(\text{Bu}')\text{C}(\text{H})\}_2]$, which abstracted hydrogen from the reaction solvent or dimerized, respectively. However, no spectroscopic evidence for either species was forthcoming.

Using a very similar methodology to that of Weber, Segawa et al. described the reduction of the bulkier 1,3,2-diazaborole, $[\text{BrB}\{\text{N}(\text{Dip})\text{C}(\text{H})\}_2]$ (**1**), with lithium metal in DME in the presence of a catalytic amount of naphthalene. This led to the formation (28.3% yield) of the thermally

Scheme 1



sensitive, dimeric lithium boryl complex, **2**, as a crystalline solid (Scheme 1).²⁶ The importance of this result to boron chemistry cannot be understated, and several highlight articles confirming this point appeared shortly after its publication.^{27,28} The X-ray crystal structure of **2** revealed it to have B–Li bonds (2.291(6) Å) that are 8.5% longer than the sum of the covalent radii for the two elements. In addition, the intraring geometry of the anion was found to be close to that calculated for the parent boryl anion, $[\text{B}\{\text{N}(\text{H})\text{C}(\text{H})\}_2]^-$. Both observations suggested a highly polarized B–Li interaction with significant anionic character at boron. NMR spectra of solutions of **2** in d_8 -THF were consistent with the replacement of Li coordinated DME by THF in the compound. The ^{11}B and ^7Li NMR spectra displayed broad signals at δ 45.4 ppm and δ 0.46 ppm, respectively, and no resolvable coupling to other nuclei was observed. In contrast, calculations on the model system $[(\text{H}_2\text{O})\text{LiB}\{\text{N}(\text{H})\text{C}(\text{H})\}_2]$ gave a $^1J_{\text{BLi}}$ coupling constant of 92.5 Hz,²⁹ though in that compound the Li center is two-coordinate, as opposed to the likely higher Li coordination number of **2** in THF solutions.

Subsequent to this initial report, the same group prepared a variety of closely related lithium boryl complexes using similar synthetic methodologies to that used in the preparation of **2** (Figure 2).^{20,21,30} These include the “Wanzlick” boryl complexes, **4** and **7**, and the benzannulated heterocycle **5**. It is of note that the mesityl-substituted systems, **6** and **7**, are less thermally stable than the bulkier Dip-substituted compounds and can decompose via intramolecular processes, for example, C–H activation of the mesityl *ortho*-methyl groups. The spectroscopic data for all the lithium boryl complexes are comparable, but it is of note that the B–Li distances in the solid-state structures of three-coordinate **3–5**, are significantly shorter than those in four-coordinate **2**. However, all are greater than the sum of the covalent radii for B and Li.

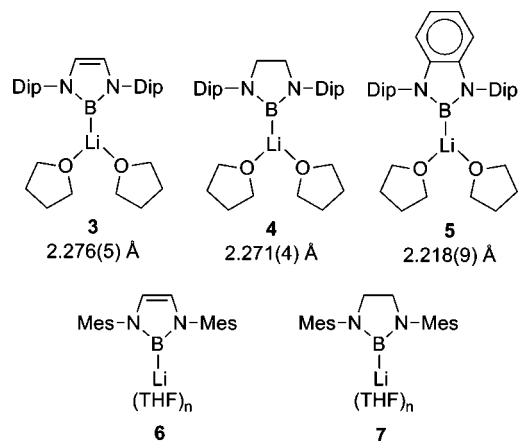


Figure 2. Boryl–lithium complexes (solid-state B–Li distances given where known).

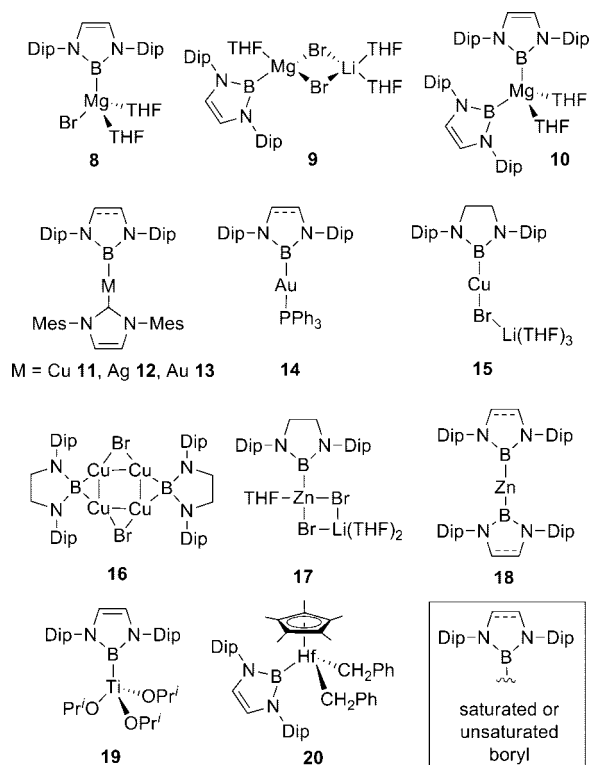


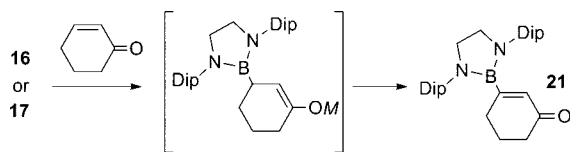
Figure 3. Magnesium and d-block metal boryl complexes.

Although the further chemistry of isolable lithiated boryl heterocycles is only in its infancy, the predicted ability of these complexes to act as sources of very nucleophilic boryl anions has been amply demonstrated by their reactions with a wide range of organic electrophiles, for example, aldehydes, alkyl halides, acyl halides, esters, etc.^{2,20,26,30} The synthetic transformations resulting from these are generally moderate to high yielding.

The availability of lithium boryl complexes as sources of boryl anions has also opened up a new synthetic route to other metal boryl complexes, namely, nucleophilic attack on metal halide complexes, leading to lithium halide elimination. This has led to the synthesis of several new classes of metal boryls, which themselves can be used for synthetic transformations. The formation of these metal boryl complexes (which are summarized in Figure 3) has so far largely mirrored the well-developed metal–gallyl chemistry derived from the gallyl anion, $[\text{Ga}\{\text{N}(\text{Dip})\text{C}(\text{H})\}_2]^-$ (see section 2.3.2). The reactions of **3** with MgBr_2 under varying stoichiometries have given a series of magnesium boryl complexes, **8–10**, which contain the first structurally characterized Mg–B bonds in molecular compounds.³¹ The Mg–B distances and intraheterocyclic geometries in these complexes indicate that the Mg–B bonds have high ionic character. This was seemingly confirmed by the reaction of the boryl “Grignard” reagent **8** with benzaldehyde, which led to nucleophilic attack at the substrate and the formation of the first fully characterized acylborane, $[\text{Ph}(\text{O})\text{CB}\{\text{N}(\text{Dip})\text{C}(\text{H})\}_2]$. Surprisingly, none of the corresponding alcohol, $[\text{Ph}(\text{OH})(\text{H})\text{CB}\{\text{N}(\text{Dip})\text{C}(\text{H})\}_2]$, was formed in this reaction, though it was the major product in the analogous reaction with the lithium boryl, **3**.

A handful of transition metal boryl complexes have also become available by using lithium boryl complexes in salt metathesis reactions. These include the mixed NHC/boryl group 11 complexes, **11–13**, and the gold boryls, **14**, all of

Scheme 2



which can contain either saturated or unsaturated boron heterocycles.³⁰ Compounds **12–14** were the first structurally characterized silver or gold boryl complexes, while a pinacoloboryl copper complex had previously been reported by Sadighi et al. and shown to act as a nucleophile toward carbonyl substrates.^{32,33} An examination of the structural and spectroscopic features of these complexes indicated that their boryl ligands, like those in previously reported boryl complexes,³² have high trans influences and are, in fact, some of the strongest σ -donors known. Interestingly, however, there was little discernible difference between the trans influences of the saturated and unsaturated boryls, despite the expected greater nucleophilicity of the former. Subsequently, a range of other copper and zinc boryl complexes, **16–18**, were prepared and fully characterized.³⁴ Two of these were allowed to react with an α,β -unsaturated ketone, yielding conjugate addition products, **21** (Scheme 2). In contrast, the reaction of the lithium boryl, **3**, with the substrate gave only the borane, $[\text{HB}\{\text{N}(\text{Dip})\text{CH}_2\}_2]$. The intermediate copper enolate in Scheme 2 was also trapped by addition of SiMe_3Cl .

More recently, the first examples of group 4 boryls, **19** and **20**, were prepared via the elimination of lithium isopropoxide (**19**) or lithium chloride (**20**).³⁵ DFT calculations on models of both complexes revealed them to possess polar covalent M–B σ -bonds, associated with their HOMO-1. An admixture of **20** with $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ was shown to have a similar activity toward the polymerization of either ethylene or hex-1-ene as do other hafnium half-sandwich catalyst systems.

Although in its infancy, the chemistry of nucleophilic five-membered boryl lithium complexes holds much potential in organic and inorganic synthesis. Saying this, the thermal instability and steric bulk of such systems will likely hinder the rapid advancement of their use by a broad range of chemists. Perhaps, the more stable but less nucleophilic magnesium, copper, and zinc boryls derived from these systems will be more attractive to synthetic chemists, though, at least in the case of copper, well characterized and less bulky boryl complexes are already at hand. It is noteworthy that a carbene-coordinated, five-membered, nitrogen free boryl anion, $\text{K}[\{(\text{H}_2\text{C}(\text{Mes})\text{N})_2\text{C} \rightarrow \text{BC}_4\text{Ph}_4\}]$, has recently been reported and shown to act as a π -nucleophile.³⁶ A major challenge for synthetic chemists will be to apply the nucleophilic boryl complexes described here to catalytic organic transformations, for example, diboration reactions.

2.1.3. Six-Membered Rings

No examples of N-heterocyclic boron(I) systems have yet been isolated, despite analogous systems being known for all of the group 13 metals. Several theoretical studies of heterocycles of the type $[\text{B}\{[\text{N}(\text{R})\text{C}(\text{R}')_2\text{CH}]\}]$ ($\text{R} = \text{H}, \text{Me}$ or Ph ; $\text{R}' = \text{H}$ or Me), have been carried out.^{37,38} These have revealed that such heterocycles have much smaller singlet–triplet energy separations (<3.5 kcal/mol) than their heavier homologues and should, therefore, be difficult to prepare and very reactive if synthetically accessible. It has been predicted

that they will readily participate in C–H activation reactions of alkanes and, thus, the isolation of examples of such compounds remains a substantial synthetic challenge.

2.2. Aluminum(I) Heterocycles

2.2.1. Four-Membered Rings

No examples of four-membered N-heterocyclic aluminum(I) compounds have been reported in the literature. One DFT theoretical study (BP86) of the guanidinato-coordinated Al(I) complex, $[\text{Al}\{(\text{PhN})_2\text{CNMe}_2\}]$, showed its singlet lone pair to be associated with the HOMO while the LUMO largely comprises the empty p-orbital at the aluminum center, orthogonal to the heterocycle.³⁹ Because the HOMO–LUMO gap calculated for the heterocycle was 61.8 kcal/mol, it was predicted that such species could act as σ -donor ligands, but they would be weak π -acids in complexes with late transition metal fragments.

2.2.2. Five-Membered Rings

Theoretical studies have been carried out on models of anionic five-membered aluminum(I) heterocycles, for example, $[\text{Al}\{\text{N}(\text{H})\text{C}(\text{H})_2\}]^-$.^{15,16,18} These showed the electronic structure of the heterocycles to be similar to that of all their heavier group 13 analogues but significantly different from that of corresponding boryl anions. Because of the electronegativity difference between Al and N, they possess heavily polarized $\delta^+\text{Al}–\text{N}^{\delta-}$ bonds and an effectively empty p-orbital at aluminum, orthogonal to the heterocycle plane. As a result, there is little electronic delocalization over the N–Al–N fragment. Moreover, the singlet–triplet energy gaps calculated for the models, 41.3–45.3 kcal/mol, are considerably greater than, for example, those for $[\text{B}\{\text{N}(\text{H})\text{C}(\text{H})_2\}]^-$. The Al center of the singlet heterocycles can be viewed as being close to sp-hybridized and having a directional lone pair of electrons. Taken as a whole, these results indicate that $[\text{Al}\{\text{N}(\text{H})\text{C}(\text{H})_2\}]^-$ is best represented by the canonical form, **E**, that is, a diamido complex of Al^+ , rather than **D**, which possesses covalent Al–N bonds (Figure 4).

Although anionic five-membered aluminum(I) heterocycles are predicted to have greater singlet–triplet energy gaps than their boron cousins, it is surprising that none have been isolated in the laboratory. That is not to say that their preparation has not been attempted. For example, treating the paramagnetic aluminum(III) heterocycle, $[\text{I}_2\text{Al}\{[\text{N}(\text{Dip})\text{C}(\text{H})_2]^*\}]$, with potassium metal led not to an aluminum(I) species but the deposition of aluminum metal.⁴⁰

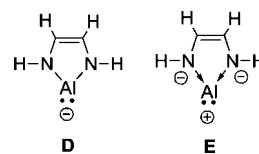


Figure 4. Canonical forms of $[\text{Al}\{\text{N}(\text{H})\text{C}(\text{H})_2\}]^-$.

2.2.3. Six-Membered Rings

Computational studies of models of aluminum(I) heterocycles incorporating β -diketiminate (Nacnac) ligands, for example, $[\text{Al}\{[\text{N}(\text{R})\text{C}(\text{R}')_2\text{CH}]\}]$ ($\text{R} = \text{H}, \text{Me}, \text{Ph}$, or Dip ; $\text{R}' = \text{H}$ or Me),^{7,37,38,41,42} have shown their electronic structure to be substantially different from that of their boron analogues but similar to those of heavier group 13 metal(I)

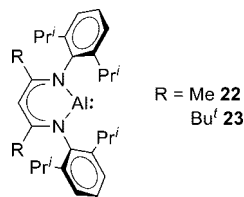


Figure 5. The six-membered aluminum(I) heterocycles, **22** and **23**.

heterocycles (*vide infra*). That is, there is a substantial positive charge on the Al center and the Al–N bonds are heavily polarized. The singlet–triplet energy separation in these models has been calculated to have values in the range 34.3–45.7 kcal/mol, which are much higher than those for similar boron(I) heterocycles but comparable to the values reported for the anionic five-membered aluminum(I) heterocycle mentioned above. The HOMO of $[\text{Al}\{\text{N}(\text{R})\text{C}(\text{R}')_2\text{CH}\}]$ incorporates an sp-like hybridized singlet lone pair of electrons at Al, and there is an effectively empty p-orbital at the metal, orthogonal to the heterocycle plane, that has little overlap with the adjacent filled N p-orbitals. As a result, it was suggested that such heterocycles have the potential to exhibit both nucleophilic and electrophilic character,⁴¹ a hypothesis that was later confirmed. This empty p-orbital is not associated with the LUMO of the heterocycle (which is ligand based) but the LUMO+1. The value of the HOMO–LUMO+1 gap in model heterocycles has been calculated to be from 82.8–98 kcal/mol.^{7,38,42}

The synthesis of two examples of six-membered aluminum(I) heterocycles, **22** and **23** (Figure 5), was achieved by the potassium metal reduction of the corresponding aluminum(III) iodide complexes, $[\text{I}_2\text{Al}(\text{DipNacnac})]$ or $[\text{I}_2\text{Al}(\text{Bu}^{\text{Nacnac}})]$ ($[\{\text{N}(\text{Dip})\text{C}(\text{R})_2\text{CH}\}]^-$ R = Me (DipNacnac), R = Bu' ($\text{Bu}^{\text{Nacnac}}$)), in toluene.^{41,43} The remarkable thermal stability of both compounds toward disproportionation reactions (decomp. > 150 °C) can be attributed to the steric bulk of the β -diketiminato ligands, which provide kinetic protection to the metal center of each. X-ray crystallographic analyses of the heterocycles revealed them to be monomeric with rare examples of two-coordinate aluminum centers. Interestingly, the ^{27}Al NMR spectrum of **22** displayed the largest downfield shifted resonance known at the time of its preparation, namely, $\delta = 590 \pm 40$ ppm with a half-height width of ca. 30 kHz.⁴⁴

With their singlet lone pairs, the neutral heterocycles **22** and **23** can be viewed as being isolobal to NHCs and thus have the potential to exhibit carbene-like reactivity or to act as strong reducing agents. In practice, these characteristics have been demonstrated in a variety of studies, the results of which have been reviewed on several occasions.^{3–6,45,46} Saying this, the coordination chemistry of **22** is only poorly developed and that of **23** is so far nonexistent. The reaction of $[\text{Pd}_2(\text{dvds})_3]$ (dvds = 1,1,3,3-tetramethyl-1,3-divinyldisiloxane) with an excess of **22** yielded **24** in which the aluminum heterocycle acts as a terminal ligand, whereas in the product of the 1:1 reaction, **25**, it symmetrically bridges two Pd centers (Figure 6).^{47,48} The dvds ligands of **25** are readily displaced by the gallium(I) diyl, $:\text{GaCp}^*$, to give the related complex, **26**.⁴⁷ A comparison of C–C bond lengths of the dvds ligands of **24** and **25** with those of related NHC complexes indicated that **22** has a similar σ -donor ability to the NHCs. The solid-state structure of the only other crystallographically characterized complex incorporating **22** as a Lewis base, namely, **27** (Figure 6), shows that the

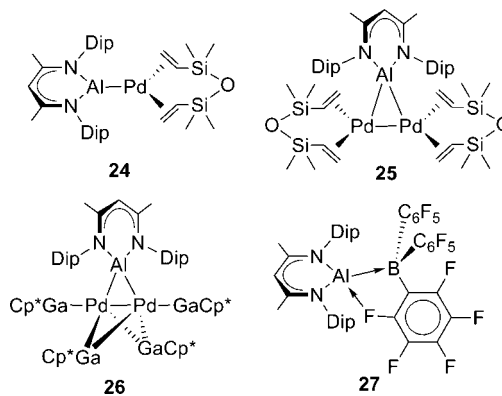


Figure 6. Complexes derived from $[\text{Al}(\text{DipNacnac})]$ **22**.

heterocycle also possesses electrophilic character, and considerably more so than NHCs. While it acts as a σ -donor ligand to the strong Lewis acidic fragment, $\text{B}(\text{C}_6\text{F}_5)_3$ (Al–B distance 2.183(5) Å), it concomitantly accepts electron density from one of the *ortho*-fluoro substituents of that fragment into an empty orbital of high p-character (according to an NBO analysis of a geometry-optimized model complex) at Al (Al...F distance 2.156(3) Å).⁴⁹ This interaction is strong enough to persist in solution, as determined by ^{19}F NMR spectroscopy, and highlights the Lewis amphoteric nature of the aluminum heterocycle.

More developed than the coordination chemistry of **22** and **23** is their redox chemistry. Not surprisingly, this is also more extensive than that of the less reducing heavier group 13 analogues of **22** (*vide infra*) and has shown the worth of aluminum(I) heterocycles as reagents for inorganic synthesis, small molecule activations, organic transformations, etc. A summary of some of the syntheses that have exploited **22** and **23** is given in Scheme 3. With regard to their reactions with p-block elements, the aluminum center of **22** is readily oxidized with elemental oxygen to give the oxide-bridged species, $[\{\text{DipNacnacAl}(\mu\text{-O})\}_2]$ (**28**), which was further reacted with water to yield the oxide/hydroxide complex, $[\{\text{DipNacnacAl}(\text{OH})_2(\mu\text{-O})\}_2]$ (**29**).⁵⁰ The corresponding reaction with elemental sulfur did give the expected sulfide-bridged complex, $[\{\text{DipNacnacAl}(\mu\text{-S})\}_2]$ (**30**), but also generated a low yield of the S_3 bridged complex, $[\{\text{DipNacnacAl}(\mu\text{-S}_3)\}_2]$ **31**, which crystallography showed to have a central Al_2S_6 crown-like ring, which was described as a homobimetallic derivative of the sulfur crown, S_8 .⁵¹ Similarly, the partial reduction of P_4 with **22** led to a good yield of the P_4^{4-} bridged species, $[\{\text{DipNacnacAl}\}_2(\mu\text{-P}_4)]$ (**32**), which was formed by the insertion of the aluminum center of **22** into two P–P edges of the P_4 tetrahedron.⁵² This result is especially interesting given that the activation of P_4 with NHCs has been recently studied in some detail and is seen as a potential entry to new organophosphorus compounds.^{53–55}

The carbene-like ability of **22** and **23** to undergo cycloaddition reactions, in combination with their reducing power, has led to the heterocycles being particularly reactive toward unsaturated substrates. Most success has been had in their reactions with organic azides. Treatment of compound **22** with the very bulky azide Ar^*N_3 ($\text{Ar}^* = \text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}^i_{3-2,4,6})_2-2,6$) afforded the first monomeric aluminum imide, $[\{\text{DipNacnacAl}=\text{NAr}^*\}]$ (**33**), which was not crystallographically characterized.^{44,56} When a slightly less bulky terphenyl azide, $\text{Ar}'\text{N}_3$ ($\text{Ar}' = \text{C}_6\text{H}_3(\text{C}_6\text{H}_3\text{Pr}^i_{2-2,6})_2-2,6$), was reacted with **22**, it was presumed that a similar monomeric aluminum imide was formed as an intermediate in the reaction. This

aluminum-containing materials has not been touched upon yet but is certainly a worthwhile area to explore.

2.3. Gallium(I) Heterocycles

2.3.1. Four-Membered Rings

A DFT computational study (BP86) of the guanidinato-coordinated Ga^I complex, $[\text{Ga}\{(\text{PhN})_2\text{CNMe}_2\}]$, showed its electronic structure to be similar to that of its Al analogue (*vide supra*) but with a higher HOMO–LUMO gap (67.4 kcal/mol).³⁹ Although the singlet lone pair (HOMO) at the gallium center does have high s-character ($4s^{1.90}4p^{0.37}$) it exhibits sufficient directionality to suggest that four-membered gallium(I) heterocycles may behave as σ -donor ligands. The high energy of the LUMO (empty p-orbital at Ga) of the model indicates that these heterocycles will be weak π -acceptor ligands.

Only one example of a four-membered gallium(I) heterocycle, **47**, has so far been reported.³⁹ This was prepared from the salt elimination reaction of the bulky lithium guanidinate complex, $[\text{Li}(\text{Giso})]$ ($\text{Giso} = [(\text{DipN})_2\text{CNCy}_2]^-$, Cy = cyclohexyl)⁶⁵ with “GaI”,^{66,67} a reagent that is known to act as a source of gallium(I) in its reactions (Scheme 4). It is of note that previous attempts to form related heterocycles stabilized by bulky amidinate ligands were not successful and instead gallium(II) products were obtained by disproportionation reactions.⁶⁸ Compound **47** is monomeric in the solid state with a two-coordinate Ga center. It is very thermally stable and does not decompose below 155 °C. The remarkable stability of the heterocycle is thought to be derived from the considerable steric bulk and electron richness of the Giso ligand. It is, however, air- and moisture-sensitive and its gallium center has been shown to be readily oxidized by, for example, I_2 and SiMe_3I to give the gallium(III) heterocycles $[(\text{Giso})\text{GaI}_2]$ and $[(\text{Giso})\text{Ga}(\text{I})(\text{SiMe}_3)]$, respectively.⁶⁹

The nucleophilicity of $[\text{Ga}(\text{Giso})]$, **47**, has been demonstrated by its use as a ligand in the formation of a small number of coordination complexes. These are summarized in Table 1, and all were prepared by the displacement of labile ligands from transition metal precursor complexes. In general, the coordination chemistry of these heterocycles is similar to that of gallium diyls, :GaR , in that both can act as terminal or bridging ligands. However, spectroscopic and other evidence indicates that $[\text{Ga}(\text{Giso})]$ is significantly less

Scheme 4

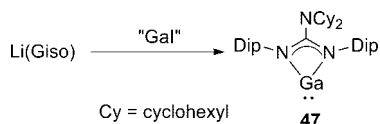


Table 1. Transition Metal Complexes Derived from the Gallium(I) Heterocycle, $[\text{Ga}(\text{Giso})]$ ($\text{Giso} = [(\text{DipN})_2\text{CNCy}_2]^-$)

complex	$d(\text{Ga}-\text{M})$, Å	ref
$[\text{Fe}(\text{CO})_4\{\text{Ga}(\text{Giso})\}]$, 48	2.271 (1)	73
$[\text{Ru}(\text{CO})_2(\text{PPh}_3)_2\{\text{Ga}(\text{Giso})\}]$, 49		73
$[\{(\text{CO})_3\text{Co}\}_2\{\mu\text{-Ga}(\text{Giso})\}_2]$, 50	2.383 (mean)	73
<i>cis</i> - $[\text{Ni}(\text{COD})\{\text{Ga}(\text{Giso})\}_2]$, 51 ^a	2.239 (mean)	70
<i>cis</i> - $[\text{Pt}(\text{dppe})\{\text{Ga}(\text{Giso})\}_2]$, 52 ^b	2.357 (mean)	70
$[\text{Pt}\{\text{Ga}(\text{Giso})\}_3]$, 53	2.309 (mean)	70
<i>cis</i> - $[\text{Pt}(p\text{-C}_6\text{HF}_4)_2\{\text{Ga}(\text{Giso})\}_2]$, 54	2.371 (mean)	71
<i>cis</i> - $[\text{Pt}(p\text{-C}_6(\text{OMe})\text{F}_4)_2\{\text{Ga}(\text{Giso})\}_2]$, 55	2.359 (mean)	71
<i>trans</i> - $[\text{Pt}(\text{C}_6\text{H}_2\text{F}_3\text{-2,4,6})_2\{\text{Ga}(\text{Giso})\}_2]$, 56	2.346 (mean)	71

^a COD = 1,5-cyclooctadiene. ^b dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$.

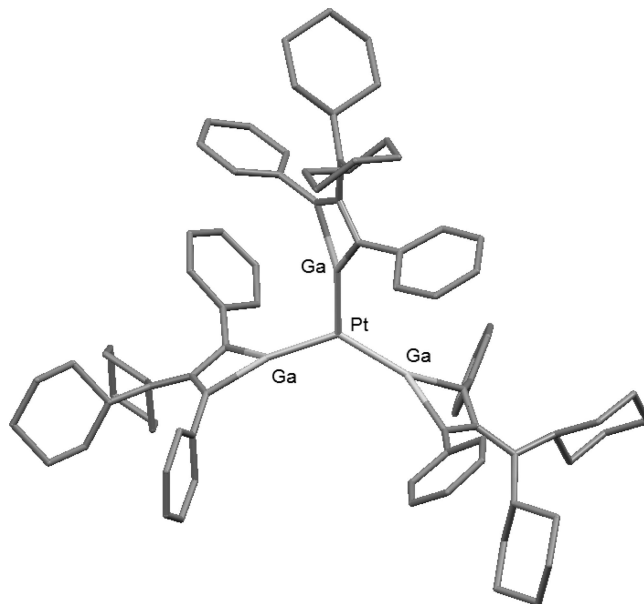


Figure 7. Molecular structure of **53** (isopropyl groups omitted). nucleophilic than gallium diyls. Indeed, the platinum complexes, **54–56**, are unstable with respect to gallium heterocycle loss in solution in the absence of excess $[\text{Ga}(\text{Giso})]$.^{70,71}

The relatively poor σ -donor properties of $[\text{Ga}(\text{Giso})]$ most probably arise from the high s-character of its gallium lone pair. Despite the relatively high HOMO–LUMO gap calculated for a model of the heterocycle, it is possible that in its late transition metal, carbonyl-free complexes some π -backbonding to the Ga center of the heterocycle might be observed. To some extent this appears to be the case in the homoleptic platinum(0) complex, **53** (Figure 7).⁷⁰ Despite the bulk of its ligands, the complex exhibited what were at the time, the shortest reported Pt–Ga bonds. DFT calculations, in combination with a charge decomposition analysis (CDA) on a model of the complex, 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 significant.⁷² However, at least in the case of **53**, the electrostatic component of the polarized Ga–Pt bonds was calculated to be greater than the covalent component, and therefore, the Pt–Ga π -bonding in the complex was not thought substantial.

There is much future scope to develop the coordination chemistry of four-membered gallium(I) heterocycles, and it can be envisaged that this will, to some extent, mirror that of their neutral six-membered counterparts (*vide infra*). Differences may arise from the less sterically protected gallium centers in the four-membered heterocycles, which could lead to greater reactivity of the heterocycles, both in the free and coordinated states. It is unlikely that transition metal complexes of such heterocycles will find many applications related to those associated with NHC–transition metal complexes, but some possibilities exist. It is more likely that the heterocycles will find function as specialist reducing agents and in the synthesis of novel gallium-containing materials and complexes, an area that is beginning to be fruitful for larger gallium(I) heterocycles.

2.3.2. Five-Membered Rings

The most developed of the group 13 metal(I) NHC analogues are the anionic, five-membered gallium(I) hetero-

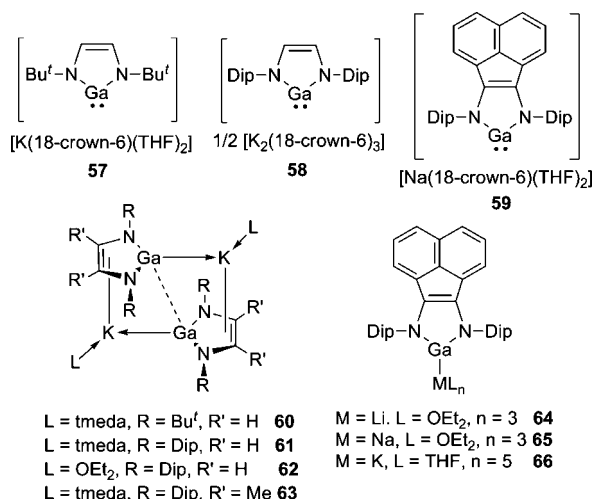


Figure 8. Alkali metal salts and complexes of anionic gallium(I) heterocycles.

cycles. Computational analyses of models of such systems, for example, $[\text{:Ga}\{\text{N}(\text{H})\text{C}(\text{H})\}_2]^-$,^{15,18,74} reveal them to have similar electronic structures to their aluminum counterparts (*vide infra*) but with slightly higher singlet–triplet energy separations (ca. 52 kcal/mol). Similar to the anionic aluminum(I) heterocycles, they have been described as possessing very polar $\delta^+\text{Ga}-\text{N}^{\delta-}$ bonds with a “quasi”-sp-hybridized singlet lone pair of electrons at their gallium centers.

To date, alkali metal salts of four anionic gallium(I) heterocycles have been isolated, either as ion-separated species, for example, **57–59**, or contact ion pairs, **60–66** (Figure 8). The first of these to be reported, **57**⁷⁴ and **60**,⁷⁵ were prepared in very low yield by the potassium reduction of the digallane(4), $[\{\text{Ga}(\text{Bu}^t\text{-DAB})\}_2]$ ($\text{Bu}^t\text{-DAB} = \{\text{N}(\text{Bu}^t)\text{C}(\text{H})\}_2$), in the presence of 18-crown-6 or tmeda, respectively. Subsequently, a high-yield synthetic route to **60** was developed, whereby the paramagnetic gallium(II) dimer, $[\{\text{Ga}(\text{Bu}^t\text{-DAB}^*)\}_2]$, was reduced with potassium metal, also in the presence of tmeda.⁴⁰ Similar reductions of the paramagnetic gallium(III) compounds, $[\text{GaI}_2(\text{Ar-DAB}^*)]^{76}$ or $[\text{GaI}_2(\text{Ar-MeDAB}^*)]^{77}$ ($\text{Ar-DAB} = \{\text{N}(\text{Dip})\text{C}(\text{H})\}_2$, $\text{Ar-MeDAB} = \{\text{N}(\text{Dip})\text{C}(\text{Me})\}_2$) gave **58** and **61–63**,^{40,77} while the alkali metal cleavage of the Ga–Ga bond of $[\{\text{Ga}(\text{Ar-BIAN})\}_2]$ ($\text{Ar-BIAN} = (\text{DipNC})_2\text{C}_{10}\text{H}_6$) afforded the alkali metal gallyl complexes, **59** and **64–66**.^{78,79} It is of note that a prior attempt to generate complexes of $[\text{:Ga}(\text{Ar-BIAN})]^-$ by reduction of paramagnetic $[\text{I}_2\text{Ga}(\text{Ar-BIAN}^*)]$ was not successful.⁸⁰ Similarly, one attempted preparation of a P-analogue of these heterocycles, $[\text{:Ga}\{\text{P}(\text{Mes}^*)\text{C}(\text{H})\}_2]^-$ ($\text{Mes}^* = \text{C}_6\text{H}_2\text{Bu}^t\text{-3,2,4,6}$), has been reported, but this was also unsuccessful.⁸¹

Although all of these complexes are very air-sensitive, they are thermally stable at ambient temperature and in general can be prepared in high yields. Crystallographic studies on **60–62** and **64–66** indicated interactions between the gallium lone pairs and the alkali metal cation, which in the cases of **64** and **65** were shown to have dative character by DFT calculations.⁷⁸ In addition, although outwardly similar, the dimeric complexes **60** and **61** differ in that they have significantly divergent Ga···Ga distances (**60**, 4.21 Å; **61**, 2.864 Å). It was postulated that the short interaction in the latter is due to partial donation of the Ga lone pair into the empty p-orbital of the opposing Ga center, though no evidence from computational studies was given for this.

Almost all the further chemistry derived from **57–66** has come from complex **61**, used as a source of the $[\text{:Ga}(\text{Ar-DAB})]^-$ anion. In fact, the only reactions reported with any of the other reagents are the treatment of **60** with methyl triflate to give $[\text{MeGa}(\text{Bu}^t\text{-DAB})]^{75}$, the oxidative coupling of **63** with thallium sulfate to give the digallane(4), $[\{\text{Ga}(\text{Ar-MeDAB})\}_2]$,⁷⁷ and the reaction of **65** with BaI_2 to give $[\text{Ba}\{\text{Ga}(\text{Ar-BIAN})\}_2(\text{THF})_5]$.⁷⁹ In contrast, compound **61** has been used in the formation of a wide array of complexes containing gallium–metal bonds, as a reducing agent in the synthesis of novel organometallic complexes, and for a variety of other purposes. A summary of compounds directly resulting from the $[\text{:Ga}(\text{Ar-DAB})]^-$ anion is given in Table 2, while further general and specific details of its chemistry and synthetic applications can be found below. The further chemistry of $[\text{:Ga}(\text{Ar-DAB})]^-$ has been partly covered in earlier reviews.^{5,8}

The versatility of the $[\text{:Ga}(\text{Ar-DAB})]^-$ anion as a ligand is evidenced by the fact that it has so far been used to form compounds exhibiting bonds between gallium and 45 elements from all blocks of the periodic table. These include complexes that displayed the first examples of bonds between gallium and 14 metallic elements (Mg, Ca, Y, V, Cu, Ag, Zn, Cd, In, Sn, Nd, Sm, Tm, and U. See Table 2 for references). A variety of synthetic methods have been utilized to access the complexes listed in Table 2. These include (i) ligation of the gallyl anion to a coordinatively unsaturated metal fragment, as in the preparation of **77**, **78**, **82**, **83**, and **99**, (ii) the displacement of a labile neutral ligand (e.g., **94**, **98**, **100**, and **101**), (iii) the elimination of a salt, KX where $\text{X} = \text{halide, hydride, Cp}^-, \text{ or alkyl}$, (iv) C–H or N–H activation (e.g., **75**, **85**, and **86**), (v) oxidative insertion of the Ga^{I} into an E–E bond (e.g., **87**, **90**, and **91**), (vi) oxidation of the Ga^{I} center (e.g., **88** and **89**), (vii) oxidative coupling (e.g., **71** and **72**), and (viii) insertion of elemental metal or a low oxidation state metal fragment into the Ga–Ga bond of the digallane(4), $[\{\text{Ga}(\text{Ar-DAB})\}_2]$, **128** (e.g., **67**, **69**, **93**, and **105**; $\text{M} = \text{Pt}$).

It should be noted that salt elimination is the most common route to the complexes in Table 2, but the reducing power of the gallyl anion can sometimes instead lead to reduction of the metal halide precursor and oxidative coupling of the gallyl anion to give either diamagnetic ($[\{\text{Ga}(\text{Ar-DAB})\}_2]$, **128**¹⁰⁴) or paramagnetic gallium(II) products (**71**). In contrast, the reaction of $[\text{:Ga}(\text{Ar-DAB})]^-$ with TmI_2 led to reduction of the heterocycle with elimination of Ga metal and formation of the Tm^{III} complex, **126**.¹⁰² Another interesting example of a gallium heterocycle modification occurred in the treatment of **110** with the phosphalkyne, $\text{P}\equiv\text{CBu}^t$ (Scheme 5), which led to the quantitative formation of the unusual P,N-heterocyclic gallyl complex, **115**. Remarkably, reaction of this compound with the isonitrile, $\text{C}\equiv\text{NBu}^t$, proceeded via the quantitative elimination of the phosphalkyne to give complex **114**.⁹⁹

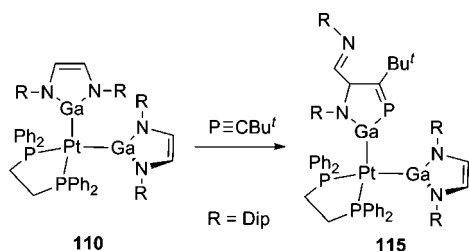
It is apparent that the steric bulk and nucleophilicity of $[\text{:Ga}(\text{Ar-DAB})]^-$ are contributing factors to its ability to stabilize low oxidation state complexes, for example, the zirconium(III) complex **93**, and what would normally be considered as very thermally labile systems, for example, the indium hydride complex **74**. In fact, spectroscopic and crystallographic analyses of a variety of group 9–11 complexes incorporating the heterocycle have allowed its *trans* influence to be placed in the series, $\text{B}(\text{OR})_2 > \text{H}^- > \text{PR}_3 \approx [\text{:Ga}(\text{Ar-DAB})]^- > \text{Cl}^-$.^{97,99} That is, its *trans* influence

Table 2. Complexes Derived from the Anionic Gallium(I) Heterocycle, $[\text{Ga}(\text{Ar-DAB})]^-$ ($\text{Ar-DAB} = [\text{N}(\text{Dip})\text{C}(\text{H})_2]^{2-}$)

complex	$d(\text{Ga-E}), \text{\AA}^a$	ref
s-block		
$[\text{K}_2(18\text{-crown-6})_3][\text{Ga}(\text{Ar-DAB})_2]$, 58		40
$[\{(\text{tmeda})\text{KGa}(\text{Ar-DAB})\}_2]$, 61	2.875(2)	40
$[\{(\text{Et}_2\text{O})\text{KGa}(\text{Ar-DAB})\}_2]$, 62	2.864(1)	40
$[\text{Mg}(\text{THF})_3\{\text{Ga}(\text{Ar-DAB})\}_2]$, 67	2.722 (mean)	82
$[\text{Mg}^{(\text{Dip})\text{Nacnac}}(\kappa^1\text{-tmeda})\{\text{Ga}(\text{Ar-DAB})\}]$, 68	2.747(1)	83
$[\text{Ca}(\text{THF})_4\{\text{Ga}(\text{Ar-DAB})\}_2]$, 69	3.159 (mean)	82
$[\text{M}(\text{tmeda})_2\{\text{Ga}(\text{Ar-DAB})\}_2]$ ($\text{M} = \text{Ca}, \text{Sr}$ or Ba), 70	3.228, 3.224, 3.464 (all mean)	83
p-block		
$[\{\text{GaX}(\text{Ar-DAB}^*)\}_2]$ ($\text{X} = \text{Br}$ or I), 71	2.466(1), 2.576(2)	84
$[\{\text{Ga}(\text{Ar-DAB})\}_2\{\mu\text{-CpK}(\text{tmeda})_2\}]$, 72	2.446(1)	85
$[\text{K}(\text{tmeda})_2][\text{H}_2\text{Ga}\{\text{Ga}(\text{Ar-DAB})\}_2]$, 73	2.407 (mean)	86
$[\text{Li}(\text{tmeda})_2][\text{H}_2\text{In}\{\text{Ga}(\text{Ar-DAB})\}_2]$, 74	2.595 (mean)	86
$[\text{HGa}(\text{Ar-DAB})(\text{IMes})]$, 75^b		87
$[(\text{C}_6\text{H}_2\text{Pr}^h\text{-2,4,6})\text{Ga}(\text{Ar-DAB})]$, 76		88
$[\text{K}(\text{tmeda})][\text{Ge}\{\text{CH}(\text{SiMe}_3)_2\}_2\{\text{Ga}(\text{Ar-DAB})\}]$, 77	2.540(1)	88
$[\text{K}\{\text{Ge}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2\}\{\text{Ga}(\text{Ar-DAB})\}]$, 78	2.460(1)	89
$[\text{Ge}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2(\text{SiMe}_3)\{\text{Ga}(\text{Ar-DAB})\}]$, 79	2.431(1)	89
$[(\text{Priso})\text{GeGa}(\text{Ar-DAB})]$, 80^c	2.516(1)	88
$[(\text{Priso})\text{SnGa}(\text{Ar-DAB})]$, 81^c	2.689(1)	88
$[\text{K}(\text{tmeda})][\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2\{\text{Ga}(\text{Ar-DAB})\}]$, 82	2.719(1)	88
$[\text{K}(\text{tmeda})][\text{Sn}(\text{C}_6\text{H}_2\text{Pr}^h\text{-2,4,6})_2\{\text{Ga}(\text{Ar-DAB})\}]$, 83	2.666(2)	88
$[\text{K}(\text{tmeda})][\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2\{\text{Ga}(\text{Ar-DAB})\}_2]$, 84	2.648 (mean)	88
$[\text{K}(\text{Ar-DAB})\text{Ga}(\text{H})\{\kappa^1\text{-N}(\text{Dip})\text{C}(\text{H})\text{N}(\text{Dip})\}]$, 85	1.904(3)	90
$[\text{K}(\text{tmeda})(\text{OEt}_2)][\{\text{PhNN}(\text{H})(\text{C}_6\text{H}_4)\}\{\text{Ga}(\text{Ar-DAB})\}]$, 86	1.964(4)	91
$[\text{K}(\text{tmeda})][\{\kappa^2\text{-P,P}-(\text{PhP})_4\}\{\text{Ga}(\text{Ar-DAB})\}]$, 87	2.402 (mean)	91
$[\text{K}(\text{tmeda})_2][\{\text{Ga}(\text{Ar-DAB})(\mu\text{-O})\}_2]$, 88	1.814(3)	92
$[\text{K}(\text{THF})_2][\{\text{Ga}(\text{Ar-DAB})(\mu\text{-Te})\}_2]$, 89	2.618 (mean)	92
$[\text{K}(\text{PhSe})_2\text{Ga}(\text{Ar-DAB})]$, 90	2.417 (mean)	92
$[\text{K}(\text{OEt}_2)_3][(\text{PhTe})_2\text{Ga}(\text{Ar-DAB})]$, 91	2.618 (mean)	92
d-block		
$[\text{Y}\{\text{Ga}(\text{Ar-DAB})\}\{\text{C}[\text{P}(\text{Ph})_2\text{N}(\text{SiMe}_3)]_2(\text{THF})_2]$, 92	3.1757(4)	93
$[\text{Li}(\text{THF})_4][\text{Cp}_2\text{Zr}\{\text{Ga}(\text{Ar-DAB})\}_2]$, 93	2.737 (mean)	94
$[\text{K}(\text{tmeda})][\text{CpV}(\text{CO})_3\{\text{Ga}(\text{Ar-DAB})\}]$, 94	2.462(1)	95
$[\text{Cp}'_2\text{V}\{\text{Ga}(\text{Ar-DAB})\}]$, 95^d	2.530(1)	95
$[\text{K}(\text{tmeda})][\text{Cp}'_2\text{V}\{\text{Ga}(\text{Ar-DAB})\}_2]$, 96^d	2.509 (mean)	95
$[\text{Cp}'_2\text{Cr}\{\text{Ga}(\text{Ar-DAB})\}]$, 97^d	2.423(1)	95
$[\text{K}(\text{tmeda})][\text{Cp}'\text{Mn}(\text{CO})_2\{\text{Ga}(\text{Ar-DAB})\}]$, 98^d	2.311(1)	95
$[\text{K}(\text{tmeda})][\text{Mn}\{\text{CH}(\text{SiMe}_3)_2\}_2\{\text{Ga}(\text{Ar-DAB})\}]$, 99	2.666(1)	95
$[\text{K}(\text{tmeda})][\text{Fe}(\text{CO})_4\{\text{Ga}(\text{Ar-DAB})\}]$, 100	2.307(1)	96
$[\text{K}(\text{tmeda})][\text{CpCo}(\text{CO})\{\text{Ga}(\text{Ar-DAB})\}]$, 101	2.235(1)	95
$[\text{M}\{\text{Ga}(\text{Ar-DAB})\}(\text{IMes})(\text{COD})]$ ($\text{M} = \text{Rh}$ or Ir), 102^{b,e}	2.426(1), 2.469(1)	97
$[\text{K}(\text{tmeda})][\text{CpNi}\{\text{Ga}(\text{Ar-DAB})\}_2]$, 103	2.217 (mean)	98
$[\text{Ni}\{\text{Ga}(\text{Ar-DAB})\}_2\{\text{C}[\text{N}(\text{Me})\text{C}(\text{Me})_2]_2\}]$, 104	2.324 (mean)	98
$\text{trans-}[\text{M}\{\text{Ga}(\text{Ar-DAB})\}_2(\text{PEt}_3)_2]$ ($\text{M} = \text{Ni}, \text{Pd}$, or Pt), 105	2.361, 2.451, 2.440 (all mean)	99
$\text{cis-}[\text{Pt}\{\text{Ga}(\text{Ar-DAB})\}_2(\text{PEt}_3)_2]$, 106	2.431 (mean)	99
$\text{trans-}[\text{Pt}\{\text{Ga}(\text{Ar-DAB})\}\text{Cl}(\text{PEt}_3)_2]$ ($\text{M} = \text{Ni}$ or Pd), 107	2.355, 2.288 (both mean)	99
$\text{cis-}[\text{M}\{\text{Ga}(\text{Ar-DAB})\}_2(\text{tmeda})]$ ($\text{M} = \text{Ni}$ or Pd), 108	2.305, 2.350 (both mean)	99
$\text{cis-}[\text{M}\{\text{Ga}(\text{Ar-DAB})\}_2(\text{dppm})]$ ($\text{M} = \text{Pd}$ or Pt), 109^f	2.396, 2.417 (both mean)	99
$\text{cis-}[\text{Pt}\{\text{Ga}(\text{Ar-DAB})\}_2(\text{dppe})]$, 110^g	2.416 (mean)	99
$\text{cis-}[\text{Pt}\{\text{Ga}(\text{Ar-DAB})\}_2(\text{COD})]$, 111^c	2.384 (mean)	99
$\text{cis-}[\text{Pt}\{\text{Ga}(\text{Ar-DAB})\}\text{Cl}(\text{dppe})]$, 112^g	2.393(1)	99
$\text{cis-}[\text{Pt}\{\text{Ga}(\text{Ar-DAB})\}\text{Cl}(\text{dcpe})]$, 113^h	2.415(1)	99
$\text{trans-}[\text{Pt}\{\text{Ga}(\text{Ar-DAB})\}_2(\text{CNBu}^i)_2]$, 114		99
$\text{cis-}[\text{Pt}\{\text{Ga}(\text{Ar-DAB})\}\{\text{Ga}(\text{P,N-gallyl})\}(\text{dppe})]$, 115ⁱ	2.426(1), 2.406(1) ^j	99
$[\text{Cu}(\text{ICy}^{\text{Me}})\{\text{Ga}(\text{Ar-DAB})\}]$, 116^k		97
$[\text{M}(\text{IMes})\{\text{Ga}(\text{Ar-DAB})\}]$ ($\text{M} = \text{Cu}, \text{Ag}$ or Au), 117^h	2.307(1), 2.416(1), 2.378(1)	97
$[\text{M}(\text{IPr})\{\text{Ga}(\text{Ar-DAB})\}]$ ($\text{M} = \text{Cu}, \text{Ag}$ or Au), 118^l	2.281(1), 0.411(1)	97
$[\text{Zn}(\text{tmeda})\{\text{Ga}(\text{Ar-DAB})\}_2]$, 119	2.441 (mean)	100
$[(\text{Priso})\text{ZnGa}(\text{Ar-DAB})]$, 120^c	2.323(1)	100
$[(\text{Dip})\text{Nacnac}]\text{ZnGa}(\text{Ar-DAB})]$, 121	2.384(1)	83
$[(\text{tmeda})\text{Zn}(\text{Br})\{\text{Ga}(\text{Ar-DAB})\}]$, 122	2.383(1)	83
$[\{(\text{tmeda})\text{Cd}(\text{I})[\text{Ga}(\text{Ar-DAB})]\}_n]$ ($n = 1$ or 2), 123	2.528 (mean)	83
f-block		
$[\text{Nd}\{\text{N}(\text{SiMe}_3)_2\}(\text{Iamid})\{\text{Ga}(\text{Ar-DAB})\}(\text{THF})]$, 124^m	3.2199(3)	101
$[\text{M}\{\text{Ga}(\text{Ar-DAB})\}_2(\text{tmeda})_2]$ ($\text{M} = \text{Sm}, \text{Eu}$, or Yb), 125	3.312, 3.312, 3.226 (all mean)	102
$[\text{Tm}\{\text{Ga}(\text{Ar-DAB})\}(\text{Ar-DAB})(\text{tmeda})]$, 126	2.974(2)	102
$[\text{U}\{\text{Ga}(\text{Ar-DAB})\}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3\}(\text{THF})]$, 127	3.211(1)	103

^a Where no value is given, (i) the compound does not possess an E–Ga(Ar-DAB) bond ($\text{E} = \text{any element}$), (ii) the compound only possesses E–Ga(Ar-DAB) ($\text{E} = \text{H}$ or C) bonds, or (iii) the compound has not been structurally characterized; where more than one value is given, unless otherwise stated, the order of values relates to the listed compounds. ^b IMes = $:\text{C}\{\text{N}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})\text{C}(\text{H})\}_2$. ^c Priso = $\{\text{N}(\text{Dip})\}_2\text{CNPr}^2$. ^d Cp' = $\text{C}_5\text{H}_4\text{Me}$. ^e COD = 1,5-cyclooctadiene. ^f dppm = $(\text{Ph}_2\text{P})_2\text{CH}_2$. ^g dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$. ^h dcpe = $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2$ ($\text{Cy} = \text{cyclohexyl}$). ⁱ P,N-gallyl = $\text{PC}(\text{Bu}^i)\text{C}(\text{H})\{\text{N}(\text{Dip})\}\text{C}(\text{H})\text{N}(\text{Dip})$. ^j Values for two different Ga–Pt bonds. ^k ICy^{Me} = $:\text{C}\{\text{N}(\text{Cy})\text{C}(\text{Me})\}_2$. ^l IPr = $:\text{C}\{\text{N}(\text{Dip})\text{C}(\text{H})\}_2$. ^m Iamid = $\text{Bu}^i\text{NCH}_2\text{CH}_2\{\text{C}(\text{NCSiMe}_3\text{CHN}^i\text{Bu}^i)\}$.

Scheme 5



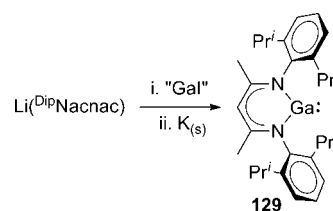
is similar to that of tertiary phosphines, despite the results of the aforementioned computational studies, which indicate a significant positive charge at its gallium center. It will certainly be interesting to follow the future development of the coordination chemistry of the isostructural, but presumably more nucleophilic, boryl anion, $[\text{B}(\text{Ar-DAB})]^-$, and to compare it with that of $[\text{Ga}(\text{Ar-DAB})]^-$. Indeed, comparisons between the chemistry of the latter and less bulky boryls have already appeared in the literature.^{97,99}

It is clear that the anion, $[\text{Ga}(\text{Ar-DAB})]^-$, acts as an excellent σ -donor ligand, but given the empty p-orbital at its gallium center, it could potentially participate in $d \rightarrow p$ π -backbonding with suitable transition metal fragments. One study has thoroughly examined this possibility using the results of crystallographic, spectroscopic, and computational analyses of the complex series $[(\text{C}_5\text{H}_4\text{R})\text{M}(\text{CO})_n\{\text{Ga}(\text{Ar-DAB})\}]^-$ ($\text{R} = \text{H}$ or Me ; $\text{M} = \text{V}$ (**94**), Mn (**98**), or Co (**101**); $n = 3, 2$, or 1 , respectively). The conclusion of this study was that there is no more π -backbonding in these complexes than there is in corresponding neutral NHC complexes, $[\text{CpM}(\text{CO})_n(\text{NHC})]$, for which $d \rightarrow p$ bonding is known to be negligible.⁹⁵ In this respect, it is interesting to note that a theoretical analysis of the bonding in the first complex to contain an unsupported $\text{Ga}-\text{U}$ bond, **127** (Figure 9), indicated that its gallyl ligand acts as a weak π -donor to an empty f-orbital on the U center.¹⁰³ Such a phenomenon has not been seen in the bonding in more electrostatic gallium–lanthanoide interaction (as in **124**),¹⁰¹ but the ability of NHCs themselves to engage in π -donation has been recognized.¹⁰⁵

2.3.3. Six-Membered Rings

Computational analyses of models of neutral six-membered gallium(I) heterocycles, for example, $[\text{Ga}\{\text{N}(\text{R})\text{C}(\text{R}')_2\text{CH}\}]$ ($\text{R} = \text{H}$, Me , Ph or Dip ; $\text{R}' = \text{H}$ or Me),^{7,37,38,42} have revealed their electronic structures to be similar to that

Scheme 6



of their Al counterparts but with higher singlet–triplet energy separations (51.7–55.5 kcal/mol),^{37,38} reflecting a lower energy of the metal lone pair in the gallium heterocycles. As with the Al heterocycles, the p-orbital is associated with the LUMO+1, but the HOMO–LUMO+1 separation is somewhat larger (95.3–110 kcal/mol).^{7,38,42}

Only one six-membered gallium(I) heterocycle, $[\text{Ga}(\text{DipNacnac})]$, **129** (Scheme 6), has so far been synthesized.¹⁰⁶ It is very thermally stable (mp 202–204 °C), and an X-ray crystal structure showed it to be monomeric and isostructural with its aluminum counterpart. The coordination chemistry of **129** has been developed further than that of $[\text{Al}(\text{DipNacnac})]$, **22**, but its use in the transformation of unsaturated organic substrates has not. Presumably, these differences are derived from **129** being more weakly reducing than **22**. A summary of complexes resulting directly from **129** is given in Table 3. Some chemistry of **129** has been previously reviewed.^{5,7,8}

The synthetic routes to the complexes listed in Table 3 are similar to those available for the anionic gallium(I) heterocycle, $[\text{Ga}(\text{Ar-DAB})]^-$, except that salt elimination reactions are obviously not available for $[\text{Ga}(\text{DipNacnac})]$, **129**. The general reaction types for which **129** has been utilized are (i) coordination to unsaturated fragments (e.g., in the formation of **130**), (ii) displacement of labile ligands from transition metal complexes (e.g., **152**, **154**, **156**, and **158**), (iii) insertion of its Ga^{I} center into $\text{E}-\text{X}$ bonds ($\text{E} = \text{hydrogen}$ or a p- or d-block element; $\text{X} = \text{halide}$, alkyl, hydrogen, etc.) (e.g., **131**–**135**, **149**, **150**, **165**, **167**, and **169**), (iv) reduction of main group halides or pseudohalides (e.g., **136**, **137**, and **145**), (v) formation of gallium imides and amides from organo-azides (e.g., **141**–**143**), and (vi) oxidation of its Ga^{I} center (e.g., **144** and **146**). Moreover, further reactions of complexes derived from $[\text{Ga}(\text{DipNacnac})]$, **129**, can be used to access other complexes incorporating this ligand. These include the oxidative addition of H_2 or HSiEt_3 to the Pt^0 center of complexes of **129** (e.g., to give **161** and **162**), as is well-known for homoleptic NHC–group 10 complexes, and halide abstraction from gallyl complexes (e.g., **164** and **167**) to yield cationic species (e.g., **166** and **168**).

The electronic properties of **129** are related to those of its aluminum counterpart, **22**, in that its gallium center is nucleophilic, while having the potential to be electrophilic. Its nucleophilicity has been determined to be greater than several gallium and aluminum diyls, for example, $:\text{GaCp}^*$, $:\text{GaAr}^*$, and $:\text{AlCp}^*$, based on the pyramidalization of the boron centers of the complexes of these Lewis bases with $\text{B}(\text{C}_6\text{F}_5)_3$.^{107,117} It seems likely, however, that the electrophilicity of $[\text{Ga}(\text{DipNacnac})]$, **129**, is less than that of $[\text{Al}(\text{DipNacnac})]$, **22**, because its borane complex, **130**,¹⁰⁷ does not exhibit strong intramolecular $\text{M} \cdots \text{F}$ interactions in solution or the solid state, as the analogous aluminum compound, **27**,⁴⁹ does. This is not surprising based on the greater Lewis acidity of aluminum relative to gallium. That

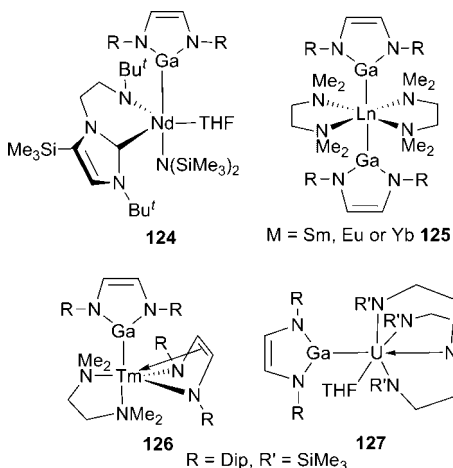


Figure 9. f-Block complexes derived from $[\text{Ga}(\text{Ar-DAB})]^-$.

Table 3. Complexes Derived from the Gallium(I) Heterocycle, [Ga(DipNacnac)] (DipNacnac = [{N(Dip)C(Me)}₂CH][−])

complex	<i>d</i> (Ga–E), Å ^a	ref
p-block		
[^(Dip) Nacnac]GaB(C ₆ F ₅) ₃ , 130	2.156(1)	107
[^(Dip) Nacnac]Ga(Me)GaMe ₂ , 131	2.451(2)	108
[{ ^(Dip) Nacnac]Ga(X)} ₂ (μ-GaX)] (X = Me or Cl), 132	2.504, 2.441 (both mean)	108
[{ ^(Dip) Nacnac]Ga(Cl)} ₂ (μ-SnMe ₂), 133	2.628 (mean)	108
[^(Dip) Nacnac]Ga(Cl)(R)] (R = SiMe ₃ , Bu'), 134	2.386(1)	108
[^(Dip) Nacnac]Ga(H)(X)] (X = SnPh ₃ , OEt, NEt ₂ , PPh ₂ , OH, H), 135	2.602(1), 0.792(3), 1.948(2), 363(1)	109
[Sn ₇ {Ga(Cl)(^(Dip) Nacnac)} ₂], 136	2.589 (mean)	110
[Sn ₁₇ {Ga(Cl)(^(Dip) Nacnac)} ₄], 137	2.584 (mean)	110
[Me ₃ Pb{Ga(Cl)(^(Dip) Nacnac)}], 138	2.597(1)	111
[Pb(THF){Ga(O ₃ SCF ₃)(^(Dip) Nacnac)} ₂], 139	2.792 (mean)	111
[Pb{Ga(O ₃ SCF ₃)(^(Dip) Nacnac)} ₂ (μ-OH ₂)], 140	2.725 (mean)	111
[^(Dip) Nacnac]Ga{N(SiMe ₃)N} ₂ , 141	1.947 (mean)	112
[^(Dip) Nacnac]Ga(N ₃){N(SiMe ₃) ₂ }, 142	1.918(1), 1.884(1)	112
[^(Dip) Nacnac]Ga=NAr*, 143 ^b	1.742(3)	56
[^(Dip) Nacnac]Ga(PPh ₂)(O ₃ SCF ₃), 144	2.312(3) (Ga–P)	113
[{ ^(Dip) Nacnac]Ga(OR)Bi] ₂] (R = C ₆ F ₅ or SO ₃ CF ₃), 145	2.693, 2.655 (both mean)	114
[{ ^(Dip) Nacnac]Ga(μ-E)] ₂] (E = O or S), 146	1.851, 2.262 (both mean)	115
[Ga(H)(^(Dip) Nacnac)(OH)Li(THF) ₃][Ga ₃ SiR' ₃ (SiMe ₃) ₃], 147 ^c	1.820(5)	116
d-block		
[Fe(CO) ₄ {Ga(^(Dip) Nacnac)}], 148	2.2851(3)	117
[Rh(PPh ₃) ₂ (μ-Cl){Ga(^(Dip) Nacnac)}], 149	2.387(1)	118
[Rh(COE)(C ₆ H ₆){Ga(Cl)(^(Dip) Nacnac)}], 150 ^d	2.404(1)	118
[Ni(cdt){Ga(^(Dip) Nacnac)}], 151 ^e	2.348(1)	119
[Ni(II) ₂ {Ga(^(Dip) Nacnac)}] (II = C ₂ H ₄ , styrene, or 1/2 dvds) ^f , 152	2.284(1), 2.280(2), 2.246(2)	119
[Ni ₂ (C ₂ H ₄) _n {μ-Ga(^(Dip) Nacnac)}] (n = 3 or 4), 153	2.326, 2.328 (both mean)	119
[Ni ₂ (PhCCPh) ₂ (COD){μ-Ga(^(Dip) Nacnac)}], 154 ^g	2.434 (mean)	119
[Ni ₃ H(C ₂ H ₄)(C ₂ H ₃){μ-Ga(^(Dip) Nacnac)} ₂], 155	2.333 (mean)	119
[Pd(dvds){Ga(^(Dip) Nacnac)}], 156 ^f	2.396(1)	48
[Pd ₂ (L) ₂ {Ga(^(Dip) Nacnac)} ₂] (L = CO or Bu'NC), 157	2.489, 2.478 (both mean)	48
[Pt(L){Ga(^(Dip) Nacnac)} ₂] (L = 1,3-COD or CO), 158 ^h	2.344	48
[Pt ₂ (L) ₂ {Ga(^(Dip) Nacnac)} ₂] (L = CO or Bu'NC), 159	2.503, 2.460 (both mean)	48
[(PtH ₂) ₂ {Ga(^(Dip) Nacnac)} ₂], 160	2.470 (mean)	48
<i>trans</i> -[PtH ₂ {Ga(^(Dip) Nacnac)} ₂], 161	2.304 (mean)	48
<i>cis</i> -[PtH(SiEt ₃){Ga(^(Dip) Nacnac)} ₂], 162	2.370 (mean)	48
[{Cu(X)[Ga(^(Dip) Nacnac)] ₂] (X = O ₃ SCF ₃ or Br), 163	2.460 (mean)	120
[Au{Ga(^(Dip) Nacnac)}{Ga(Cl)(^(Dip) Nacnac)}], 164	2.412 (mean)	121
[Au(PPh ₃){Ga(Cl)(^(Dip) Nacnac)}], 165	2.411(1)	121
[Au{Ga(^(Dip) Nacnac)} ₂][BAR ^f ₄], 166 ^f	2.392 (mean)	118
[ZnCl(THF) ₂ {Ga(Cl)(^(Dip) Nacnac)}], 167	2.392(1)	122
[{ZnCl(THF)[Ga(THF)(^(Dip) Nacnac)] ₂][BAR ^f ₄], 168 ^f	2.396 (mean)	122
[Zn{Ga(Me)(^(Dip) Nacnac)} ₂], 169	2.462 (mean)	122
<i>anti</i> - or <i>gauche</i> -[Hg{Ga(SC ₆ F ₅)(^(Dip) Nacnac)} ₂], 170	2.534, 2.533 (both mean)	111

^a Where no value is given, (i) the compound only possesses E–Ga(^(Dip)Nacnac) (E = H, C, or halide) bonds, or (ii) the compound has not been structurally characterized; where more than one value is given, the order of values relates to the listed compounds. ^b Ar* = C₆H₃(C₆H₂Pr^f₃-2,4,6)₂-2,6). ^c R' = Si(SiMe₃)₃. ^d COE = cyclooctene. ^e cdt = 1,5,9-cyclododecatiene. ^f dvds = 1,1,3,3-tetramethyl-1,3-divinylidisiloxane. ^g COD = 1,5-cyclooctadiene. ^h 1,3-COD = 1,3-cyclooctadiene. ⁱ Ar^f = C₆H₃(CF₃)₂-3,5.

is not to say that the empty p-orbital of the Ga center of **129** is inaccessible, as evidenced by the bent terminal gallium imide complex, **143**.⁵⁶ Crystallographic, spectroscopic, and computational analyses of this compound support the presence of a weak Ga–N π -bond in this compound.

With regard to the function and application of [Ga(^(Dip)Nacnac)], **129**, and its complexes, a number of specific points about the chemistry of the complexes listed in Table 3 should be noted here. Although **129** can be used as an unconventional Lewis base in the formation of complexes with dative bonds between Ga and p- or d-block metals (cf. NHC coordination chemistry), it has been equally effective in the formation of covalent Ga–E bonds via the insertion of its Ga^I center into E–X bonds. Such chemistry is only poorly developed for four- and five-membered gallium(I) heterocycles. In these insertion reactions, **129** is acting as a reducing agent, and when E is a metal, the formed gallyl (i.e., {–Ga(X)(^(Dip)Nacnac)}) complexes have been described as intermediates on the way to elimination of more thermodynamically favorable [Ga^{III}X₂(^(Dip)Nacnac)].^{110,114} The

usefulness of **129** as a reducing agent has been recently demonstrated with the preparation of complexes bearing the first structurally characterized Ga–Pb (**138–140**)¹¹¹ and Ga–Hg (**170**)¹¹¹ bonds, and the dimeric compound, **163**,¹²⁰ which displayed the shortest known Cu^I...Cu^I contact (2.277(3) Å) at the time of its publication.

Several remarkable experimental “snapshots” of such oxidative insertion/reductive elimination processes involving **129** have also been taken. For example, the rhodium complex, **149**, can be considered as an intermediate in the insertion of the Ga^I center of **129** into the Rh–Cl bond of Wilkinson’s catalyst, after displacement of one of its PPh₃ ligands by **129**.¹¹⁸ Perhaps more impressive has been the treatment of SnCl₂ with 2 equiv of **129**. This reaction afforded the tin cluster compounds, **136** and **137**, which are presumably intermediates in the decomposition of [Sn{Ga(Cl)(^(Dip)Nacnac)}₂] to tin metal, [GaCl₂(^(Dip)Nacnac)], and [Ga(^(Dip)Nacnac)].¹¹⁰ Compounds **136** and **137** can be thought of as containing Zintl-type anionic cores, Sn₇^{2−} and Sn₁₇^{4−}, respectively, stabilized by coordination to two or four

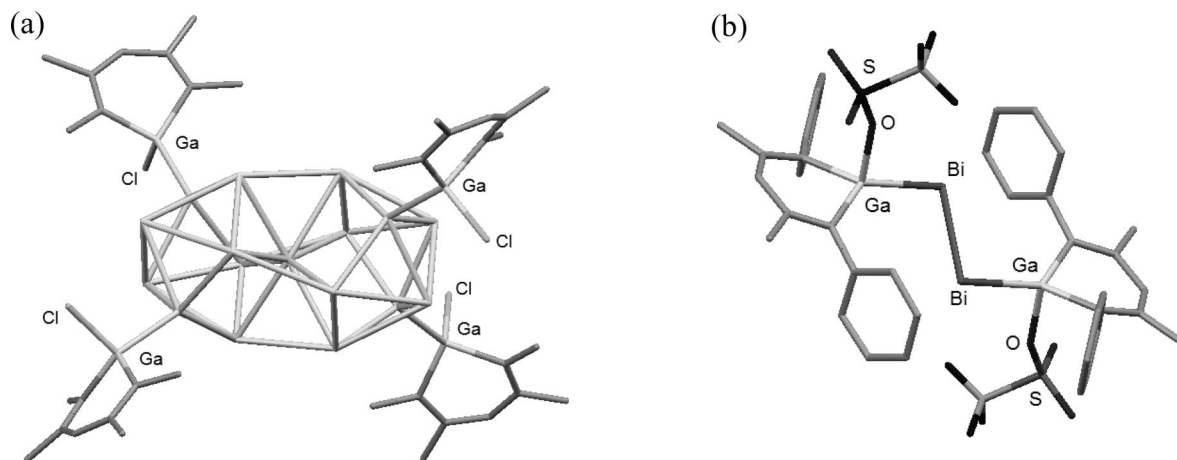


Figure 10. Molecular structures of (a) compound **137** (Dip groups omitted) and (b) compound **145** (isopropyl groups omitted).

electrophilic gallyl fragments, $\{-\text{Ga}(\text{Cl})(\text{DipNacnac})\}$. Compound **137** is the largest known tin cluster, and its structure (Figure 10) can be viewed as having a Sn_{17} core consisting of two Sn_9 tricapped trigonal prisms, sharing one common vertex. The cluster has 40 valence electrons according to the Jellium model,¹²³ an electron count that is favored by that model. Similarly, the reactions of **129** with $\text{Bi}(\text{OR})_3$ ($\text{R} = \text{O}_2\text{SCF}_3$ or C_6F_5) have given the galla-dibismuthenes, **145**, as isolated intermediates on the way to full reduction to bismuth metal.¹¹⁴ The structures of these compounds (see Figure 10 for **145**, $\text{R} = \text{O}_3\text{SCF}_3$) show them to contain $\text{Bi}=\text{Bi}$ double bonds with effectively covalent $\text{Ga}-\text{Bi}$ single-bonded interactions and $\text{Ga}-\text{Bi}-\text{Bi}$ angles of close to 90° . They were thus formulated as containing bismuth in the +1 oxidation state. The syntheses of **136**, **137**, and **145** highlight the potential of using **129** as a reducing agent in the preparation of novel materials, metalloid clusters, and subvalent “metastable” species.

Other functions that the gallium(I) heterocycle has demonstrated are its ability to activate a variety of element–element bonds, including that of dihydrogen¹⁰⁹ (cf. the facile activation of NH_3 and H_2 by NHCs¹²⁴), and its use in the construction of novel heterocycles, for example, **141**.¹¹² Its late transition metal complexes have been shown to participate in small molecule (e.g., ethylene) C–H activation processes,¹¹⁹ and have been used as precursors in the formation of heterometallic clusters (e.g., **153–155**,¹¹⁹ **157**, and **159**⁴⁸). The latter have been described as potential soluble models for the study of alloys, heterogeneous catalysts, etc. There is clearly significant scope to further explore the use of **129** and related neutral and anionic gallium(I) heterocycles as ligands, as reagents in organic and organometallic synthesis, as specialist reducing agents for the preparation of materials, low-valent “metastable” clusters, etc.

2.4. Indium(I) Heterocycles

2.4.1. Four-Membered Rings

The electronic structure of the guanidinato-coordinated $\text{In}(\text{I})$ complex $[\text{In}\{(\text{PhN})_2\text{CNMe}_2\}]$ has been calculated (DFT-BP86) to be very similar to those of its Al and Ga counterparts with an intermediate HOMO–LUMO gap of 63.5 kcal/mol.³⁹ Although the singlet lone pair (HOMO) at the metal center has an almost identical hybridization ($5s^{1.90}5p^{0.36}$) to that of $[\text{Ga}\{(\text{PhN})_2\text{CNMe}_2\}]$, the lone pair would be expected to be more diffuse due to the greater size

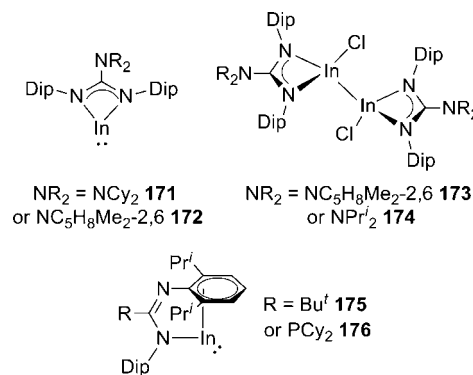


Figure 11. Indium(I) and indium(II) heterocycles incorporating bulky guanidinate, amidinate, or phosphaguanidinate ligands.

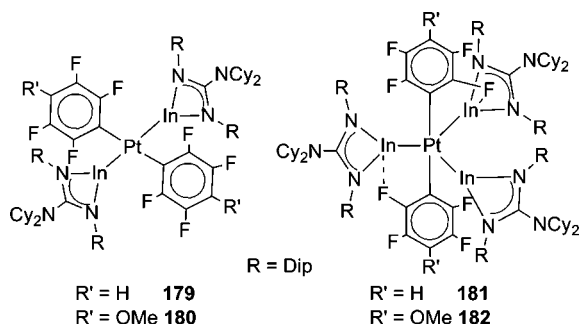
of the metal. Accordingly, four-membered indium heterocycles should be weaker σ -donors than their Al or Ga cousins.

All efforts to prepare four-membered indium(I) heterocycles have involved the reaction of bulky N-Dip-substituted amidinate, guanidinate, or phosphaguanidinate alkali metal complexes⁶⁵ with InCl . The outcomes of these salt elimination reactions are strongly dependent on the nature of the ligand backbone C-substituent.⁶⁹ That is, the four-membered heterocycle **171** (Figure 11) is formed in good yield when the backbone amino substituent is very bulky.³⁹ A mixture of the related heterocycle **172** and the partial disproportionation product **173** resulted from the reaction involving a guanidinate of less bulk, while only an indium(II) product, **174**, was isolated from the reaction with a smaller guanidinate.⁶⁹ In two reactions involving an amidinate or a phosphaguanidinate ligand, the “five-membered” N-Dip-chelated complexes **175** and **176** were obtained.^{69,125} It appears that very bulky ligand backbone substituents are required to prevent disproportionation processes from occurring and to sterically enforce N,N-chelation of the indium center. In this respect, the Giso ligand is the most stabilizing, and all further chemistry of four-membered indium(I) heterocycles reported to date has come from $[\text{In}(\text{Giso})]$, **171**.

The chemistry of **171** has been restricted to the formation of late transition metal complexes and to some extent mirrors that reported for the $[\text{Ga}(\text{Giso})]$, **47**, ligand. A summary of all complexes derived from **171** is given in Table 4. Spectroscopic and crystallographic studies of these complexes have shown that the indium heterocycle is a weaker nucleophile than its gallium counterpart, and in its complexes,

Table 4. Transition Metal Complexes Derived from the Indium(I) Heterocycle, [In(Giso)] (Giso = [(DipN)₂CNCy₂][−])

complex	<i>d</i> (In–M), Å	ref
[Ru(CO) ₂ (PPh ₃) ₂ {In(Giso)}], 177	2.555(1)	73
<i>cis</i> -[Pt(dppe){In(Giso)} ₂], 178^a	2.533 (mean)	70
<i>trans</i> -[Pt(<i>p</i> -C ₆ H ₄ F ₄) ₂ {In(Giso)} ₂], 179	2.518 (mean)	71
<i>trans</i> -[Pt(<i>p</i> -C ₆ (OMe)F ₄) ₂ {In(Giso)} ₂], 180	2.541 (mean)	71
<i>trans</i> -[Pt(<i>p</i> -C ₆ H ₄ F ₄) ₂ {In(Giso)} ₃], 181	2.577 (mean)	71
<i>trans</i> -[Pt(<i>p</i> -C ₆ (OMe)F ₄) ₂ {In(Giso)} ₃], 182	2.575 (mean)	71
[Pt(norbornene)] ₃ {μ ₃ -In(Giso)} ₂ , 183	2.744 (mean)	71

^a dppe = Ph₂PCH₂CH₂PPh₂.**Figure 12.** Platinum(II) complexes derived from [In(Giso)].

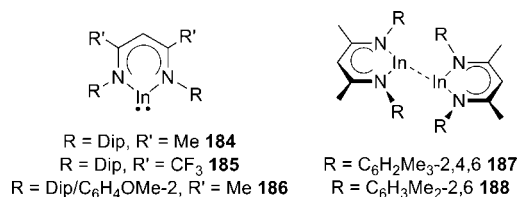
it is generally very labile. In contrast, evidence is beginning to emerge that **171** is a stronger electrophile than **47**, which is perhaps not surprising given the greater Lewis acidity of In relative to Ga. For example, the 3:1 complexes of **171** with electrophilic platinum(II) fragments, **181** and **182**, exhibit strong intramolecular In...F interactions in both the solid state (ca. 2.50 Å) and solution (Figure 12).⁷¹ These interactions presumably help stabilize the complexes toward ligand loss and the formation of the 2:1 complexes, **179** and **180**. That no similar 3:1 complexes with [Ga(Giso)] could be formed was put down to its lower tendency to form strong Ga...F interactions. It is of note that the In...F interactions in **181** and **182** are reminiscent of the close Al...F contacts in **27**,⁴⁹ and they highlight the Lewis amphoteric nature of the indium heterocyclic ligand.

2.4.2. Five-Membered Rings

The electronic structure of the model anionic indium(I) heterocycle [In{N(H)C(H)}₂]^{−15,18} has been computed to be similar to that of its Al and Ga analogues (*vide supra*), but with a slightly smaller but still substantial singlet–triplet energy separation (38.8 kcal/mol, DFT B3LYP). Although its In lone pair is more diffuse than those of the lighter metals in the other heterocycles, it still exhibits significant directionality and therefore was predicted to act as a good nucleophile.¹⁸ This has yet to be tested in practice as there are no examples of anionic five-membered indium(I) heterocycles in the literature. Attempts to prepare salts of [In(Ar-DAB)][−] (cf. [Ga(Ar-DAB)][−]) by alkali metal reductions of the paramagnetic indium(II) dimer [{InCl(Ar-DAB•)}₂] were reported to be unsuccessful.¹²⁶

2.4.3. Six-Membered Rings

Computational studies of the model neutral six-membered indium(I) heterocycles [In{N(R)C(R')₂CH}] (R = H, Me, Ph, or Dip; R' = H, Me, or CF₃)^{7,37,38,42} have shown their electronic structures to be broadly similar to those of the corresponding Al and Ga systems but with higher singlet–triplet energy separations than the lighter heterocycles (55.1–67.1

**Figure 13.** Neutral six-membered indium(I) heterocycles.

kcal/mol).^{37,38} In all systems, the In lone pair is represented by the HOMO, while the In based empty p-orbital is associated with the LUMO+1. Interestingly, it has been calculated (DFT B3LYP) that a change of the backbone methyl substituents of [In{N(Dip)C(Me)₂CH}] to electron-withdrawing CF₃ groups (to give [In{N(Dip)C(CF₃)₂CH}]), causes a reduction in the HOMO energy by 21 kcal/mol.⁴² Therefore, it would be expected that the CF₃-substituted heterocycle would be the less nucleophilic of the two.

An early attempt to prepare [In(DipNacnac)], **184**, by the reaction of [Li(DipNacnac)] with InCl, instead led to partial disproportionation and the formation of the indium(II) dimer, [{InCl(DipNacnac)}₂].¹²⁷ The synthesis of **184** was eventually achieved using a “one-pot” reaction of InI, KN(SiMe₃)₂, and DipNacnacH in THF.¹²⁸ A range of other related heterocycles have since been reported, and it has been found that in the solid state, sterically bulkier ligands stabilize species that are monomeric, **184**–**186**,^{42,128} while less bulky ligands result in dimeric complexes, **187** and **188** (Figure 13).^{129,130} The long In...In distances in the latter complexes (3.1967(4) Å and 3.3400(5) Å, respectively) suggest that their In...In interactions are weak at best, as borne out by DFT calculations, which indicated that <2 kcal/mol is required to dissociate them into monomeric singlet fragments.¹²⁹ Indeed, NMR studies have shown that both **187** and **188** exist in their monomeric forms in solutions of noncoordinating solvents.¹³⁰ It is noteworthy that a report of a related linear In–In bonded, hexameric complex, which incorporates less bulky β-diketiminato N-substituents than those of **184**–**188**, has come forward. While the complex I(L)In{In(L)}₄In(L)I (L = [N(C₆H₃Me₂-3,5)CMe]₂CH) is a mixed valence species, it does contain four In^I centers.¹³¹

The reactivity of six-membered indium(I) heterocycles has been poorly studied, and there is much scope to extend this and compare it with the well-developed chemistry of similar Al and Ga species. Although no coordination complexes of **184**–**188** are known, the indium centers of **184** and **187** have been shown to insert into the Fe–I bond of [CpFe(CO)₂I] to give [CpFe(CO)₂{In(I)[N(Ar)C(Me)₂CH}]} (Ar = Dip or mesityl).¹³² Attempts to abstract the halide from these compounds resulted in complex product mixtures. Similarly, a range of alkyl halides can oxidatively add to the indium center of **184** to give complexes of the type [(DipNacnac)In(R)(X)] (X = Br or I).¹³³ The only other reported reaction of an indium(I) heterocycle is the aerobic oxidation of **188**, which yielded the crystallographically characterized trimeric complex [{In(O){In(N(*o*-xylyl)C(Me)₂CH}]₃], which contains a In₃O₃ six-membered ring.¹³⁰

2.5. Thallium(I) Heterocycles

2.5.1. Four-Membered Rings

It is apparent that no computational studies have examined the structure or bonding of four-membered thallium(I) heterocycles with unsaturated backbones. All attempts to prepare examples of such species via the reaction of alkali

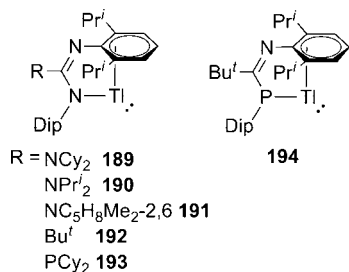


Figure 14. N-Dip- and P-Dip-chelated thallium(I) complexes.

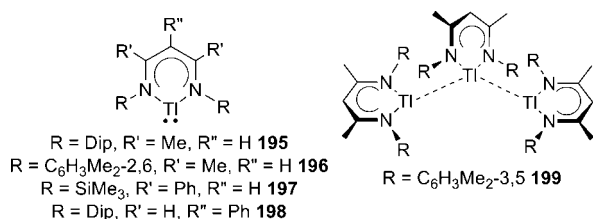


Figure 15. β -Diketiminato thallium(I) complexes.

metal complexes of N-Dip-substituted amidinates, guanidinates or phosphaguanidinates instead gave the N,Dip-chelated “five-membered” isomers, **189–193** (Figure 14), all of which are extremely air-sensitive.^{39,69,125} It is likely that the N,N-chelated isomers are not accessible in these reactions due to the larger covalent radius of thallium(I) relative to those of the lighter group 13 metals. Similarly, a recent attempt to form a P,N-heterocyclic thallium(I) species using an aza-phosphaallyl ligand afforded **194**, which is closely related to **189–193**.¹³⁴ No further chemistry has been reported for any of these complexes.

2.5.2. Five-Membered Rings

No theoretical investigations of anionic five-membered thallium(I) heterocycles have been reported. Moreover, no examples of the preparations of such species have been described in the literature.

2.5.3. Six-Membered Rings

Calculations on the model neutral six-membered thallium(I) heterocycles, $[\text{Ti}\{[\text{N}(\text{R})\text{C}(\text{R}')]\text{CH}\}]$ (R = Ph or Dip; R' = Me),^{38,42} have shown their electronic structures to differ compared with those of the aforementioned β -diketiminato coordinated Al^I and Ga^I systems in that their HOMOs are entirely ligand-based and their metal lone pairs are now associated with the HOMO-2. Similarly, the empty p-orbital at thallium constitutes the LUMO, and the HOMO-2–LUMO gap is ca. 115 kcal/mol (DFT B3LYP). These differences were attributed to the increased stability of the thallium(I) cation, relative to the monovalent state of the lighter members of the group, which is a manifestation of the “inert pair” effect.¹³⁵

A handful of thallium(I) β -diketiminato complexes, **195–199** (Figure 15), have appeared in the literature, and all were prepared via salt elimination reactions.^{42,136,137} In the solid state, all but **199** were found to be monomeric. The aggregation of **199** into a weakly Tl \cdots Tl bonded (ca. 3.58 and 3.80 Å) trimer likely results from the lesser steric protection the xyllyl groups of each ligand provide to the thallium centers.^{137b} It is evident that the only mention of the further reactivity of an N-heterocyclic thallium(I) compound is the use of **196** as a ligand transfer reagent in the formation of a β -diketiminato copper(I) complex.¹³⁶ Con-

sidering the low energy of the thallium lone pairs of these heterocycles, it seems unlikely that their coordination and redox chemistry will develop to any great extent.

3. Group 14 Element(II) N-Heterocycles

This second section will focus on the N-heterocyclic systems of group 14 with the exception of carbon. Carbene chemistry has received significant attention and has been thoroughly reviewed.¹³⁸ By and large the discussion will be limited, as with the previous section, to the compounds of type **F**, **G**, and **H** (Figure 16). The discussion of the four-membered amidinate and guanidinate species¹³⁹ and six-membered β -diketiminato (Nacnac) species¹⁴⁰ will be expanded to include compounds of type **I** and **J** as well. This is done because the element remains in the +2 oxidation state, which can be clearly seen in the resonance structures **I'** and **J'**. Additionally these types of species have a rich and interesting chemistry whereas there are relatively few examples of the cationic species of type **F** and **H**. Some aspects of low-valent group 14 compounds have been reviewed elsewhere^{3,141} with particular attention on neutral silylene systems.¹⁴² However, herein we will strive to update and give a complete account of the latest work on low-valent group 14 N-heterocycles in the +2 oxidation state.

3.1. Silicon(II) Heterocycles

3.1.1. Four-Membered Rings

To date, the four-membered cationic amidinate silylenes of type **F** are unknown although theoretical studies have been undertaken.¹⁴³ However, the covalently bonded neutral analog of type **I** has been synthesized by Roesky et al.¹⁴⁴ Compound **200**, which can also be viewed as an imine-stabilized amino chloro silylene (**I'**), was synthesized by reduction of the trichloride precursor **201a** (Scheme 7). Unfortunately the reduction step yields only 10% of **200**. However, recently it has been reported that the yield can be significantly increased by using an N-heterocyclic carbene (NHC) (35%) or simply LiN(TMS)₂ (90%) starting from the dichlorosilane precursor **201b**.¹⁴⁵ Dehydrochlorination using NHCs was previously reported to generate several other stable or metastable silylenes and appears to be a powerful method for generating low-valent silicon species.¹⁴⁶ The substitution at both nitrogens and the ring carbon are highly important; thus to date only the system with the *N-tert*-butyl *C*-phenyl substitution pattern has been reported. The sterics at the nitrogen group

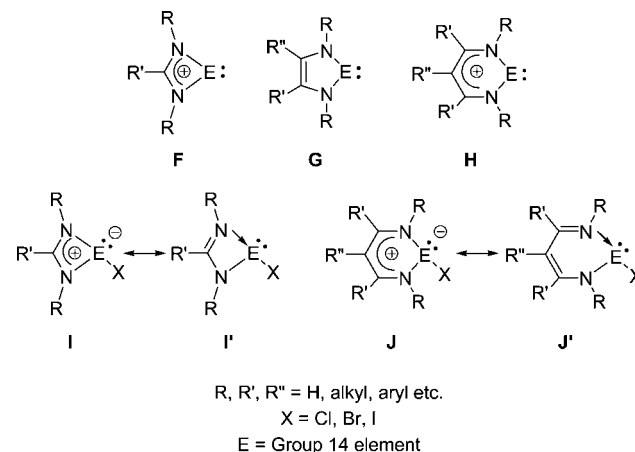
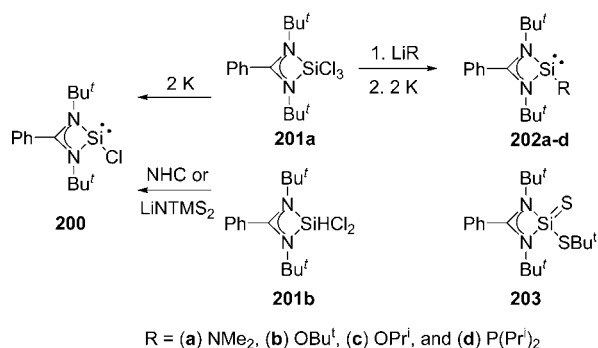


Figure 16. General structures of group 14 element(II) N-heterocycles.

Scheme 7



appear to be of great importance because analogues with isopropyl and cyclohexyl groups or even the slightly less bulky trimethylsilyl group did not yield stable species. At the same time, the electronics of the phenyl group appear to be significant because isopropyl or *tert*-butyl substitution at this remote position also led to unsuccessful reductions.¹⁴⁷

One chlorine from the precursor **201a** can be substituted with nitrogen, oxygen, and phosphine bases. Subsequent reduction with elemental potassium leads to the corresponding heteroleptic silylenes **202a–d** in reasonable yields (41–52%).¹⁴⁷ A lithium thiolate can also successfully substitute one chlorine from **201a**. Interestingly, reduction with 2 equiv of potassium metal leads to the silicon thioester species **203** rather than the thio-substituted silylene (Scheme 7).¹⁴⁸ Heteroleptic silylenes like **202a–d** were rare making this synthetic pathway, starting from a common precursor, an important step in further investigation of their chemistry. Already this has led to the report of a coordination complex. The reaction of the *tert*-butoxy-substituted silylene **202b** with diironnonacarbonyl in THF leads to the silylene iron carbonyl complex Fe(**202b**)(CO)₄, which has been isolated and entirely characterized.¹⁴⁹

The reactivity of **200** is still nascent, in large part because of the initial low yield. Shortly after the new synthetic method (starting from **201b**) was revealed the reactivity of **200** with diphenylacetylene was reported. The resultant disilacyclobutene **204** was isolated, and it was postulated that after an initial cyclopropanation reaction, a typical reaction of carbenes and their heavier analogues, that insertion of a second equivalent of **200** into one of the Si–C bonds yields this novel disilane, which is one of the first examples of a compound containing two pentacoordinate silicon atoms directly bonded (Figure 17).^{145a} There has been only one other

such species reported.^{145b} Also the reaction of **200** with benzophenone has been reported.¹⁵⁰ In this case, the siloxirane **205**, with a pentacoordinate silicon center, could be isolated. This is only the second example of an isolable siloxirane¹⁵¹ and the first with a pentacoordinate silicon atom. The new high yield synthesis should lead to rapid advances in this new and interesting chemistry.

One final example of an amidinate-stabilized silylene is known. The bis(silylene) **206** was isolated in low yield (5.2%) from the reduction of trichlorosilane **201a** with 3 equiv of potassium graphite.¹⁵² Compound **206** has two silicon(I) centers but is included here for completeness and because of the structural similarities to all the silylenes discussed in this section. Additionally, the bromine-substituted silylene analogue of **200** is accessible by bromination (with Br₂) of the bis(silylene) **206**.¹⁵³ No alternative synthesis has been reported for this bromo silylene. The reactivity of both of these species is very promising but will be significantly hindered by the low yields. However, very recently the reaction of **206** with N₂O and benzophenone has been reported to give the siloxy compounds **207** and **208**, respectively (Figure 17). These two species were fully characterized and a mechanism for the formation of both species was suggested by the authors.¹⁵⁴ Also the addition of 2 equiv of diphenylacetylene to **206** has recently been published.¹⁵⁵ Both diphenylacetylene equivalents add across the Si–Si, with concomitant Si–Si bond rupture, to give the 1,4-disilabenzene derivative **209** (Figure 17). This disilabenzene species is nearly planar in the solid state despite the tetrahedral silicon centers, and calculations show that there is some aromatic character to the system [NICS(1) = –3.6].

3.1.2. Five-Membered Rings

Isolable five-membered N-heterocyclic silylenes (NHSi) are clearly the largest group of silylenes and provide the largest diversity in structure and reactivity. As such, they have been previously reviewed several times.¹⁴² They have also been the focus of several theoretical studies.^{15,156} The first silylene, **210a**, was reported by Denk et al. in 1994 (Figure 18).¹⁵⁷ In the 15 years since this initial report, 11 other isolable silylenes have been reported and can be broadly classified into three groups. First are unsaturated silylenes like the first example **210a**, which for a long time stood alone until the recent report of two aryl-substituted versions **210b** and **210c**.¹⁵⁸ The second are the saturated silylenes of type

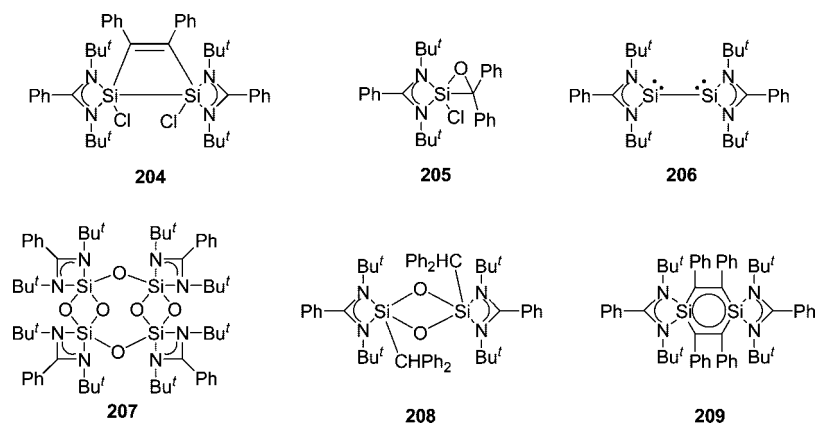


Figure 17. Products of the reaction of **200** with diphenyl acetylene (**204**), benzophenone (**205**), and KC₈ (**206**) and the products of the reaction of **206** with N₂O (**207**), benzophenone (**208**), and 2 equiv of diphenyl acetylene (**209**).

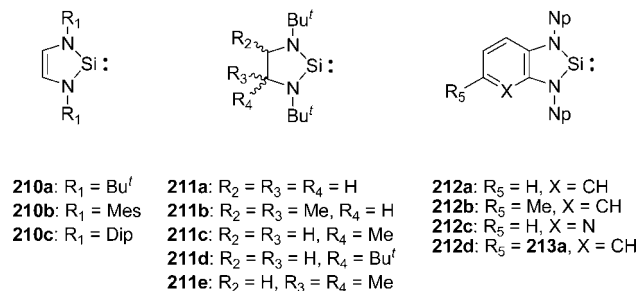
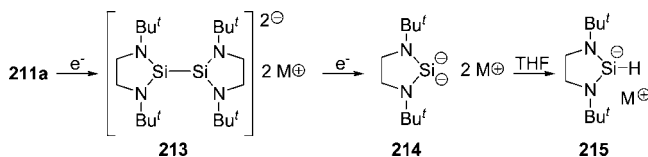


Figure 18. Known five-membered NHSi.

Scheme 8



211, the first of which (**211a**) was also reported by Denk et al. (Figure 18).¹⁵⁹ Interestingly, **211a** is stable in dilute solutions; however, in more concentrated solutions and in the solid state, it undergoes reversible tetramerization, which has also been studied.¹⁶⁰ More recently the substituted saturated silylenes **211b–e** have been reported, all of which are stable and do not undergo oligomerization.^{161,162} The third group are the benzo-fused models of type **212** (Figure 18), which includes the only example of a bis-silylene **212d**.^{163–165} The silylenes **210a** and **211a** have also been the subject of cyclic voltametric studies.^{156b} The electronic structure of each type of silylene has also been further probed by photoelectron,¹⁶⁶ Raman,¹⁶⁷ and core excitation spectroscopy.¹⁶⁸

The synthesis of all these silylenes was performed by reduction of a dihalosilane precursor (dichloro or dibromo) in polar solvents such as THF or DME. In some cases, it was found that addition of 10% triethylamine prevented over-reduction.^{161,169} The reducing agent of choice has been potassium; the element, sodium–potassium alloy, or more often with recent examples, potassium graphite. There are two notable exceptions: first, silylene **210c** is synthesized from the hexachlorodisilyldiamine precursor by reduction with six equivalents of potassium graphite (it has been proposed that polymeric silicon halide is extruded),¹⁵⁸ and second, silylenes **210a** and **210b**, in addition to the standard reduction procedure, have been generated by dehydrochlorination of the corresponding chlorosilanes with a bulky NHC.^{146a}

The electrochemistry of silylenes has received some attention over the years. During the synthesis of saturated silylene **211a**, it was noted that the further reduction of the silylene competed with the reduction of the starting material.¹⁶⁹ As mentioned previously, triethylamine was used to limit this problem; however, **211a** can be directly reacted with sodium potassium alloy or potassium graphite to yield the silylene radical anion that dimerizes to the dianion **213** (Scheme 8). This dianion is not sufficiently stable to be characterized but can be trapped by proton sources or trimethylsilylchloride (TMSCl). Two electron reduction of **211a** yields the monomeric dianion **214**, which is stable at -20°C and can be trapped by 2 equiv of a proton source or TMSCl. At room temperature the dianion slowly deprotonates THF to give the anionic **215**, which has also been trapped with 1 equiv of a proton source or TMSCl.¹⁷⁰

The unsaturated silylene **210a** can also be further reduced; however no anionic products have been observed or trapped.

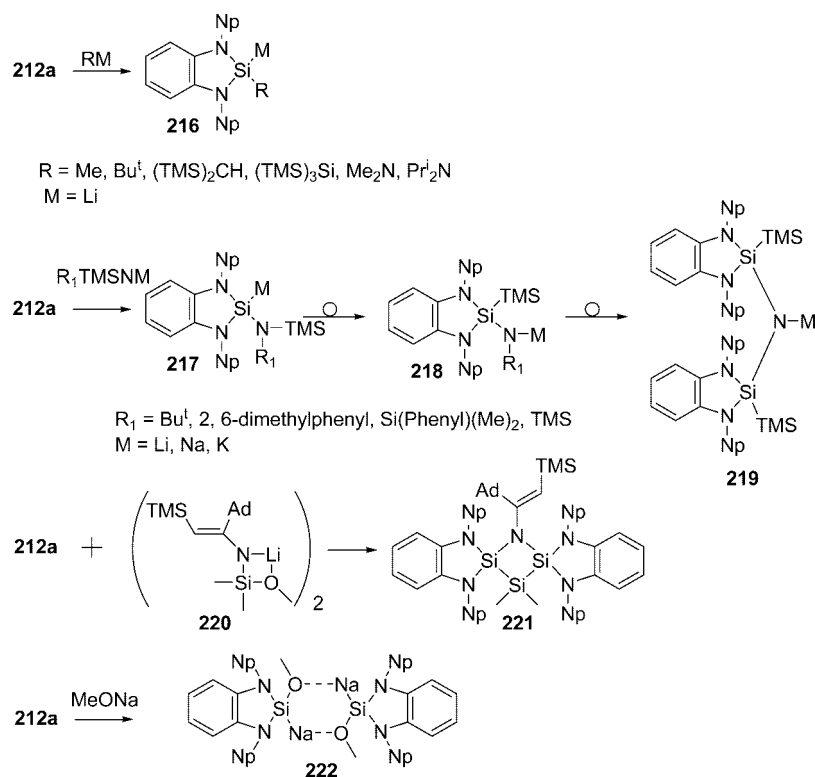
Attempts to reduce **210a** have led to the tetraamino spirocyclic silane, which indicates that the reduction breaks the Si–N bond liberating the diimine, which then reacts with **210a**. The reaction of the diimine with **210a** has been reported independently to give the same tetraamino spirocyclic silane.¹⁷¹ This reaction has also been studied theoretically.¹⁷² The only silylene that undergoes reduction to give stable isolable and well-characterized products is benzo-fused silylene **212a**. Reduction with excess sodium or potassium yields the dianionic dimeric salt similar to the single-electron reduction of **211a**. In this case, the potassium salt could be crystallized and fully characterized by multinuclear NMR and X-ray diffraction. This dianion was also trapped with TMSCl. Addition of **212a** to the dianion, or in one case by careful control of the stoichiometry, resulted in fractional reduction products. A cyclic trimeric radical anion was isolated and characterized by EPR and X-ray crystallography. The cyclic tetrameric dianion was also isolated and fully characterized.^{173,174}

The behavior of silylene **210a** with TEMPO, (O)P(OPr^{*i*})₂, MCP(CO)₃ (M = Mo, W), and Re(CO)₅ radicals has been studied.¹⁷⁵ In all cases, it was found that the radical was delocalized into the ring system. Recently **210a** has also been reacted with muonium to give muoniated radical species.^{176,177}

The reaction of benzo-fused silylene **212a** with a large number of alkali metal bases has been reported. Reactions of this type are only reported with **212a**. Lithium alkyl and silyl bases [MeLi, *tert*-BuLi, (TMS)₂CHLi, (TMS)₃SiLi] lead to addition products where the base adds to the silylene center, which is also coordinated to Li(sol)_x (sol = THF, Et₂O) yielding the corresponding silyllithium salt of type **216** (Scheme 9).¹⁷⁸ This reaction also occurs with R₂NLi (R = Me or Pr^{*i*}).¹⁷⁹ The use of amides with one silyl group [*tert*-Bu(TMS)NLi, 2,6-dimethylphenyl(TMS)NLi] lead to new lithium amides **218**, which are the result of the addition of the base followed by migration of the TMS group to the silylene center.^{180,181} This mechanistic pathway was confirmed in the case of the latter where the addition product of type **217** was isolated, and the migration product **218** was isolated only upon heating.¹⁷⁹ Similar amide products were observed with MN(TMS)₂ (M = Li, Na, or K); however in the case of LiN[Si(Phenyl)(Me)₂](TMS) a 2:1 silylene to base, doubly migrated product, **219**, was isolated as the only product. Using the correct stoichiometry LiN(TMS)₂ and NaN(TMS)₂ also gave the double addition/migration products **219**.¹⁸⁰ The lithium enamide **220** has also been reported to react with 2 equiv of **212a** to give azatrissilacyclobutane **221**.¹⁸² There is also only one report of reaction with an oxygen base. The addition of MeONa to **212a** gives the methoxy-substituted sodium silanide as the dimer **222** (Scheme 9). This same product was also isolated by reacting **212a** with Na[CH(TMS)(SiMe₂OMe)], however in very low yield (16%).¹⁷³ Despite the isolation of all these silyl anions there has been no report of their further reactivity as nucleophiles or ligands to transition metals.

Silylenes **210a**, **211a**, **211d**, **211e**, and **212a** all reacted with various alcohols by inserting into the H–O bond to produce the corresponding diaminosiloxanes of type **223** (Figure 19). Additionally, water has been reacted with **211a**, **212a**, and **212e** to yield the oxo-bridged silane **224** resulting from insertion of 2 equiv of silylene into the H–O bonds.^{161–163,169,171} This chemistry has limited further use but rather serves as a trapping reaction for silylenes and to demonstrate typical and expected reactivity.

Scheme 9



The reaction of silylenes with alkyl halides was initially another predictable and typical trapping reaction. For example, silylenes **210a**, **211a**, and **212a** all insert into the C–I bond of MeI to yield the expected halosilanes of type **225** (Figure 20).^{163,169,171} More recently, a wider variety of halocarbons were reacted with **210a** giving unexpected results. The reaction with dichloromethane, chloroform, carbon tetrachloride, and benzyl chloride led exclusively to 2:1 disilane adducts of type **226** while phenyl bromide led to both the disilane and insertion products.¹⁸³ Further studies investigated an even larger variety of halocarbons with not

only silylene **210a** but also **211a**.¹⁸⁴ The ratio of disilane to insertion product varied based on the nature of the halocarbon, but more importantly in all cases the results were best explained by free-radical chain mechanisms. Silylene **212a** was also independently reacted with a wide variety of halocarbons with similar results.¹⁸⁵ There were some important differences: first, it was found that upon heating the disilanes of type **226** would yield the addition product **225** and free silylene; second, di- and trihalocarbons were found to insert 2 equiv of **212a** to form carbon-bridged halosilanes; third, reaction with (bromomethyl)cyclopropane led to product mixtures indicative of the free radical chain mechanism (inasmuch as cyclopropylmethyl radical converts rapidly into the more stable 1-butenyl isomer). There have been several computational studies to investigate the mechanism of disilane formation;¹⁸⁶ however, one study focused on the differences between concerted and radical mechanisms found that the radical pathway was 16–23 kcal/mol lower in energy, which agrees with the experimental results.¹⁸⁷ Interestingly, the reaction of **212a** with silyl halides (SiCl_4 , SiBr_4 , PhSiCl_3 , and MeSiCl_3) also led to a similar array of

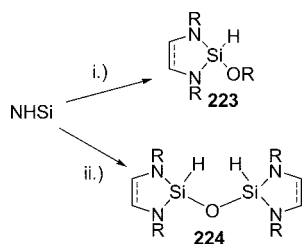
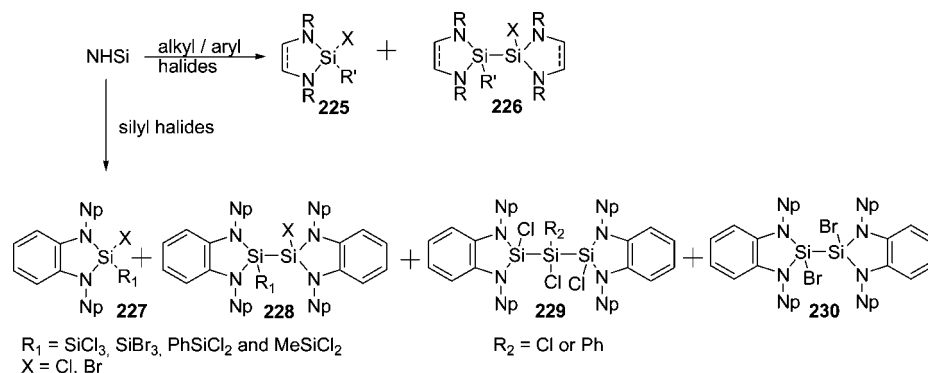
Figure 19. Reactivity of NHSi: (i) ROH and (ii) H₂O.

Figure 20. Reactivity of NHSi with alkyl, aryl, and silyl halides.

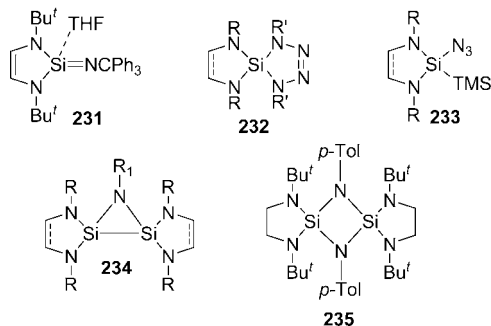


Figure 21. Products obtained by reacting NHSi's with azides.

products, that is, insertion to give compounds **227** in all cases, disilanes **228** with both tetrahalosilanes, and insertion of two silylenes to form trisilanes **229** with SiCl_4 and PhSiCl_3 . When SiBr_4 was used two additional products are also observed, the dibromodisilane **230** and the dibromosilane (the silylene precursor) (Figure 20).¹⁸⁸ All of these products are also best rationalized by a free radical chain mechanism. Activation of C–H bonds has been reported using silylene **210a** and PhI .¹⁸⁹ It was found that the expected addition product, while present, was a minor product and that C–H bonds of various solvents were activated with elimination of benzene and formation of solvent iodide adducts of the silylene. This activation occurs with alkanes, ethers, and tertiary amines. This type of activation has precedence with heavier silylene analogues (specifically germanium and tin),¹⁹⁰ however this is the first report using silylenes.

The reaction of NHSi with azides has been thoroughly investigated. The intense interest is due to the possibility of isolating a stable silaimine. This was the goal when West et al. reacted Ph_3CN_3 with silylene **210a** shortly after it was first reported.¹⁹¹ The results were very encouraging because the silaimine **231** was isolated; however one molecule of THF was coordinated to the silicon center (Figure 21). The use of a noncoordinating solvent did not lead to the free species but rather to silatetrazolines **232** not only with PhCN_3 but also PhN_3 , $p\text{-tolN}_3$, Ph_3SiN_3 , and Adamantyl N_3 .^{159,192} These silatetrazolines appear to be the result of a 2 + 3

cycloaddition of the desired silaimine with a second equivalent azide. Similar silatetrazolines were also isolated with silylenes **210a**,¹⁹² **211d**,¹⁶² and **212a**.¹⁹³ There are several exceptions. Two equivalents of TMSN_3 also react with silylenes **210a**,^{191,192} **211a**,¹⁹² and **212a**,¹⁹⁴ but rather than the silatetrazoline, the TMS group migrates to give the isomeric azidosilane **233**. Azadisilacyclopropanes **234** were isolated when 1 equiv of RN_3 ($\text{R} = \text{Ad}$ or TMS) was added to 2 equiv of **212a**.^{193,194} The azadisilacyclopropane was the only product isolated, quantitatively, by reacting MesN_3 with silylene **211d**.¹⁶² Mechanistically, the intermediate nature of the silaimine is reinforced by the isolation of the 2 + 2 cyclodimerization product **235** as a minor product when silylene **211a** is reacted with $p\text{-TolN}_3$.¹⁹²

There have been numerous studies into the reactivity of NHSi with unsaturated organic species. However, C–C double and triple bonds do not show significant reactivity, most likely because of the nonpolar multiple bond. Silylenes **210a** and **211a** undergo 4 + 1 cyclization reactions with dienes (1,4-diphenyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene, respectively).^{159,169} Cycloadditions to 1,3-heterodienes have also been documented. NHSi **211a** and **212a** react with 1,4-diaza-1,3-butadiene to form the corresponding spirocyclic tetraaminosilanes of type **236** (Figure 22, $\text{E}_1 = \text{E}_2 = \text{NR}$).^{171,195} Additionally, **212a** reacts with 1,4-diphenyl-1-azabutadiene, cinnamyl ketone, and benzil to give the corresponding spirocyclic compounds of type **236**.^{195,196} Silylene **212a** also reacts with phenyl(trimethylsilyl)acetylene presumably in a first step to give a silacyclopropene, which immediately reacts with a second equivalent of **212a** to give the disilacyclobutene **237** (Figure 22).¹⁹³

There has also been one report of the reactivity of silylene **212a** with a heavy alkene analogue. The transient silene $[\text{Ad}=\text{Si}(\text{TMS})_2]$ reacts with **212a** to give the expected 2 + 1 disilane **238**, which could be isolated in good yield and was fully characterized (Figure 22).¹⁹⁷ Additionally, NHSi **210a**, **211a**, and **212a** react with 1,3,5-triphenylbenzene, not with the P–C double bond but rather to form the 2.2.1 bicyclic adducts **239**.¹⁹⁸ This reaction also allows the silylene intermediate in the tetramerization of **211a** to be trapped.

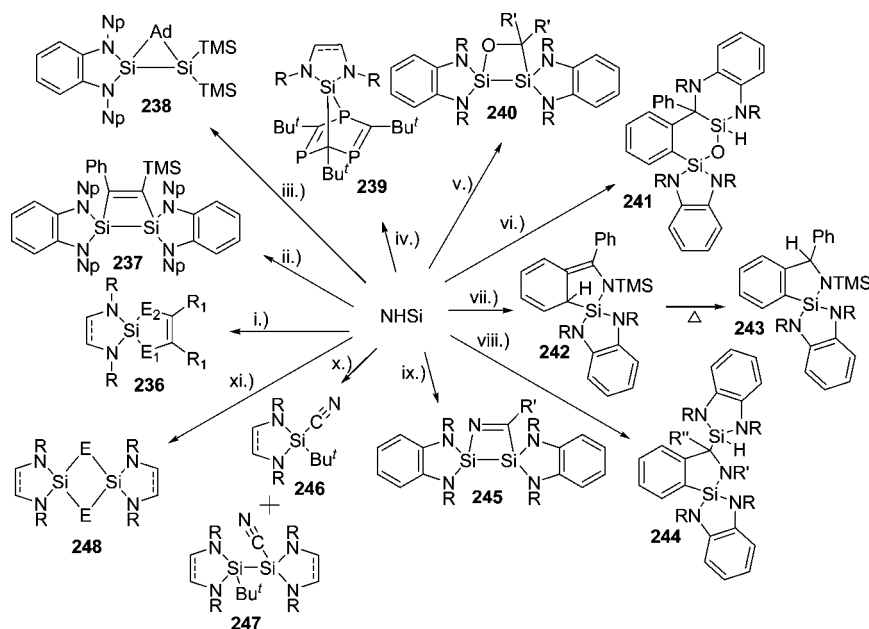


Figure 22. Reactivity of NHSi: (i) dienes and heterodienes; (ii) an alkyne; (iii) $\text{Ad}=\text{Si}(\text{TMS})_2$; (iv) 1,3,5-triphenylbenzene; (v) ketones; (vi) benzophenone/reflux; (vii) $\text{TMSN}=\text{CPh}_2$; (viii) $\text{R}'\text{N}=\text{CPhR}''$; (ix) nitriles; (x) *tert*-butylisocyanide; (xi) O_2 , S, Se, or Te.

Both imines and ketones react with NHSi **212a** but in different ways. Gehrhuis and Lappert proposed that in both cases an initial heterocyclopropanation reaction takes place.¹⁹³ In the case of ketones, a second equivalent of **212a** inserts into the Si–O bond to form a stable four-membered disilaoxetane **240** (Figure 22). When benzophenone was reacted with 2 equiv of **212a** in refluxing benzene a different adduct, **241**, was isolated, which is unrelated to the disilaoxetane inasmuch it cannot be thermally transformed into the second adduct.¹⁹⁶ A mechanism for this reaction was suggested by the authors. Interestingly, pyridine and quinoline react with **212a** to give disilazabutanes.¹⁹⁹ In the case of pyridine, the disilazabutane formed is labile probably because of the energy gained by rearomatization. However, upon heating, the pyridine-substituted disilane is isolated, which can be seen as the addition of the C–H bond across the Si–Si bond. The 2:1 adduct formed with quinoline is thermally stable. The reactions of imines are less straightforward. One equivalent of $\text{Ph}_2\text{C}=\text{NTMS}$ reacts with **212a** presumably to form the unstable silaziridine, which then undergoes ring expansion to give the isolable **242**, which over the course of several months at room temperature (or several hours in refluxing benzene) isomerizes to give the rearomatized product **243**. Adding a second equivalent of **212a** to **243** gives compound **244**, which is the only product isolated when $\text{Ph}(\text{H})\text{C}=\text{NBu}^t$ is used.¹⁹⁵

Nitriles (1-adamantanecarbonitrile and trimethylacetone-trile) react with **212a** to give compounds of type **245** (Figure 22). Once again the transient three-membered ring reacts with a second equivalent of silylene to form the disilazabutene **245**.^{193,194} *tert*-Butylisocyanide is also reported to react with **212a**. When **212a** was added to the isonitrile the silanitrile **246** was isolated.¹⁹³ When the isonitrile is added to the silylene, the 1:2 acyclic disilane adduct **247** is isolated with a *tert*-butyl group on one silicon and a nitrile on the other. Mechanistically, Lappert et al. explained this reactivity not by an intermediate three-membered ring but rather by the formation of a silaketenimine followed by migration of a *tert*-butyl group.¹⁹⁴ West et al. mentioned the reaction of NHSi **210a** with the same isonitrile to give the silanitrile addition product, which was reported to be in equilibrium with the isonitrile.^{142g} However, these preliminary results were never fully reported.

The Lewis acid/base properties of NHSi have received some interest and have been studied theoretically.^{200–202} The Lewis acid properties of **212a** have been demonstrated by the formation of a stable carbene adduct, which was serendipitously discovered while trying to synthesize a mixed carbene/silylene Ni complex.²⁰³ The crystal structure clearly shows that the carbene lone pair donates into the formally vacant $p\pi$ orbital on Si. Variable-temperature NMR studies demonstrated that this adduct was thermally labile and that the free species were observable in solution at 358 K.²⁰⁴ In contrast, silylene **210a** acts as a Lewis base to $\text{B}(\text{C}_6\text{F}_5)_3$ to form a metastable adduct that undergoes phenyl migration only after several months in solution.²⁰⁵ Interestingly, addition of the Lewis basic 4-methylpyridine to the adduct resulted in formation of the free silylene and the pyridine–borane adduct.

There are examples of group 16 elements reacting with NHSi. The hope was to isolate the monomeric $\text{Si}=\text{E}$ ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{or Te}$) heavy carbamide analogues. However, in all cases, the 2 + 2 dimer of type **248** has been isolated (Figure 22). Saturated NHSi **210a** reacts with elemental

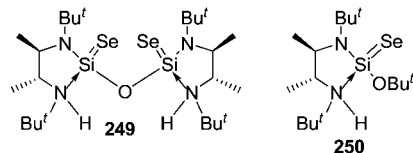
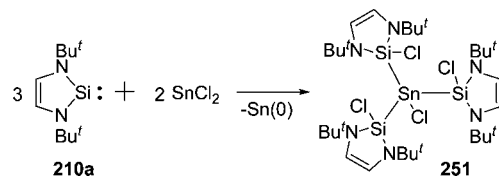


Figure 23. Acid anhydride and carbamate analogues from silylene **211e**.

Scheme 10



sulfur and selenium to give the stable dimers.¹⁷¹ In this same publication, West et al. were also able to observe the same type of dimeric species upon reaction with O_2 . Unfortunately, they were unable to isolate sufficient quantities for full characterization because separation from an apparently polymeric product was not feasible. Silylene **212a** reacts in the same fashion with sulfur, selenium, and tellurium.²⁰⁶ There are no examples with the saturated silylene **211a** perhaps because of the equilibrium with the tetramer. However, the advent of the monomeric saturated silylene **211e** has led to a stable O_2 dimer of type **248**.¹⁶¹ The selenium dimer is also isolable and interestingly reacts with water and *tert*-butanol, which add across the Si–N bond to give the amine-stabilized carbamic acid anhydride **249** and the carbamate selenium analogue **250** (Figure 23).²⁰⁷ From group 15 there is only a brief mention that attempts to react **210a** with P_4 yielded no isolable product although they proposed that amorphous red phosphorus was formed.¹⁷¹

Several heavy group 14 halides react with NHSi **210a** and **212a**. The divalent halides SnCl_2 and PbCl_2 react with **210a**. Two equivalents of SnCl_2 react with 3 equiv of **210a** to give the light-sensitive tris(silyl)stannyl chloride **251** (Scheme 10).²⁰⁸ Apparently **251** is the result of insertion of an equivalent of **210a** into each Sn–Cl bond and the third equivalent coordinating to the tin center followed by dechlorination of the second tin(II) chloride to yield **251** and tin metal, which visibly precipitates from the reaction mixture. Upon heating of **251**, the dichlorosilane, dichlorodisilane, and free silylene **210a** are observed with the deposition of tin metal. Under photolytic conditions, only the dichlorodisilane is observed as well as some SnCl_2 and tin metal.

Lead(II) chloride is reduced by **210a** to the metal accompanied by the formation of dichlorosilane. Similar redox reactions were reported for the reaction of NHSi **212a** with GeCl_4 and SnCl_4 .¹⁸⁸ In both cases, the dichlorosilane was isolated, and in the case of tin, the corresponding reduced tin(II) chloride was observed. Presumably the germanium(II) chloride was also transiently formed, but because it is unstable without an additional donor ligand, it reacted further to give unidentified products. Several other low-valent group 14 species have been reacted with NHSi. A saturated N-heterocyclic germylene (NHGe) was added to the unsaturated NHSi **211a**. The 1:1 silagermene acid/base complex was not observed but may be an intermediate in the formation of digermene analogue of the stable tetramer of **211a**.²⁰⁹ The reaction pathway is presumed to be similar to that of the tetramer but unfortunately no trapping reactions of the intermediate germylene have been reported. In the same

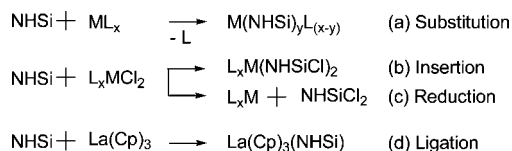


Figure 24. Possible reaction of NHSi with transition metals.

publication, the reaction of **211a** with $\text{Sn}[\text{N}(\text{TMS})_2]_2$ is also reported. Two equivalents of silylene inserted into the Sn–N bonds to give an intermediate disilastannylene, which subsequently inserts into the C–H bond of one methyl group. The same reaction is reported for **212a** with slightly different results. In the case of addition of **212a** to $\text{Ge}[\text{N}(\text{TMS})_2]_2$, the same result was found, but in the case of both $\text{Sn}[\text{N}(\text{TMS})_2]_2$ and $\text{Pb}[\text{N}(\text{TMS})_2]_2$, 2 equiv of silylene **212a** inserted into both M–N bonds to form new stable disila-substituted M(II) species.²¹⁰ When one or two $\text{N}(\text{TMS})_2$ groups are replaced with aryl groups [Ar = 2,6-bis(dimethylamino)phenyl] on tin(II) [$\text{Sn}(\text{Ar})\text{N}(\text{TMS})_2$ and $(\text{SnAr})_2$], respectively] the monoinsertion products are found.²¹¹ In the case of $\text{Sn}(\text{Ar})[\text{N}(\text{TMS})_2]$, the insertion occurs exclusively in the Sn–N bond. The stability of the monoinsertion products is attributed to weak interactions with the dimethylamino groups that can be seen in the respective crystal structures. In all of these cases, a $\text{Si}=\text{M}$ intermediate is proposed but none can be directly observed. There is also one report of an isoelectronic divalent phosphorus compound, a phosphonium tetrachloroaluminate [$(\text{Cy}_2\text{N})_2\text{P}^+ \cdot \text{AlCl}_4^-$], reacting with NHSi **210a**.²¹² The resulting species is a phosphinochlorosilane and aluminum trichloride. Calculations indicate that the $\text{Si}=\text{P}$ species is not likely an intermediate in the reaction.

The ability of NHSi to form transition metal complexes has been well documented with a wide variety of metals ranging from group VI to group XI, as well as several lanthanides. A large number of these complexes are formed by ligand substitution reactions of hemilabile ligands such as phosphines, carbon monoxide, and 1,4-cyclooctadiene (Figure 24, path a). Additionally, there are insertion and reduction reactions of NHSi with transition metals and ligation reactions of NHSi to lanthanides (Figure 24, paths b, c, and d, respectively).

The ligand properties of NHSi have been widely discussed and their relation to phosphines and NHCs has been examined.²¹³ In order to compare σ -donor and π -acceptor properties of NHSi, phosphines, and NHCs (L), group VI complexes of type $\text{M}(\text{L})_2(\text{CO})_4$ (M = Cr, Mo, and W) have been synthesized, and the carbonyl stretching frequencies were measured by IR.²¹⁴ The $\text{M}(\text{210a})_2(\text{CO})_4$ and $\text{M}(\text{211b})_2(\text{CO})_4$ complexes were readily prepared by reaction of the free silylene with the hexacarbonyl metal complex under photolytic conditions ($h\nu = 254 \text{ nm}$). The results show that the NHSi's are electronically similar to phosphines; however they are not as strongly donating as NHCs. These results are in line with several theoretical studies of NHCs, NHSi's and other heavy carbene analogs.^{15,215,216} Sterically, NHSi's are more like NHCs, which are often described as "fences",²¹⁷ as opposed to phosphines, which have been described as "cones".²¹⁸ However, there are several important steric differences between NHSi and NHCs. The smaller N–E–N (E = Si or C) bond angle ($\sim 90^\circ$ vs $\sim 100^\circ$), as well as the longer N–E bond length ($\sim 1.73 \text{ \AA}$ vs $\sim 1.37 \text{ \AA}$), creates a marked decrease in steric congestion at the metal center, which has been investigated experimentally and theoretically.^{219,220}

As mentioned, the substitution method (path a) is the most widely applicable method for synthesis of NHSi metal complexes. In fact, the first metal complex was formed in this fashion and reported preliminarily in the first NHSi publication¹⁵⁷ and fully reported shortly thereafter.²²¹ Two equivalents of **210a** were reacted with $\text{Ni}(\text{CO})_4$ to substitute two CO and form the stable $\text{Ni}(\text{210a})_2(\text{CO})_2$ complex. The monosubstituted complex could not be synthesized. Substitution of CO at metal(0) centers has been also used to make the aforementioned group VI disilylene tetracarbonyl complexes as well as $\text{Fe}(\text{210a})(\text{CO})_4$ and $\text{Ru}(\text{210a})_2(\text{CO})_3$ from $\text{Fe}_2(\text{CO})_9$ and $\text{Ru}_3(\text{CO})_{12}$, respectively.²¹⁴ Other metal(0) complexes are also common reagents. For example, $\text{Ni}(\text{COD})_2$ (COD = 1,5-cyclooctadiene), an excellent source of nickel(0) and much less toxic, reacts with silylenes **210a–c**, **211a**, and **212a** to form silylene complexes albeit in three different ways. Three equivalents of silylenes **210a** and **211a** substitute both COD ligands to give the corresponding 16 electron complexes,²²² while four equivalents of **212a** coordinate to give the expected 18 electron species.²²³ The difference can be best explained by the sterically larger *tert*-butyl groups on **210a** and **211a** compared with the neopentyl group on **212a**. Finally, 2 equiv of **210b** and **210c** replace only one COD to give the heteroleptic $\text{Ni}(\text{210b})_2(\text{COD})$ and $\text{Ni}(\text{210c})_2(\text{COD})$ complexes, respectively.¹⁵⁸ Substitution of the COD groups is not limited to metal(0) complexes; both COD ligands of the cationic $[\text{Rh}(\text{I})(\text{COD})_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ are substituted by 4 equiv of both **210a** and **211a** to give the corresponding cationic homoleptic Rh(I) complexes.²²⁴ In this case, the larger metal center can accommodate four silylenes although the products are still unsaturated 16 electron species.

As pointed out previously, NHSi are stronger ligands than phosphines according to experimental and theoretical results.^{15,215,216} This indicates that metal phosphine complexes should undergo substitution reactions of type a with NHSi. This was found to be the case in numerous examples. The most straightforward examples are those of $\text{Pt}(\text{PPh}_3)_4$ and $\text{CuI}(\text{PPh}_3)_3$ with 3 and 1 equiv of **212a**, respectively, to give $\text{Pt}(\text{212a})_3(\text{PPh}_3)$ and $\text{CuI}(\text{212a})(\text{PPh}_3)_2$.²²⁵ Silylene **210a** also substitutes PEt_3 of $\text{Mo}(\text{Cp})_2(\text{PEt}_3)$ under photolytic conditions to give $\text{Mo}(\text{210a})(\text{Cp})_2$, which adds water across the Mo–Si bond to form the hydrido(silanolato) complex **252** (Figure 25).²²⁶ With palladium(0) phosphines, the results are more complicated. The first example was the reaction of **210a** with $\text{Pd}(\text{PPh}_3)_4$, which gives, not the homoleptic palladium species, but rather the dimeric silylene bridging complex **253a** with two terminal PPh_3 (Figure 25).²²⁷ Silylenes as bridging ligands have been well established,²²⁸ but this represented the first example of an NHSi as the bridging silylene. Subsequently both **210a** and **211a** reacted with $\text{Pd}(\text{P}^i\text{Bu}_3)_4$ to give the similar bridged complexes **253b** and **254**, respectively.²²⁹ However, in both cases the homoleptic $\text{Pd}(\text{210a})_3$ and $\text{Pd}(\text{211a})_4$ complexes can be seen by multinuclear NMR studies but undergo reaction with the free phosphine to form the isolated species. When 2 equiv of **210a** are added to $\text{Pd}(\text{P}^i\text{Bu}_3)_2$ the homoleptic species $\text{Pd}(\text{210a})_3$ can once again be observed followed by the formation of a new species identified as **255** by NMR, but any attempts to isolate this species led only to the more stable species **253b**.

While the substitution of phosphines is in accordance with theoretical and experimental results relating to the ligand strength of these species, there is one surprising example of NHSi **210a** substituting an NHC.²³⁰ When 3 equiv of **210a**

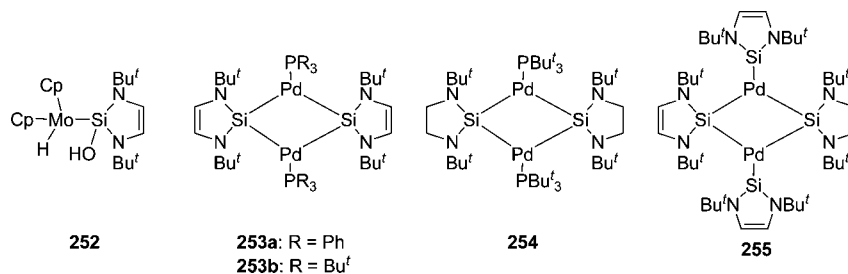


Figure 25. Transition metal silylene complexes.

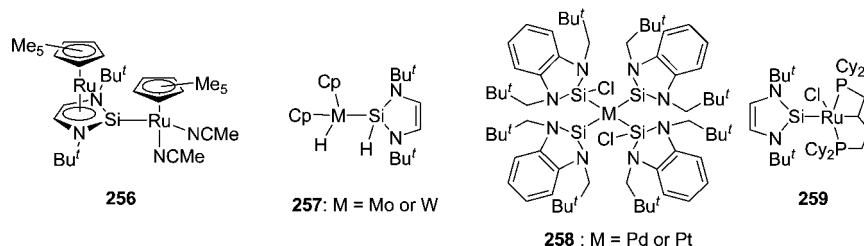


Figure 26. Silylene transition metal complexes.

are added to $\text{Pd}(\text{NHC})_2$, ligand substitution occurs and the corresponding $\text{Pd}(\mathbf{210a})_3$ and free NHC can be isolated. These results were also thoroughly theoretically investigated, which revealed that the NHSi metal bond was 3.6 kcal/mol more stable. This is primarily due to the slightly decreased steric encumbrance at the silylene center. There are three further examples of NHSi complexes formed by a substitution reactions of type a. First, silylene **210a** substitutes one acetonitrile from the cationic $\text{Ru}(\text{Cp}^*)(\text{NCMe})_3$ triflate complex (Cp^* = pentamethylcyclopentadienide) to give the stable $\text{Ru}(\mathbf{210a})(\text{Cp}^*)(\text{NCMe})_3$ triflate. Interestingly, heating of this complex leads to elimination of two additional acetonitrile groups and 1 equiv of **210a** to form the first η^6 NHSi complex **256** (Figure 26).²³¹ Second, NHSi **212a** substitutes an ethylene ligand of a $\text{LRuCl}_2(\text{ethylene})$ [$\text{L} = 2,6-(\text{MesN}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$] to give the corresponding complex.²³² Finally, the triphosphabenzene adduct of **239** (Figure 22), reacts with $\text{Mo}(\text{CO})_4(\text{nbd})$ (nbd = nobornadiene) to give the $\text{Mo}(\mathbf{212a})_2(\text{CO})_4$ as well as the η^6 -triphosphabenzene molybdenum complex.¹⁹⁸

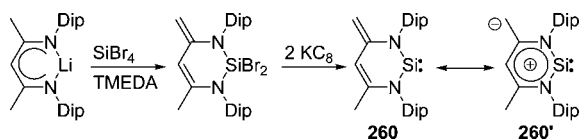
The insertion pathway b (Figure 22) is rarely observed as an end product and in fact is only observed alone for the reaction of $\text{M}(\text{Cp})_2(\text{H})_2$ ($\text{M} = \text{Mo}$ and W) with silylene **210a** where 1 equiv inserts into one $\text{M}-\text{H}$ bond to give **257** (Figure 26).²²⁶ There are also two examples where pathways a and b occur in conjunction. The reaction of 4 equiv of **212a** with $\text{PdCl}_2(\text{PPh}_3)_2$ and $\text{PtCl}_2(\text{PPh}_3)_2$ give similar products. Two equivalents insert into the $\text{M}-\text{Cl}$ bond and 2 equiv substitute the phosphines to give the mixed silylchloride silylene complexes **258**.^{223,225} The (bis)silylene complexes are unknown, and therefore it appears that the first step is in fact insertion and only then does the substitution occur.

Another pathway that is typically combined with substitution is the reduction pathway c (Figure 22). This combination was initially seen in the first attempts to synthesize nickel(II) chloride complexes of **212a** starting from $\text{NiCl}_2(\text{PPh}_3)_2$.^{223,225} When either 4 or 5 equiv of **212a** reacted with the nickel chloride, a nickel(0) complex was obtained [$\text{Ni}(\mathbf{212a})_3(\text{PPh}_3)$ and $\text{Ni}(\mathbf{212a})_4$, respectively]. The “missing” silylene equivalent was isolated as the dichlorosilane and serves as the redox partner to the metal center. This occurs by an initial insertion step followed by reductive elimination of the dichlorosilane.

Alternatively, excess NiCl_2 could be reduced to give $\text{Ni}(\mathbf{212a})_4$.²²⁵ Homoleptic $\text{Pd}(\mathbf{210a})_3$ and $\text{Pd}(\mathbf{211a})_4$ complexes, which were not accessible by substitution of phosphines, were accessible by a reduction/substitution pathway. When $\text{Pd}(\text{COD})(\text{Me})_2$ reacts with 6 equiv of **210a** or **211a**, the complexes $\text{Pd}(\mathbf{210a})_3$ and $\text{Pd}(\mathbf{211a})_4$, respectively, are isolated.²²⁹ Interestingly, the unsaturated silylene **210a** adds only 3 equivalents and eliminates 1 equiv of the dimethylsilane whereas **211a** adds 4 equivalents and eliminates the dimethyldisilane, once again demonstrating the different electronic and steric properties of **210a** and **211a**. Furthermore, the $\text{Pd}(\mathbf{210a})_3$ was found to be in equilibrium with free silylene **210a** and the dibridged silylene complex **255** (Figure 25). The reductive elimination pathway of methyl palladium(II) NHC and NHSi species has also been investigated theoretically.²¹³ There is also one reported case where the reduction of the metal is accompanied by the elimination of the HCl adduct of **210a**. The reaction of **210a** with $[(\text{dcypb})(\text{H})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{dcypb})(\text{N}_2)]$ [$\text{dcypb} = \text{Cy}_2\text{P}(\text{CH}_2)_4\text{PCy}_2$] gives the novel η^3 - dcypb ruthenium chloride complex **259** and the corresponding chlorosilane redox partner (Figure 26).²³³ There is one exceptional example of the reverse reaction occurring wherein a chlorosilane oxidatively adds to a metal center to give the NHSi complex. When the HCl adduct of **212a** is mixed with ruthenium(0) precursor $\text{RuL}(\eta^6\text{-C}_6\text{H}_6)$ or LRuN_2RL [$\text{L} = 2,6-(\text{MesN}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}$] the corresponding $\text{LRu}(\mathbf{212a})(\text{H})(\text{Cl})$ complex could be isolated.²³² In the same publication, the authors reported that the dichlorosilane precursor of **212a** reacts with the same ruthenium complexes to give the free silylene and a dichlororuthenium complex. These results are intriguing because oxidative addition of $\text{Si}-\text{Cl}$ bonds is rare²³⁴ and as mentioned this is the lone case where an NHSi complex is accessible from a precursor other than the free NHSi .

The last pathway, the ligation pathway d (Figure 22), also yields several examples. Both YCp_3 and YbCp_3 react with **212a** to give the corresponding $\text{M}(\mathbf{212a})\text{Cp}_3$ complexes.²³⁵ It was found that these complexes were in equilibrium in solution with the starting materials. Silylene **210a** also ligates $\text{Sm}(\text{Cp}^*)_2$ directly to give $\text{Sm}(\mathbf{210a})(\text{Cp}^*)_2$.²³⁶ In this case, there is no equilibrium, but the silylene is easily substituted by 2 equiv of THF. There are also several examples where NHSi are used to ligate transition metal dimers or oligomers

Scheme 11



resulting in the monomeric silylene complexes. A ruthenium(II) complex is available by the reaction of the tetrameric $[\text{Ru}(\text{Cp}^*)(\mu\text{-Cl})_4]$ with 4 equiv of **210a** to give the $\text{Ru}(\text{210a})(\text{Cp}^*)\text{Cl}$.²³¹ Allylpalladium chloride dimer has also been reported to react with **210a** to give the monomeric $\text{Pd}(\text{210a})\text{Cl}(\text{allyl})$ complex.²³⁷ Unfortunately this complex is not fully characterized and lacks X-ray crystallographic analysis and ^{29}Si NMR, although the other analytical data is in line with the attributed structure.

These N-heterocyclic silylene complexes have found limited application as ancillary ligands in homogeneous catalysis. In fact, to date, there appears to be only two examples where an NHSi is used as an ancillary ligand in a catalytic reaction. The first reported catalytic reaction mediated by a silylene complex is the Suzuki coupling of aryl bromides with aryl boronic acids mediated by palladium complex **253a**.²²⁷ The yields reported (66–88%) and catalyst loading (5 mol %) are good for an initial communication. Unfortunately, there have been no further reports into the actual active species other than the suggestion that the dimeric species may be the resting state of the catalyst and in equilibrium with the catalytically active species.²²⁹ In fact the only other example involves the $\text{Pd}(\text{210a})\text{Cl}(\text{allyl})$ complex, which has been used in Heck coupling reactions.²²⁷ The reported yields of 40–100% with a relatively low catalyst loading (1 mol %) are promising. The optimism that these results bring is somewhat tempered because, as previously mentioned, the catalyst is somewhat ill-defined (no X-ray structure, ^{29}Si NMR, or melting point) and further studies have yet to be reported.

3.1.3. Six-Membered Rings

The chemistry of six-membered N-heterocyclic low-valent silicon species began very recently with the advent, in 2006, of the neutral silylene **260** (Scheme 11).²³⁸ Since that time there have been no other six-membered silylenes that are not based on this Nacnac system. In fact, as with the five-membered systems, changing of the substituents has proven difficult and to date the Nacnac backbone cannot be altered. The N-substituent has been changed to *tert*-butyl and 2,6-dimethylphenyl, but in both cases no stable free silylene could be isolated.^{239,240} There have been theoretical investigations into pyridine²⁴¹ and perimidine based silylene species.^{156d,242}

The straightforward synthesis of **260** begins with the deprotonation of the well-known Nacnac ligand followed by reaction with $\text{SiBr}_4/\text{TMEDA}$ (TMEDA = tetramethylethylenediamine) to give the dibromo precursor (Scheme 11). Interestingly the TMEDA not only activates the SiBr_4 but also performs the dehydrohalogenation to give the neutral species rather than a hypervalent cyclic Nacnac- SiBr_3 compound or cyclic cation $[(\text{NacnacSiBr}_2)^+(\text{Br})^-]$. Therefore, the reduction with KC_8 directly yields the neutral species rather than the cationic Nacnac silicon(II) of type **H**. Silylene **260** and its structural isomers have been theoretically studied and compared with carbon and germanium analogues.²⁴³

The reactivity of **260** has proven to be quite rich primarily because of the charge-separated resonance structure **260'**.

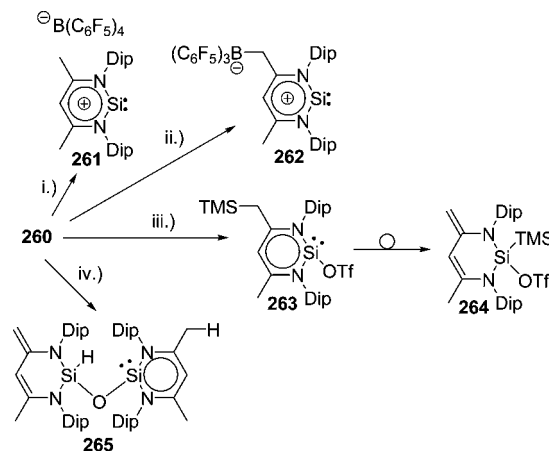


Figure 27. Reactivity of **260** with (i) $[\text{H}(\text{OEt}_2)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, (ii) $\text{B}(\text{C}_6\text{F}_5)_3$, (iii) TMSOTf , and (iv) H_2O .

This resonance structure emphasizes that there are two possible nucleophilic centers in the system; the typical nucleophilic silicon center and the unsaturated backbone. This second nucleophilic site gives access to the cationic silylene **261** by addition of $[\text{H}(\text{OEt}_2)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ to the neutral silylene **260** (Figure 27).²⁴⁴ Additionally, the zwitterionic silylene **262** is accessible by addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **260**, which once again adds exclusively to the backbone. Cationic silylenes of type **261** have also been extensively treated theoretically.^{244,245} Despite these results the generalization that nucleophiles react exclusively at the carbanionic center cannot be made. In fact, upon addition of TMSOTf to **260**, the TMS group does add to the carbon while the triflate coordinates to the silicon center to give **263**; however this 1,4 addition product is unstable and slowly undergoes isomerization to the 1,1 adduct **264** over the course of several days at room temperature.²³⁸ Density functional calculations indicate that these two species are the kinetic and thermodynamic products, respectively. It is this subtle difference between the reactive centers that leads to a rich reactivity that at times mirrors that of five-membered NHSi but is often significantly different. For this reason, it is especially instructive to compare the reactivities of these two types of silylenes. Therefore, where possible and relevant, explicit comparisons will be made in the rest of this section.

The reaction of **260** with organic or silyl halides is similar to that of the five-membered NHSi. The 1,1 insertion product is always the major product. The only other products found are the dihalosilanes (in the case of CH_2Br_2 , CHCl_3 , and MeCCl_3) and the monohalosilanes (in the case of SiHCl_3 and MeSiCl_3). However, contrary to other NHSi, no disilanes have been observed, and thus one of the major arguments for a radical mechanism can be excluded. Additionally, calculations show once again that a 1,4 addition could be the kinetic product, which then isomerizes to give the observed products. However, contrary to the TMSOTf example, no intermediate could be observed. Clearly there are significant steric concerns as well because PhBr , CMe_2Cl_2 , PhSiCl_3 , and Ph_2SiCl_2 do not react at all.²⁴⁶ There has been no significant mechanistic studies; however, as opposed to five-membered NHSi's, the radical mechanism seems to be less likely, although further theoretical and experimental studies are required.

The reaction of **260** with water once again has similarities to other NHSi. The product is an oxo-bridged species with two silicon Nacnac equivalents. The difference is that the

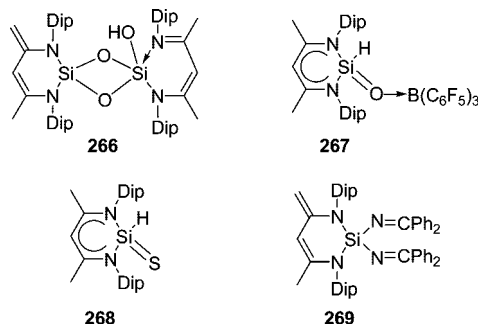


Figure 28. 2,4-Dioxa-1,3-disiletane **266**, silaformamide-borane complex **267**, donor-stabilized silathioformamide **268**, and diimynsilane **269**.

O—H bond adds once in a 1,1 fashion to the silylene center and once by the 1,4 pathway.²⁴⁷ The resulting compound **265** has one normal silicon(IV) center and one silicon that can be viewed as a donor (imine)-stabilized oxo-amino silylene (Figure 27). Even though this silylene center is donor-stabilized, it remains reactive as has been demonstrated by the formation of a silanoic ester,²⁴⁸ as well as the sulfur, selenium, and tellurium analogues by reaction with N_2O (or CO_2), S, Se, and Te, respectively.²⁴⁹ Despite the fact that the $Si=E$ bond is donor-stabilized, careful analysis of the analytical data indicates that there is significant double bond character in these species. The nature of these double bonds has been thoroughly investigated by solid-state NMR and high-level calculations.²⁵⁰ Attempts to oxidize **265** with O_2 led to a 2,4-dioxa-1,3-disiletane **266**, which is formally the result of one oxygen adding between the two silicon centers and one oxygen inserting into the $Si-H$ bond (Figure 28).²⁴⁸ Perhaps more interesting is the reaction of **260** with the water-borane adduct $H_2O[B(C_6F_5)_3]$. In this case, the water adds either 1,1 or 1,4 to only 1 equiv of silylene, while the borane remains coordinated to the oxygen atom. Subsequent proton migration leads to the isolated product, the silaformamide-borane complex **267**, which proved stable enough to be isolated and completely characterized.²⁴⁷ Hydrogen sulfide also reacts with **260** to give the donor-stabilized silathioformamide **268**.²⁵¹ This reaction most probably proceeds by the same mechanism as the silaformamide-borane complex, that is, consecutive 1,1 or 1,4 addition/proton migration.

Silylene **260** reacts with 2 equiv of trimethylsilylazide to give the corresponding silatetrazoline, as is often the case with five-membered $NHSi$'s. The first reaction of a silylene with a diazo compound was also reported. Silylene **260** reacts

exclusively with 2 equiv of diphenyldiazomethane to eliminate 1 equiv of N_2 and give diimynsilane **269** in nearly quantitative yield (Figure 28).²⁵²

Unsaturated C—C bonds react with **260** in several different ways. The common diene 2,3-dimethyl-1,3-butadiene reacts in the expected 4 + 1 fashion to give the desired spirocyclic compound; however sterically larger dienes do not react with **260** even at elevated temperatures.²⁵³ While the 4 + 1 cyclization reaction is well established in silylene chemistry, the 2 + 1 cyclization reaction is only a proposed intermediate. There is only one example of an alkyne reacting with an $NHSi$, but once again the cyclopropene is only a proposed intermediate. The reaction of **260** with acetylene, phenylacetylene, and diphenylacetylene at low temperature gives the corresponding silacyclopropene **270** as a stable isolable species (Figure 29).²⁵⁴ Interestingly, when the reaction with acetylene or phenylacetylene is done at room temperature, the C—H insertion product **271** was isolated, and in the case of acetylene, a second equivalent of **260** could be reacted to form a disilylacetylene. The mechanism of these two reactions was studied by theoretical means, and an autocatalytic pathway was suggested. Silacyclopropenes **270** are quite robust and can be heated in solution to 110 °C without decomposition. These species also give access to donor-stabilized silacyclopropenyl cations, once again by using the nucleophilicity of the methylene group in the backbone. Both Lewis $[B(C_6F_5)_3]$ and Brønsted $\{[H(OEt)_2]^+[B(C_6F_5)_4]^- \}$ acids react on the backbone to give the corresponding cationic species. In the case of the latter, the cation is only stable at low temperature. At room temperature, 1 equiv of Et_2O reacts with the cationic silicon center to open the silacyclopentene ring, eliminate ethylene, and give the (ethoxy)vinylsilane.²⁵⁵

Silylene **260** reacts with $C=O$ and $C=N$ bonds. The reaction with diphenylketone is similar to other $NHSi$'s. Initially, a 4 + 1 cyclization product is observed but over the course of several days the phenyl ring rearomatizes as has been previously reported for **212a**.¹⁹³ Silylene **260** also reacts with a conjugated ketone to give the 4 + 1 product.²⁵⁶ A significantly different reactivity is observed when acetophenone is used. In this case, the product is the O—H insertion product of the enolate of the ketone **272** (Figure 29); however whether or not the enolate plays an important role in the mechanistic pathway could not be determined because donor/acceptor intermediates are also viable. Transient silylenes have been known to give similar products.^{151,257} There are no reports of typical imines reacting with **260**;

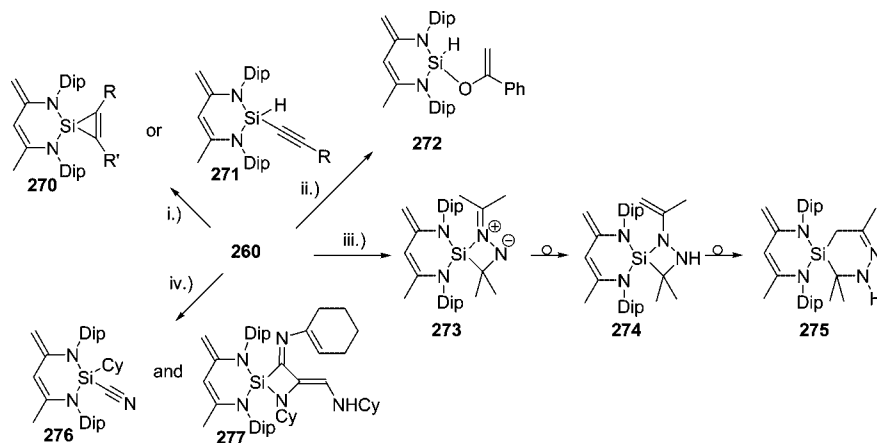
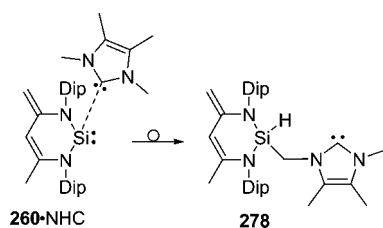


Figure 29. Reactivity of **260** with (i) alkynes, (ii) acetophenone, (iii) 2,3-diazabuta-1,3-diene acetone azine, and (iv) cyclohexylsilyl cyanide.

Scheme 12



however diphenyl hydrazone reacts in nearly the same fashion as diphenylketone except the 4 + 1 cyclization product is indefinitely stable, that is, it does not undergo isomerization/rearomatization.²⁵⁸ The unsaturated conjugated 2,3-diazabuta-1,3-diene acetone azine reacts not by an expected 2 + 1 or 4 + 1 pathway but rather by a 3 + 1 to give the ylide-like adduct **273**.²⁵³ This species can be isolated and is stable at 0 °C but at room temperature slowly undergoes first a proton shift to give **274** followed by ring expansion to give the 1-sila-4,5-diazacyclohex-3-ene **275**.

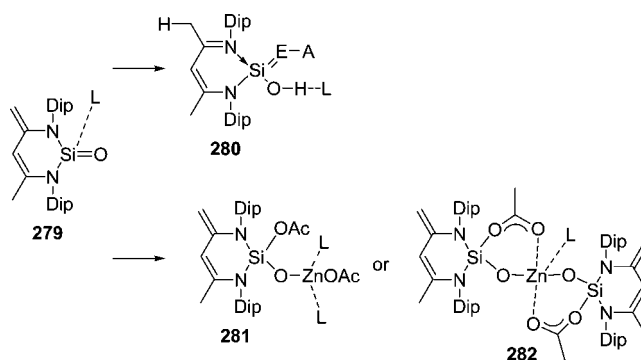
Unlike NHSi **212a**, silylene **260** is chemically inert to acetonitrile and *tert*-butyl cyanide. What has been reported is the reaction of **260** with cyclohexyl isonitrile.²⁵² The isonitrile most likely forms a donor/acceptor complex followed by migration of the cyclohexyl group to the unsaturated silicon center to form cyclohexylsilyl cyanide **276** in low yield (32%) (Figure 29). Another unexpected product was also found in the reaction mixture in low yield (41%). This product could also be isolated and was proven to be the adduct of **260** with 3 equiv of the isonitrile, the azasilacyclobutane **277**. A mechanism for this reaction was also proposed.

Silylene **260** demonstrates reactivities that were unprecedented for other stable silylenes. The activation of ammonia is one of the most interesting cases. When dry NH₃ is passed through a solution of **260**, a reaction rapidly takes place and the 1,1 N–H bond insertion product was isolated in high yield (90%).²⁵⁹ A similar activation of NH₃ occurs with cyclic(alkyl)(amino)carbenes (CAACs) and a six-membered diamido carbene but not with the Arduengo-type NHC or five-membered NHSi.¹²⁴ Additionally, **260** activates N–H bonds of hydrazine and methylhydrazine to give the 1,1 insertion products.²⁵⁸

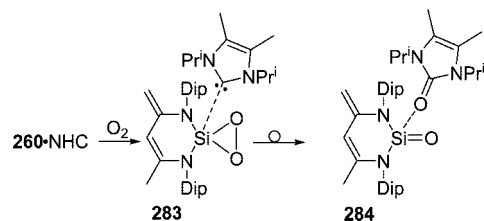
The electrophilic character of **260** has also been investigated. The low-valent silicon center can act as an electron acceptor for several Lewis bases. The reaction of **260** with the NHCs 1,3-dimethyl-3,4-dimethylimidazol-2-ylidene or 1,3-diisopropyl-3,4-dimethylimidazol-2-ylidene lead to coordination of the NHC to the silicon center.^{260,261} In the first case, the adduct is not stable at room temperature and slowly inserts into one C–H of an N-methyl group. This new carbene **278** could be isolated and fully characterized (Scheme 12). The latter species is stable even at elevated temperature.²⁶¹ The less basic 4-dimethylaminopyridine (DMAP) also coordinates to the silylene center to give a stable adduct.²⁶²

Reaction of an NHC (1,3-dimethylimidazol-2-ylidene) and DMAP-stabilized silylenes with N₂O lead to base-stabilized silanones of type **279** (L = NHC or DMAP) (Scheme 13).^{260,262} The DMAP-stabilized silanone (**279**, L = DMAP) gives access to donor–acceptor-stabilized silanoic acid derivatives. Addition of H₂S gives the sulfur derivative, which is stabilized at the silicon center by the Nacnac ligand, while the DMAP coordinates to the acidic O–H proton (**280**, E = S, L = DMAP, A = not present). This acid proton can

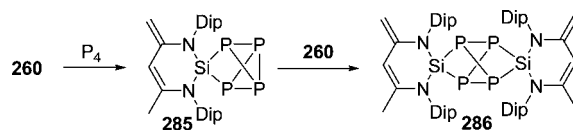
Scheme 13



Scheme 14



Scheme 15



be removed by addition of AlMe₃ to give methane and the DMAP-coordinated dimethylaluminum acid. If water is used in lieu of H₂S, decomposition occurs. However, addition of 1 equiv of H₂O·B(C₆F₅)₃ yields a donor–acceptor-stabilized silanoic acid wherein the DMAP coordinates the acidic proton and the Si=O oxygen coordinates the borane (**280**, E = O, L = DMAP, A = B(C₆F₅)₃).²⁶³ The DMAP-coordinated silanone (**279**, L = DMAP) reacts with the Lewis acid metal complexes, AlMe₃, ZnMe₂, and Zn(OAc)₂. In the case of the first two, the metal center is coordinated by the oxygen. In the case of Zn(OAc)₂, either **281** or **282** is isolated based on the stoichiometry.²⁶⁴

What is even more remarkable is that the NHC silylene complex activates O₂, first to give the isolable dioxasilirane carbene adduct **283**, which is stable at low temperature.²⁶⁵ Upon warming, the dioxasilirane rearranges by transferring one oxygen atom to the carbene center and forming the silaurea, which is stabilized by the oxygen that was transferred to the carbene, to give the complex **260** (Scheme 14). The **260**·NHC complex reacts with elemental sulfur, selenium, and tellurium to give the corresponding heavy NHC-stabilized silanone congeners.²⁶⁶

The ability of NHCs, CAACs, and even diamino cyclopropenylidenes to activate P₄ has previously been reported.^{53–55,267} However, no reaction has been reported for five-membered NHSi's aside from the brief mention that perhaps **210a** catalyzes the transformation of white phosphorus to the more stable red phosphorus allotrope.¹⁷¹ Silylene **260**, on the other hand, reacts directly with P₄.²⁶⁸ Interestingly, the product is different from those reported for carbenes. One equivalent inserts into one P–P bond of the P₄ tetrahedron to give **285**, while leaving the rest of the structure nearly untouched (Scheme 15). A second equivalent also inserts into another P–P bond to give the stable 2:1 adduct **286**. Alternatively,

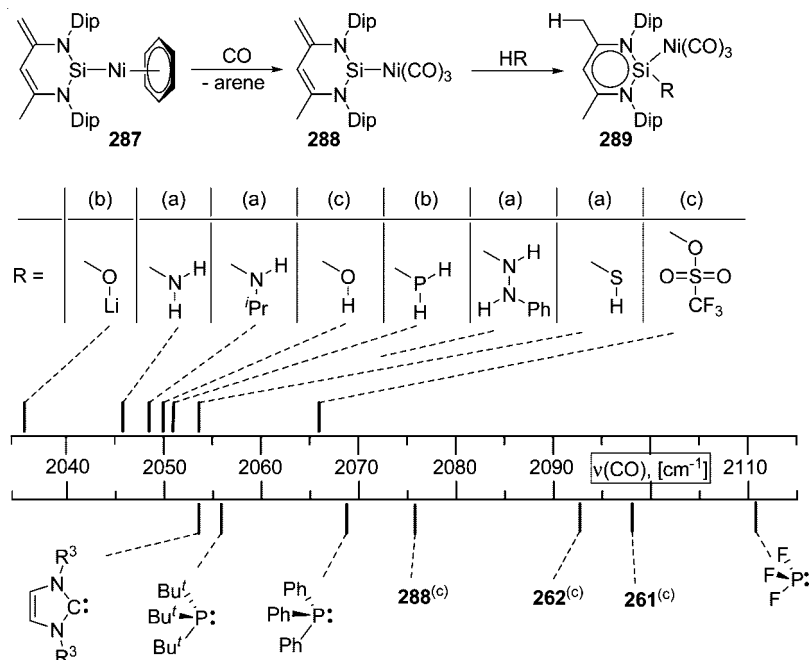


Figure 30. The IR frequency for the A1-mode of the carbonyl groups of a variety of $\text{LNi}(\text{CO})_3$ complexes: (a) see ref 251; (b) see ref 274; (c) see ref 272.

the 1:1 adduct reacts with $[\text{Ni}(\text{Nacnac})]_2 \cdot \text{toluene}$ complexes to give the diactivated mixed P_4 adduct.²⁶⁹ There have also been theoretical studies on the activation of P_4 by silylenes.²⁷⁰

The ability of **260** to act as a ligand to transition metal complexes has also been explored. Only nickel complexes of **260** have been reported to date; however the further chemistry of these nickel complexes is very extensive. The first complex was synthesized by the reaction of **260** with $\text{Ni}(\text{COD})_2$ in aromatic solvents.²⁷¹ The sterics of **260** preclude the formation of bis-, tris-, or tetrasilylene homoleptic nickel complexes; instead only 1 equiv of silylene adds to the nickel center. However, both COD groups are replaced and an η^6 arene (benzene, toluene, *para*-xylene, or mesitylene) coordinates to the nickel center to create the saturated 18-electron nickel complex **287**. While this complex is stable under inert conditions the reactivity of the silylene ligand remains, as demonstrated by the addition once again of $\text{B}(\text{C}_6\text{F}_5)_3$ to the methylene group on the backbone. In order to estimate the ligand properties and to be able to compare them to other common ligands such as phosphines and NHCs, the nickel complex was reacted with CO gas, which rapidly replaces the arene to give the corresponding $\text{Ni}(\text{260})(\text{CO})_3$ complex **288** (Figure 30).²⁷² The infrared stretching frequency can then be measured and compared with other $\text{NiL}(\text{CO})_3$ complexes inasmuch as these stretching frequencies are a well known probe to indirectly measure the donor/acceptor properties of ligands.²⁷³ The value for the A1-mode of **288** (2076 cm^{-1}) is similar to that of the triphenyl phosphine complex (2069 cm^{-1}). Again the backbone of silylene **260** remains reactive and $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{H}(\text{OEt})_2]_3^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ can be added to the nucleophilic methylene group. Importantly, this addition alters the donor properties of the ligand significantly, which is evidenced by a significant shift in the IR spectra (2095 and 2098 cm^{-1} , respectively). This indicates that the cationic silylene ligand acts as a much better π -acceptor ligand and is comparable to the PF_3 complex (2111 cm^{-1}). The ligand properties can be further altered by reaction of the **288** complex with a variety of reagents. There are numerous examples of O–H, N–H, and S–H bonds adding exclusively

1,4 to the silylene ligand to give complexes **289**, while the transition metal acts as a protecting group for the silylene lone pair.^{251,272} The stretching frequencies of all the known nickel complexes are summarized in Figure 30.

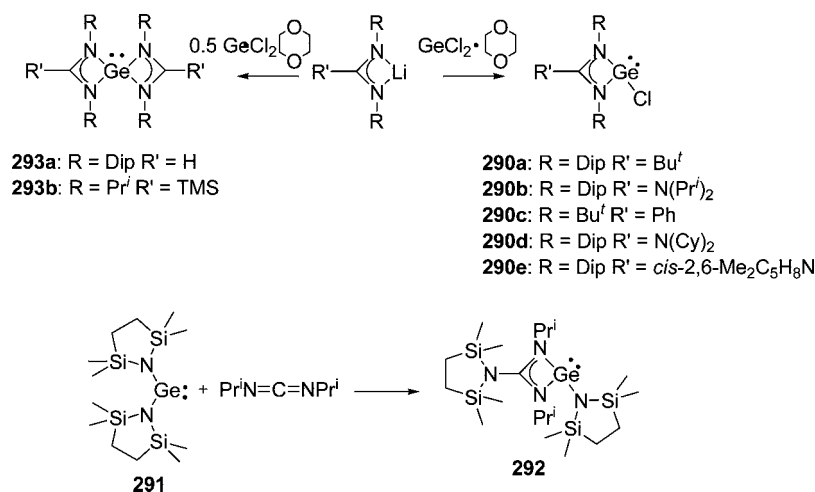
3.2. Germanium(II) Heterocycles

3.2.1. Four-Membered Ring

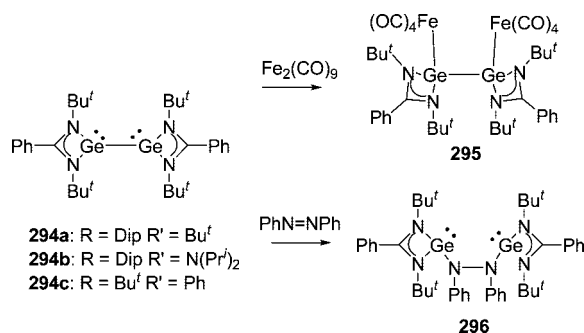
Amidinate or guanidinate germanium(II) cations of type **F** are unknown. The nearest example is the contact ion pair resulting from addition of GaCl_3 to the guanidinate germanium(II) chloride **290b** (Scheme 16).²⁷⁵ The resulting compound **290b**· GaCl_3 has a Ge–Cl bond slightly longer than that of the starting material but still within the known range for such bonds.

While the cation is unknown, it should be noted that, as with silicon, there are some notable examples of tricoordinate amidinate/guanidinate germanium(II) species. Nearly every species of this type is accessible by reaction of lithium amidinate or guanidinate salts to $\text{GeCl}_2 \cdot \text{dioxane}$. The single exception is the addition of diaminogermanium(II) **291** to diisopropylcarbodiimide, which directly yields the guanidinato(amino)germanium(II) **292** (Scheme 16).²⁷⁶ The easily accessible germanium(II) chlorides **290** undergo further substitution of the chloride when reacted with several kinds of bases. Amide bases such as $\text{LiN}(\text{TMS})_2$ ²⁷⁷ or $\text{LiN}(\text{Pr})_2$ ²⁷⁵ substitute the chloride to give stable isolable species. When an additional equivalent of lithium amidinate is added, substitution of the chloride at the germanium center also takes place; however when large substituents are on both the nitrogen and central carbon, the imine functionality of the second amidinate does not coordinate and the germanium remains tricoordinate.^{277,278} When smaller groups are used, the tetracoordinate germanium(II) can be accessed. The only two examples are **293a,b** (Scheme 16).^{275,279} The addition of 2 equiv of $\text{Li}[(\text{TMS})\text{NC}(\text{Bu}^t)\text{N}(\text{TMS})]$ to $\text{GeCl}_2 \cdot \text{dioxane}$ yielded the amidinato(amino)germanium(II) with elimination of *tert*-butyl cyanide.²⁷⁸ This reaction was studied in further

Scheme 16



Scheme 17



detail, and it was suggested that sterics play a significant role in the elimination of the nitrile as opposed to formation of tetracoordinate species, which are known in the case of **293**. Additionally, the chlorine of **290b** can be substituted by the gallium anion **60**⁸⁸ or by the anionic transition metal complex Na[FeCp(CO)₂]²⁷⁵ to give the corresponding products that could be isolated and fully characterized.

The reactivity of these species has not been thoroughly reported; however, there are several examples. The terminal chalcogenido germanium complexes can be formed by reacting many of the Ge(II) amide or amidinate species with styrene sulfide or with elemental selenium.²⁷⁷ Alternatively, the sulfur and selenium adduct of Ge[η²-CyNC(Bu^t)NCy][η¹-CyNC(Bu^t)NCy] can be formed by chalcogen atom transfer from a bis(amidinato)Sn=S and Ph₃PSe, respectively.²⁸⁰ The oxidative addition of PhEEP(E = S or Se) also occurs with three different amide- or amidinate-substituted Ge(II) species.²⁸¹ In the first two cases, the second amidinate closes to form a hexacoordinate species, while in the later case the amidinate opens to form tetracoordinate species. Finally, the lone pair of Ge[η²-DipNC(Bu^t)NDip][N(Prⁱ)₂] has been used to coordinate tungsten by addition of W(CO)₅·THF, which gives the desired tungsten pentacarbonyl complex in reasonable yield (56%).²⁷⁵

The chloro compounds **290a–c** can also be reduced to form the germanium(I) dimers **294a–c** (Scheme 17), albeit in rather low yields (13–35%).^{282,283} The first two have a typical trans-bent conformation, while the latter has a novel gauche conformation. A theoretical study of both types of dimers indicates clearly that these molecules are best viewed as digermynes although they can formally be drawn as digermynes. The reactivity reflects the digermylene nature of these species. For example, reaction

of **294a** with 2 equiv of Fe₂(CO)₉ gives the diiron complex where each germanium center is coordinated by one Fe(CO)₄ moiety to give the complex **295** (Scheme 17). The only other reactivity of this species is the addition of azobenzene across the Ge–Ge bond with concomitant bond rupture to give the new 1,2-digermylene hydrazine species **296**.²⁸⁴

3.2.2. Five-Membered Ring

Structurally, five-membered N-heterocyclic germylenes (NHGe) are more diverse than their silicon counterparts. The substituents and backbone can be widely varied and in many cases are also more readily accessible as well. The chemistry of NHGe's actually predates NHCs and NHSi by several years. The first reported examples were the benzannulated species **297a–c** of which only **297c** could be characterized by X-ray analysis, while in the following years, other species have also been characterized (**297d–f**) (Figure 31).^{164,285,286} Later, the unsaturated and saturated versions, **298** and **299**, with diverse substituents have also been reported.^{77,287–289} In addition to these typical structural motifs there are several novel backbones for NHGe. A series of acenaphthene-substituted germylenes **300** have been reported as well as the bicyclic pyridine-based version of type **301**, the latter of which are stable only one day (**301a**) or one week (**301b**).^{290,291} There are also a large number of bis(germylenes) **302**, all based on the benzo-fused system with a wide variety of linkers (Figure 32).^{292–294} Finally, there is one example of a cyclic bis(germylene) **303**.²⁹⁵

Sources of germanium(II) are readily available, and therefore the synthesis of all of the aforementioned NHGe's, aside from saturated examples **299**, involve one of these Ge(II) sources and require no final reduction step. The most widely used technique is the addition of GeCl₂·dioxane to the dilithiated diamine, which directly gives the desired germylene. For the acenaphthene germylenes **300**, magnesium is used in lieu of lithium.²⁹⁰ In the case of **302g,h** and **303**, the germylene is synthesized in one step by addition of 2 equiv of Ge[N(TMS)₂]₂ to the tetra-amino precursor with concomitant elimination of HN(TMS)₂, which is easily removed under vacuum.^{293–295} The saturated versions **298** are accessible in an analogous fashion to NHSi, that is, by reduction of a dichlorogermanium(IV) precursor.^{287,289} Germylene **299a** has been synthesized by both the GeCl₂·dioxane and reduction methods. Interestingly, the lithiation of saturated germylene **299a** with LiN(TMS)₂ leads to

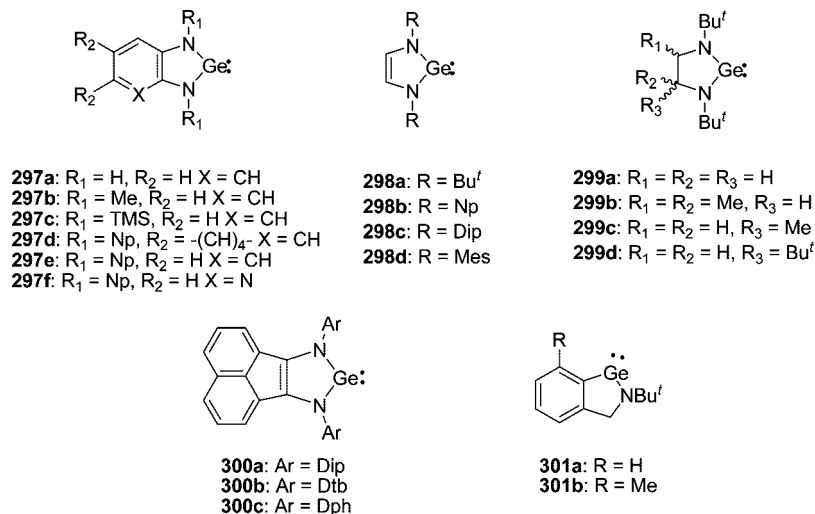


Figure 31. Five-membered N-heterocyclic germylenes (Dtb = 2,5-di-*tert*-butylphenyl, Dph = 2-Ph-phenyl).

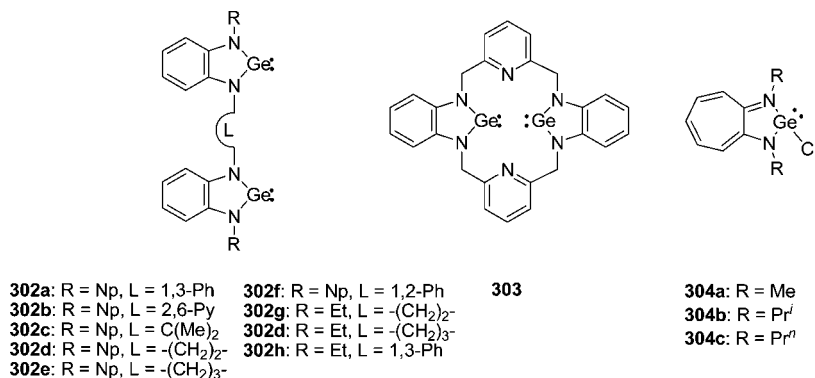


Figure 32. Reported bis(germylenes) and donor-stabilized chlorogermylene **304**.

elimination of LiH and formation of unsaturated NHGe **298a**, an unprecedented reactivity for other N-heterocyclic analogues.²⁸⁷

Stable NHGe's have been the object of several analytical and computational studies often in comparison to their lighter analogues, NHCs and NHSi. Specifically, the photoelectron spectra (PES) of all three have been compared and analyzed with the assistance of density functional calculations.^{166,296} The core excitation spectra^{168a} and electrochemistry^{156b} of NHSi and NHGe have been measured and subsequently compared once again with the assistance of theoretical calculations. The Raman spectrum of **298a** was also measured and compared with the silicon analogue.²⁹⁷ These studies are all based on the unsaturated and saturated species **298a** and **299a**. In depth discussion of the results is out of the scope of this review; however, they have shed significant light onto the structural and electronic properties of these species.

Unlike the four-membered systems, germanium(II) cations are accessible in five-membered rings. The first example is based on the tropylium cation. Deprotonation of aminotroponimines and addition of $GeCl_2 \cdot$ dioxane gives the 3.5.0 bicyclic germanium chlorides **304** (Figure 32), which can be viewed, like the amidinate or guanidinate species mentioned in the previous section, as a donor-stabilized chlorogermylene.²⁹⁸ The chlorine may be abstracted with $AgOTf$ or 2 equiv of $ZrCpCl_3$. In the solid state, the cationic germanium center of both resultant species has some weak interaction with the counterion. In the first case, the oxygen of the triflate is 2.255(2) Å from the germanium, which is slightly longer than the sum of the covalent radii (1.95 Å).

In the second case, the germanium center has longer contacts to two chlorines of two different $[Cp(Cl)_2Zr(\mu-Cl)_3Zr(Cl)_2Cp]^-$ anions (3.123 and 3.115 Å, respectively) both of which are considerably longer than the Ge–Cl bond of the starting material [2.368(2) Å]. Attempts to synthesize the cation with a large noncoordinating borate anion did not yield the free cation. The action of $Ag\{HB[3,5-(CF_3)_2Pz]_3\} \cdot$ toluene (Pz = pyrazolyl) on the germanium chloride only led to the coordination of the germanium to the silver center.^{299,300} Some further chemistry of the germanium chloride has been reported such as the substitution of the chlorine by an azide³⁰¹ and further reactivity with silver species.³⁰²

A five-membered diimine-stabilized cationic germanium(II) chloride **305** has also been reported upon reaction of $GeCl_2$ with the unsaturated germanium dichloride five-membered ring (Figure 33).³⁰³ The solid-state structure has two molecules in the unit cell with significant interaction between the cationic germanium chloride moiety and the $GeCl_3^-$ counterion. An even more astounding access to a germanium(II) cation is by the protonation of the stable NHGe **271c**. Addition of the Bronsted acids $H(OEt_2)_2^+ \cdot B(C_6F_5)_4^-$ or $[Et_3Si(C_6H_6)]^+ \cdot B(C_6F_5)_4^-$ to the germylene protonates not the low-valent germanium center but rather one of the carbons in the backbone.³⁰⁴ In both cases, the subsequent cation **306** could be isolated and fully characterized including X-ray analysis, which indicates almost no interaction with the counterion; however, in the first case, diethylether is found to be coordinated to the germanium center.

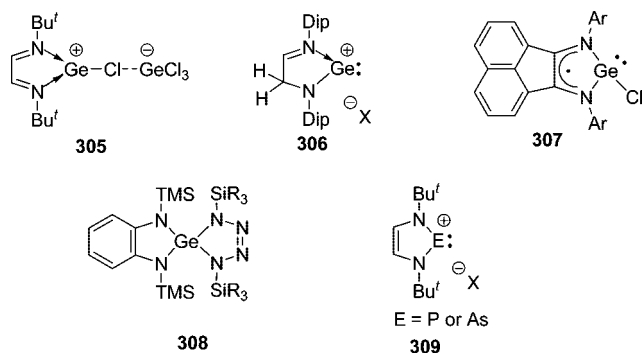


Figure 33. Cationic Ge(II) chloride **305**, germanium cation **306**, Ge(II) radical **307**, germatetrazoline **308**, and heterocyclic cations **309**.

There have been several reports of the reactivity of NHGe with radicals. Both **298a** and **299a** react with 2 equiv of TEMPO to form stable germanium(IV) species.³⁰⁵ However, further studies of the reactivity of unsaturated germylene **298a** with a variety of radicals (oxygen, carbon, silicon, and transition metal radicals) yielded radical adducts, which were investigated by EPR and density functional calculations.³⁰⁶ The consensus was that the radical is delocalized on the conjugated five-membered ring system. These results are in line with the previous study of NHSi mentioned in section 3.1.2.¹⁷⁵ The muonium radicals of **298a** were also studied with those of NHSi.¹⁷⁷ There is also one report of a Ge(II) five-membered radical **307** (Figure 33).³⁰⁷ The bis(imino)acenaphthene anion radical reacts with $\text{GeCl}_2 \cdot \text{dioxane}$ or alternatively the neutral bis(imino)acenaphthene with 2 equiv of $\text{GeCl}_2 \cdot \text{dioxane}$ to give the stable and isolable radical. ESR studies show the radical to be primarily localized on the diimine functionality with very limited electron density at the germanium center. The one electron reduction chemistry of NHGe **297d–f** and **298b** have been investigated theoretically and by cyclic voltammetry, but no reduction products were isolated.³⁰⁸

There is only one reported reaction of an NHGe with an organic reagent. In 1989, the first crystalline stable NHGe **297c** was reacted with trimethylsilylazide or triethylsilylazide to form the 1:2 germatetrazolines **308** (Figure 33).^{285b} This type of reactivity was later found to be typical for NHSi as well. Reactivity of NHGe with other typical organic reagents has not been reported.

The ability of NHGe to act as a Lewis acid has been reported. Once again in a reaction very similar to one previously discussed for an NHSi, germylene **297e** reacts with the NHC analogue as an electron pair acceptor to form a thermally labile adduct.²⁰⁴ The acid/base properties of germylenes have been investigated theoretically,²⁰¹ and the Lewis acid properties have also been briefly reviewed.³⁰⁹ There is no report of an NHGe acting as a Lewis acid to an NHSi, but as mentioned in section 3.1.2, germylene **299a** reacts with a silylene to form a digermene.²⁰⁹

Reaction of NHGe with group 16 elements is another typical reaction of NHSi that has not been reported with these heavier congeners. In fact, the only reaction involving NHGe and main group compounds is the metathesis of NHGe **298a** with PCl_3 or AsCl_3 to give the N-heterocyclic phosphonium and arsenium cations **309** (Figure 33).³¹⁰ The counterion of these species was GeCl_5^- for half of the molecules and Cl^- for the other half.

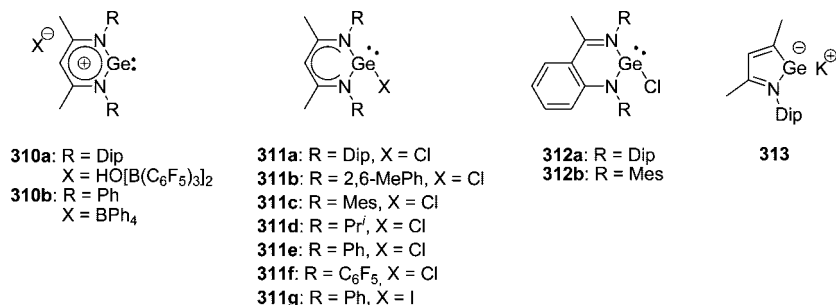
As expected, NHGe can act as a neutral ligand to transition metals. However, there are relatively few examples. The first

was reported with the synthesis of saturated germylene **299a**, which could replace one or two carbonyls of $\text{Ni}(\text{CO})_4$ to give the stable complexes $\text{Ni}(\text{299a})(\text{CO})_3$ and $\text{Ni}(\text{299a})_2(\text{CO})_2$, respectively.²⁸⁷ The homoleptic $\text{Ni}(\text{299a})_3$ complex was also accessible by using $\text{Ni}(\text{COD})_2$ and 3 equiv of **299a**. Analysis of the carbonyl stretching frequencies of the $\text{Ni}(\text{299a})_2(\text{CO})_2$ complex seemed to indicate that **299a** was a relatively good σ -donor and poor π -acceptor similar to PPh_3 . The ligand properties were investigated in depth starting with the fortuitous synthesis of the *fac*- $\text{Mo}(\text{298b})_3(\text{CO})_3$ complex as a minor product (5%) in the reaction of $\text{Mo}(\text{CO})_4(\text{NCEt})_2$ with 2 equiv of **298b**.³¹¹ The major product $\text{Mo}(\text{298b})_2(\text{CO})_4$, which was the target of this reaction, could not be isolated in crystalline form, while the minor product could be fully characterized including X-ray analysis. Following these results, two further *fac*- $\text{Mo}(\text{NHGe})_3(\text{CO})_3$ complexes were synthesized ($\text{NHGe} = \text{297d}$ and **297e**) by addition of 3 equiv of NHGe to $\text{Mo}(\text{CO})_3(\eta^3\text{-CHT})$ ($\text{CHT} = 1,3,5\text{-cycloheptatriene}$).²⁹⁶ This series of aromatic, annellated NHGe's had previously been studied with a view to understanding the effects of the more diffuse aromatic systems on the properties of the low-valent germanium center.²⁸⁸ Once again by using the carbonyl stretching frequencies comparisons of ligand strength could be made. However, comparisons to a larger variety of ligands was difficult because the carbonyl stretching frequency of $\text{MoL}_3(\text{CO})_3$ for many ligands has not been reported. Therefore, to make such comparisons theoretical techniques were used to estimate the Tolman electronic parameter (TEP), which is based on $\text{NiL}(\text{CO})_3$ complexes.³¹² Attempts to synthesize these nickel species failed, although the homoleptic $\text{Ni}(\text{297e})_4$ was accessible from $\text{Ni}(\text{COD})_2$.²⁹⁶ With this new theoretical method and the experimental results from the molybdenum complexes, it was found that NHGe's are in fact similar to phosphine ligands. However, unlike what was initially assumed, these germylenes are in fact poor σ -donors and good π -acceptors, which helps explain the lack of reported complexes with metals that do not have strong π -back-bonding properties; that is, attempts to synthesize complexes from $\text{PdCl}_2(\text{COD})$, $\text{PdCl}_2(\text{NCMe})_2$, or $[\text{RhCl}(\text{COD})]_2$ failed.²⁹⁶ There is one example that actually indicates that phosphines could be stronger ligands in certain cases. The reaction of **298d** with $(^{\text{Mes}}\text{NacnacCu})_2$ yields the expected $\text{MesNacnacCu}(\text{298d})$ complex, which was fully characterized.³¹³ Unsurprisingly, an NHC could displace the NHGe, but PPh_3 could also fully displace **298d**. Because copper(I) species are not strongly π -back-bonding, this result may give support to the theoretical and experimental results previously mentioned.

The bidentate bis(germylenes) have also been reported to form complexes with molybdenum. The reaction of $\text{Mo}(\text{NBD})(\text{CO})_4$ with 1 equiv of **302c** or **302e** eliminates NBD and gives the expected $\text{Mo}(\eta^2\text{-302c})(\text{CO})_4$ and $\text{Mo}(\eta^2\text{-302e})(\text{CO})_4$ complexes, which were fully characterized.^{293,294}

Cyclic five-membered germylenes have been found to be useful as starting materials in polymerization chemistry as well as materials chemistry, which is unlike NHSi. There are several oxidation–reduction copolymerization examples in the literature. Therein, NHGe **297c** can be used as the oxidized partner of orthoquinones,³¹⁴ thietane,³¹⁵ or enolates.³¹⁶ The resultant functional polymers could have interesting properties, but to date, no specific applications have been reported in the literature.

From a materials perspective, there have been several reports of NHGe's as starting materials for chemical vapor

**Figure 34.** Germanium(II) species.

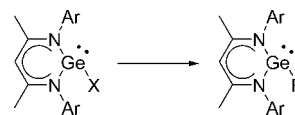
deposition. Initial reports of the thermolysis of **298a** and **299a** showed that germanium or germanium hydride films could be deposited.²⁸⁷ Later, optimization revealed that surprisingly pure amorphous germanium thin films could be prepared at relatively low temperatures (140–440 °C).³¹⁷ Additionally, NHGe **300a** could be used to deposit GeO₂ films by atomic layer deposition.³¹⁸ Germanium is an important element in many materials, and NHGe appear to be a potentially useful source of elemental germanium in materials; however, this field clearly has not been fully exploited.

3.2.3. Six-Membered Ring

The cationic germanium(II) Nacnac compound of type **H** has been reported.^{319,320} Both reported examples, **310a** and **310b** (Figure 34), are synthesized by chloride abstraction from a donor-stabilized chlorogermylene. Cation **310a** has been fully characterized including X-ray crystallography and was synthesized in low yield (21%) by the reaction of 1 equiv of B(C₆F₅)₃ with the chlorogermylene in the presence of water. The counteranion HOB(C₆F₅)₃₂ is formed in the reaction and in the solid state does not have any close contacts with the cationic species.³¹⁹ The second example **310b** is formed with a significantly better yield (82%) by straightforward salt metathesis using NaBPh₄. However, while **310b** is well characterized by multinuclear NMR, mass spectrometry, and elemental analysis, there is no reported X-ray structure.³²⁰ Despite the apparent reactive centers, there has been very little reactivity reported for these cations. The structure and reactivity of this type of cation have been investigated theoretically.²⁴⁵

The chemistry of donor-stabilized chlorogermynes is more varied than that of the cationic species. They are all easily accessible by deprotonation of the Nacnac ligand followed by addition of GeCl₂·dioxane. The substituent at nitrogen can be modified from sterically large Dip **311a**, 2,6-dimethylphenyl **311b**,³²¹ and Mes **311c**³²² groups to the relatively small Prⁱ **311d**³²³ or Ph group **311e**.³²⁰ The perfluorophenyl species **311f** has also been reported; however, no reactivity of this species is known.³²⁴ There is also one version (**312**) that has a benzo-fused backbone (Figure 34).³²⁵ The iodogermylene **311g** is also accessible by reaction of the lithium Nacnac with GeI₂.³²⁰

The largest reactivity class of these chlorogermynes can be classified as substitution that occurs exclusively at the germanium center (Scheme 18). The first example reported was that of NaN₃ with **311c** to give the azidogermanium(II) derivative.³²² Table 5 gives a summary of the reported substitution reactions that occur at the germanium center. Note that here the term substitution refers only to a comparison of the starting material and product and is not meant to imply mechanism, for example, the fluorogermylene

Scheme 18

(line 2, Table 5) is almost certainly formed by a radical mechanism, which is well-known for Me₃SnF.^{321b} A series of these PhNacnacGe-R species (R = Cl, I, Me, OMe) has also been studied by UV, PES, and DFT calculations.³²⁶ These results suggest that the halide-substituted species (**311**) can be best described as germanium cations stabilized by donation from the counterion halide rather than a halogermylene stabilized by an imine donor.

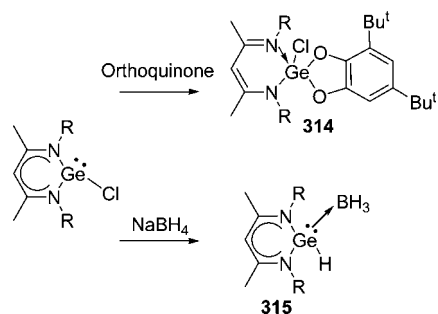
The lone pair on these species can react with elemental sulfur or selenium to give the corresponding species with germanium–element double bonds.^{320,327,336} Interestingly some examples are accessible by two different routes; the

Table 5. Reactivity of Germanium(II) Chlorides

Germanium (II) compound	Reagent(s)	R-group
311c	NaN ₃	-N ₃
311a, 311b	Me ₃ SnF	-F
311a, 311e	MeLi	-Me
311a	nBuLi	-nBu
311a	LiNMe ₂	-NMe ₂
311e	LiNTMS ₂	-NTMS ₂
311e, 312	LiOMe	-OMe
311a	LiPH ₂	-PH ₂
311a	LiPTMS ₂	-PTMS ₂
311e	AgOTf	-OTf
311a	NaBH ₄ /PMe ₃ or AlH ₃ /NMe ₃ or K[HB(iBu) ₃]	-H
311a, 311b	H ₂ O/NHC ^a	-OH
311a	K[FeCp(CO) ₂]	-FeCp(CO) ₂
313		

^a NHC = 1,3-dimesitylimidazol-2-ylidene.

Scheme 19



direct reaction of the precursor with sulfur or selenium or by substitution of the chloride after the Ge=E (E = S or Se) bond is already formed. In the case of the germanium hydride, it should be noted that a second equivalent of sulfur inserts into the Ge–H bond.³³² The result of the reaction with a single equivalent was not reported, and reaction intermediates could not be isolated. There are also two reported attempts to synthesize the stabilized germanium imine by reaction with TMSN₃. In the case of the Ge–F, the desired product could be isolated.^{321b} However, when the Ge–Me species was used, the germimine was not stable, and the product isolated was the result of a migration of a proton of one of the methyl groups to the nitrogen to give the neutral germanium(IV) species substituted with a NH–(TMS) group.³²⁷

The chlorogermynes **311e** and **312** also react with 3,5-di-*tert*-butyl-1,2-benzoquinone to give the spirocyclic cycloaddition products **314**.^{320,325} In both cases, the germanium(IV) center is pentacoordinate because the imine donor remains ligated to the germanium (Scheme 19).

There are several examples of reactivity that are exceptional. For example, both **311a** and **311c** react with NaBH₄ to eliminate NaCl and give what is formally the B–H insertion product **315** (Scheme 19; no mechanistic studies were undertaken), which is an intermediate in the synthesis of the germanium hydride (see Table 5).^{321b} In the latter case, one methyl group of the backbone can be deprotonated to give a lithium salt wherein two hydrides from the boron center coordinate the lithium. The methyl-substituted compound of **311a** reacts with MeI to give the pentacoordinate germanium(IV) insertion product.³²⁷ Additionally, the germanium chloride **311e** undergoes a ligand transfer reaction with GaCl₃ or InI₃ to give the neutral Nacnac GaCl₂ and Nacnac InI₂ compounds in reasonable yields (50% and 52%, respectively).³³⁰ There is also one report of the reduction of Ge–Cl **311a** with 2 equiv of potassium in THF to give the cyclogermylidenide derivative **313** and the germanium(II) amine derivative (Figure 34).³³⁷

The germanium hydride also displays some remarkable reactivity. Ethyl diazoacetate or trimethylsilyldiazomethane reacts with the hydride in an interesting fashion; the terminal nitrogen inserts into the Ge–H bond to give a germanium hydrazone derivative **316** (Figure 35).³³⁸ Diethyl azodicarboxylate also inserts into the Ge–H bond, in this case across the central N–N double bond, to give **317**. The germanium hydride has also been added across several C–C triple bonds to give species of type **318** and even across the C–O double bond of CO₂ to give the germylene ester **319**.³³² Finally, the PH₂ derivative can be reductively coupled to itself with Hg(Bu^t)₂ to give a diphosphane digermylene derivative **320**.³²⁹

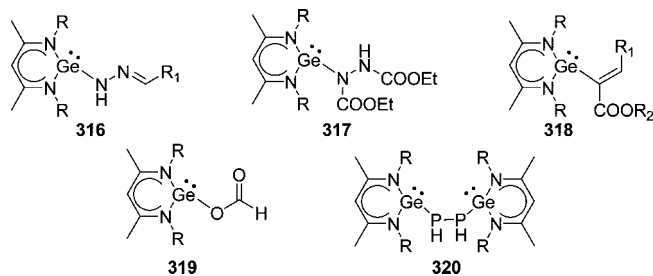
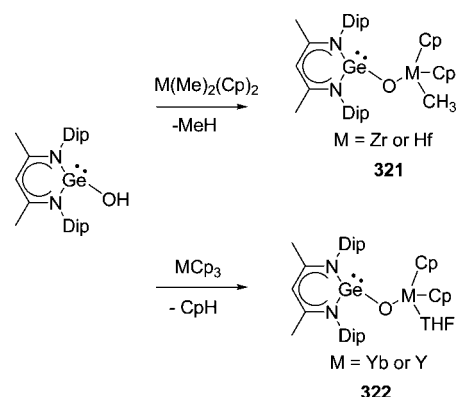


Figure 35. Insertion products of Ge–H (**316**–**319**) and diphosphane digermylene derivative **320**.

The lone pair naturally also remains available for coordination to various transition metals, which has been investigated for various substitution patterns. Germanium(II) halide transition metals are the most common. Compound **311e** reacts with Cr(CO)₅·THF, W(CO)₅·THF, or W(CO)₆ to give the corresponding M(**311e**)(CO)₅ complexes (M = Cr or W).^{320,339} The iodide **311g** also reacts with W(CO)₆ to give the expected complex. A second equivalent of **311e** can be added to the W(**311e**)(CO)₅ under irradiation to give the trans W(**311e**)₂(CO)₄.³³⁰ The Fe(**311g**)(CO)₄ complex is also accessible by reaction with Fe₂(CO)₉.³³⁹ The N-isopropyl-substituted Ge–Cl **311d** forms the only Cu complex by reaction with the Pr^tNacnacCu(NCMe) complex.³²³ In this case, the Ge–Cl could be transformed into the only Ge–H metal complex by reacting the preformed copper complex with KBHET₃. The substitution of the chloride while in the coordination sphere of a metal was previously reported by reacting the W(**311e**)(CO)₅ complex with MeLi to give the only alkyl-substituted complex.³³⁹ Transition metal complexes of cations of type **H** have been targeted by using Ge–Cl precursors. The Ge–OTf tungsten pentacarbonyl complex was accessible directly from the Ge–OTf compounds or by salt metathesis of W(**311e**)(CO)₅ with AgO–Tf.³³⁰ Unfortunately the triflate remains strongly coordinated to the germanium center, although pyridine replaces it to a certain degree in solution; however, the equilibrium prevented full characterization. Attempts to remove the chloride with NaBPh₄ or NaBPh₄/H₂O did not give the desired cationic metal complexes but rather the Ge–Ph tungsten complex and BPh₃ and the Ge–OBPh₂ tungsten complex, respectively.³³⁰ The only other metal complexes reported are from the germanium hydroxide. Interestingly, two types of complexes can be formed, the expected complexes featuring a germanium metal bond or the oxo-bridged complexes. Reaction of Ge–OH³³³ with Fe₂(CO)₆ or MnCp(CO)₃ leads to the expected iron and manganese complexes.³⁴⁰ However, the reaction of the Ge–OH with M(Me)₂(Cp)₂ (M = Zr or Hf) **321** or MCp₃ (M = Yb or Y) **322** gives the μ -oxo heterobimetallic oxides by elimination of MeH and CpH, respectively (Scheme 20).^{341,342}

The neutral germylene **323** (Figure 36), the analogue of the silylene **260** from section 3.1.3, can be accessed in several different ways. The first report was from the cation **310a** by action of amide bases LDA or LiN(TMS)₂.³⁴³ However a far simpler route was simultaneously reported starting from the Ge–Cl **311a** using 1 equiv of LiN(TMS)₂. This route remains the simplest; however, more recently an NHC has been used to eliminate HCl or HOTf to give the desired germylene **323** starting from **311a** or the corresponding triflate.^{344,345} Germylene **323** can also be obtained starting from the Ge–H by elimination of H₂ using the frustrated Lewis acid/base pair B(C₆F₅)₃/NHC.³⁴⁶ The use of frustrated

Scheme 20

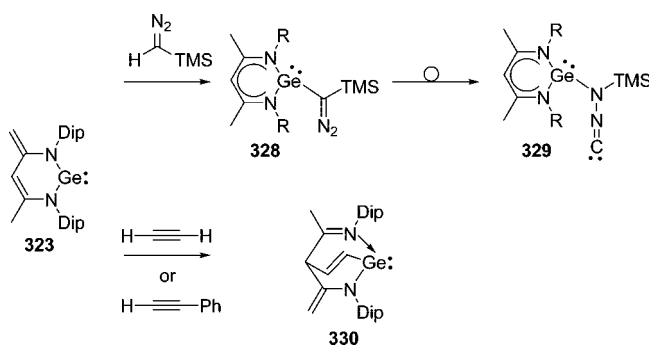


Lewis acid/base pairs to activate or eliminate H_2 has received significant attention recently.^{347,348}

Germylene **323** displays reactivity somewhat similar to that of silylene **260**. Both the germylene center and the basic methylene group in the backbone play important roles in its reactivity. The Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ adds exclusively to the methylene group to give **324** (Figure 36).³⁴⁶ This borate reacts with an NHC, which deprotonates the other methyl group to give the anionic germylene **325** (Figure 36). The 1,4 addition of various substrates has also been reported. Hydrogen–oxygen bonds of water, alcohols (HOPh or HOC_6F_5), and benzoic acid add 1,4 to **323**.³⁴⁵ Ammonia borane can be used as a hydrogen source to add H_2 and give the previously reported $\text{Ge}-\text{H}$ compound.²⁴⁶ Ammonia gas also adds 1,4 across **323** to give the germanium(II) amine.³⁴⁴ The N–H bond of bis(perfluorophenyl)amine [$\text{HN}(\text{C}_6\text{F}_5)_2$] and hydrazine add to **323** to give the germylene amine and hydrazine compounds, respectively.^{328,349} Interestingly, $\text{HN}(\text{TMS})_2$ does not add across the germylene even after extended periods of time; rather, even in the presence of catalytic amounts of $\text{HN}(\text{TMS})_2$, the new digermylene **326** was isolated (Figure 36). A possible mechanism was proposed, and calculations were performed.³⁴⁹ Trimethylsilyl triflate adds 1,4 to **323** and contrary to the silylene case is stable and does not undergo 1,4 migration.³⁴³ A novel $\text{Ge}-\text{Cl}$ is accessible by addition of Ph_2PCl to **323** to give once again the 1,4 addition product.³⁵⁰ Reaction with 1,2-dibromoethane or Br_2 leads to the dimeric germanium bromide **327**. Interestingly, two **311** units are coupled at the methyl group of the backbone presumably by a C–C homocoupling reaction, but no mechanistic details were reported (Figure 36).³⁴³

As with the silicon analogue, the neutral germylene **323** acts as an electron pair acceptor in the presence of highly donating NHCs to give the stable acid/base adducts. The

Scheme 21



reaction of these adducts with N_2O gives access to germanones. The NHC remains ligated to the germanium center during this reaction.³⁵¹

Finally, there are two somewhat exceptional reactions. First, the reaction of **323** and trimethylsilyldiazomethane proceeds by 1,4 addition as expected to give the germanium(II)-substituted diazomethane **328** (Scheme 21).³⁴⁶ However, after several months, both the silyl and germanium groups shift to the terminal nitrogen to give isocyanamide **329**. Second, **323** reacts with alkynes (acetylene or phenylacetylene), not as reported for the corresponding silylene, that is, 1,1 addition or 1 + 2 cyclopropanation, but by a 2 + 4 cycloaddition to give a [2.2.2]bicyclooctane-like structure **330**.³⁵² Additionally, in the case of phenylacetylene, the 1,4 addition product could be isolated as the minor product. These results are in stark contrast to the reactivity of the silylene analogue.

There is one other example of a neutral six-membered germylene based on 1,8-diaminonaphthalene.³⁵³ The reactivity of this species has not been extensively reported; however, it is known to undergo the typical reaction with elemental sulfur or selenium, and in both cases, the $\text{Ge}-\text{E}$ double bond dimerizes to give the heterocyclic four-membered ring system. Four equivalents of this germylene can also be ligated to a nickel(0) center by reaction with $\text{Ni}(\text{COD})_2$. The electronic structure and reactivity of this species have also been investigated theoretically.²⁴²

3.3. Tin(II) Heterocycles

3.3.1. Four-Membered Ring

Cationic amidinate species have not been reported. There are also very few examples of the chloride species of type **I**. The first example is briefly mentioned to have been synthesized by the addition of SnCl_2 to tris(trimethylsilyl)phenylamidine with elimination of trimethylsilylchloro-

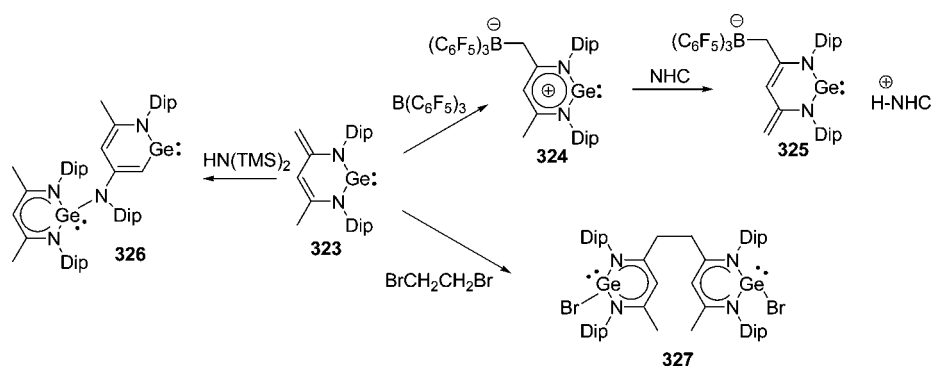


Figure 36. Neutral germylene **323** and selected reactivity.

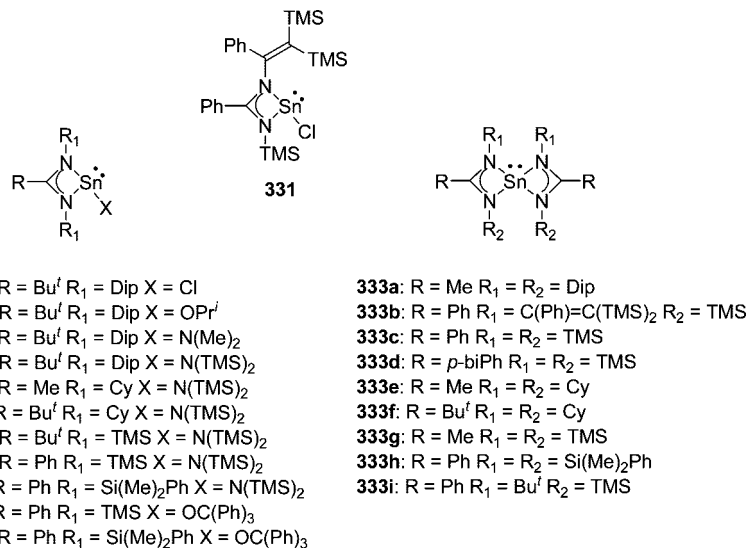


Figure 37. Mono- and bicyclic tin(II) compounds.

ride.³⁵⁴ The structure is reported to be dimeric, but no experimental details were reported. There are two other amidinate tin(II) chloride species reported, **331** and **332a**, which have been fully characterized (Figure 37).^{355,356} Both were prepared by reacting the lithium amidinate with SnCl₂. The chloride of **332a** can be substituted by using a variety of lithium bases LiR (R = OPrⁱ, NMe₂, and N(TMS)₂) to give the corresponding R-substituted compounds **332b–d**.³⁵⁶

When the *tert*-butyl group of **332d** was replaced by a methyl group, the Sn–Cl was observed but not isolated due to the formation of the spirocyclic tin(II) compound **333a** (Figure 37).³⁵⁶ Compound **333a** could be prepared directly by addition of 2 equiv of the amidine to Sn[N(TMS)₂]₂. Compound **333b**, the bicyclic analogue of **331**, was accessible by addition of 2 equiv of the lithium amidinate to SnCl₂.³⁵⁵ These two examples demonstrate the delicate steric balance required to form the Sn–Cl species. Several other substitution patterns both at carbon and at nitrogen have been reported to give this type of four-coordinate bicyclic tin(II) compound (**333a–i**), all of which are accessed by an analogous synthetic pathway.^{265,357–361}

There have been limited reports of the reactivity of these species. Both **333e** and **333f** react with styrene sulfide to give the Sn=S species; however, in the case of **333e**, the double bond dimerizes, whereas in the latter case the species is stable and isolable.³⁵⁹ The change of the seemingly remote carbon substituent makes a significant difference.

Amidinate–amide tin(II) species can be obtained by sequential addition of the lithium amidinate and lithium amide to give a series of these compounds (**332e–k**).^{268,281,360,362} In the case of **332g**, 2 equiv of the lithium amidinate are used but 1 equiv rearranges into LiN(TMS)₂ and *tert*-butylacetonitrile (which could be observed in the reaction mixture). The mechanism of this reaction has been investigated.²⁷⁸

When **332e** or **332f** was reacted with 4 equiv of sulfur, a tetrasulfido Sn(IV) complex was formed, which is a rare example of a SnS₄ five-membered ring. Addition of 3 equiv of PPh₃ yielded the dimerized Sn=S product, which could also be accessed by addition of the styrene or propylene sulfides.³⁶² Similar to the germanium analogue, **332e** reacts with (PhE)₂ (E = S or Se) by inserting into the E–E bond to give the pentacoordinate Sn(IV) species.²⁸¹ Compounds **332h** and **332i** undergo alcoholysis with Ph₃COH to give the corresponding tin ethers **332j** and **332k**.³⁶⁰

There have been several reports of some of these tin four-membered ring systems being used as catalysts. The tin(II) compounds **332g** and **333g**, as well as tetrasulfido complexes of **332e** and **332f**, catalyze the cyclotrimerization of phenyl isocyanates with the tetrasulfido complex **332e**·S₄ being the most active.^{278,362} These were the first reports of tin(II) species being used to catalyze this reaction. The amide and alkoxide tin(II) species **332b–d** and **332j,k** catalyze the ring-opening polymerization of lactide quite efficiently.^{356,360} By variation of the substituents, different kinetics were observed based on the steric hindrance at the tin center.

3.3.2. Five-Membered Ring

There have been a rather large number of tin NHC analogues reported to date. They are all synthesized using a diamine and a tin(II) source. The two most common techniques are first by deprotonation of the diamine followed by addition of SnCl₂ or second by direct addition of Sn[N(TMS)₂]₂, which acts as both a base and a tin(II) source, to the ene–diamine (this technique has only been used for unsaturated and benzo-fused systems). The three typical categories of saturated (**334**),³⁶³ unsaturated (**335**),^{172,364} and benzo-fused (**336**)^{164,286,365–368} are known, and all reported examples are found in Figure 38. The largest variety of substituents can be found in the benzo-fused class including a large variety of bis(stanylenes) **337** with different linkers.^{369–372}

Of the two saturated versions, **334a,b**, the sterically less hindered **334b** forms a dimeric species in the solid state, not as a distannene but rather as a donor–acceptor dimer between the low-valent tin center and the lone pair of one nitrogen to give a four-membered Sn₂N₂ ring. The ¹¹⁹Sn NMR indicates that this dimeric structure does not exist in solution.³⁶³ The reactivity of these two species has yet to be reported.

The chemistry of the unsaturated versions **335a–c** is quite limited. What has been reported is the transfer of the tin(II) atom to a diazadiene. For example, addition of bis(*tert*-butyl)diazadiene to **335b** gives an equilibrium mixture of **335a**, **335b**, and the corresponding diazadienes.³⁶⁴ This reaction has also been studied theoretically.^{172,364} The reaction of **335c** with elemental sulfur or selenium led to decomposition presumably to give the diazadiene, which could be

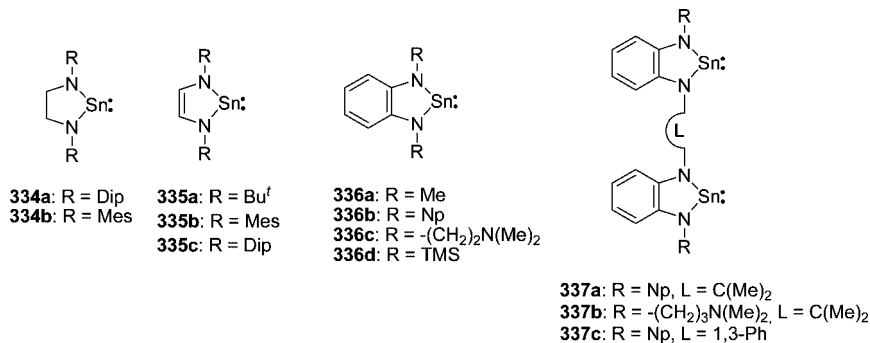


Figure 38. Examples of five-membered stannylenes.

observed by NMR, and Sn(II)S.¹⁷² Stannylene **335c** react with HgCl₂, HgBr₂, AgCl, and several organic radicals to form stable paramagnetic stannylenes that were analyzed by EPR.³⁷³

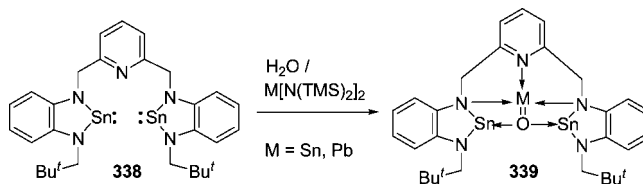
The large variety of benzo-fused systems exceeds that of both the silicon and germanium analogues. The smallest version, **336a**, like **334b**, has a dimeric donor–acceptor structure in the solid state. The nitrogen substituents can be asymmetrical, and there are numerous examples with additional donor groups (ethers or amines) on these pendant groups that coordinate to the tin center as evidenced by the ¹¹⁹Sn chemical shifts and several crystal structures.³⁶⁷ The phenyl group can also be replaced by pyridine, naphthalene, or quinoxaline groups, the last of which could only be isolated as the LiCl adduct.³⁶⁸

Stannylene **336b** reacts with its carbene congener to form a stable donor–acceptor adduct as do the Si and Ge analogues. As with both lighter analogues, variable-temperature NMR indicates that this interaction decreases at higher temperatures. This interaction appears to be stronger than that of the silicon and germanium analogues.²⁰⁴ A carbene complex of **336c** has also been reported by the addition of the dimeric NHC, *N,N,N',N'*-tetramethyl-dibenzotetraazafulvalene, to the free stannylene.³⁶⁶ The Lewis acid/base donor–acceptor complex of **336d** is also known with TMEDA (tetramethylethylenediamine). In this case, the bidentate TMEDA bridges two stannylenes.³⁶⁵

The only transition metal complexes of this type of stannylene involve the bis-stannylenes. One equivalent of **337a** and **337b** replaces the norbornadiene (nbd) of Mo(nbd)(CO)₄ to give the corresponding stable complex.³⁷² Calculations were performed to compare the bonding strength of this type of species to that of the germanium and carbon analogues. Two equivalents of **337a** form homoligated nickel(0) or platinum(0) complexes starting from Ni(COD)₂ and Pt(nbe)₃ (nbe = norbornene), respectively; in the former case, the similar **337c** complex has also been reported.^{369,371} In the case of platinum, the addition of only 1 equiv of **337a** was not possible unless triphenylphosphine and triphenylphosphine oxide were also added. In this case, the Pt(η²-**337a**)(PPh₃)₂ complex was formed; however, 1 equiv of triphenylphosphine oxide coordinates to one of the tin centers. Without the coordination of a phosphine oxide, no heteroleptic complex has been reported.³⁶⁹ The lutidine-bridged bis(stannylene) **338** reacts with M[N(TMS)₂]₂ (M = Sn or Pb) and water to trap tin(II) and lead(II) oxides to give the compounds **339** (Scheme 22). Mössbauer spectroscopy of these products shows that the tin centers retain significant stannylene character.³⁷⁰

Troponimate complexes of Sn(II) have also been reported. When Sn[N(TMS)₂]₂ was added to aminotropon-

Scheme 22



imine, the spirocyclic compound **340** could be isolated (Figure 39).³⁷⁴ When the lithium salt of the troponimine was added to SnX₂ (X = Cl or I), the base-stabilized halostannylenes **341** could be isolated.^{300,375} The reaction of **341a** with 2 equiv of Zr(Cp)Cl₃ led to the cationic compound, but weak interactions to two chlorines of the [(Cp)(Cl)₂Zr(μ-Cl)₃Zr(Cp)(Cl)₂][−] counterion were present.³⁷⁵ The action of AgOTf on **341b** also led to a similar cationic species; however, in the solid state, the triflate remains more closely coordinated to the tin center. As with the germanium analogues, when Ag{HB[3,5-(CF₃)₂Pz]₃}·toluene (Pz = pyrazolyl) was added to the tin chloride, the cation was not isolated but rather the tin silver(borate) complex.³⁰⁰

3.3.3. Six-Membered Ring

There has been one cationic tin(II) Nacnac compound reported, which could be characterized by multinuclear NMR, mass spectrometry, and elemental analysis but unfortunately lacks X-ray crystallographic data.³²⁰ The reactivity of this type of cation has not been reported but has been studied theoretically with the other group 14 analogues.²⁴⁵ As with the germanium six-membered rings, the donor-stabilized tin(II) halides **342** are well-known (Figure 40). The one reported cation is synthesized from **342a** by reaction with NaBPh₄.³²⁰

All of the Nacnac tin(II) halides, **342a–j**, have been synthesized by deprotonation of the corresponding Nacnac ligand followed by treatment with the desired SnX₂ compound (X = Cl or I). Only aryl substituents on nitrogen are known, but the aryl group can be significantly varied.³⁷⁶ The backbone can also be modified not only with the anilido-imine system, **343**,³²⁵ which is also reported for germanium, but also with the methyl groups exchanged for the larger

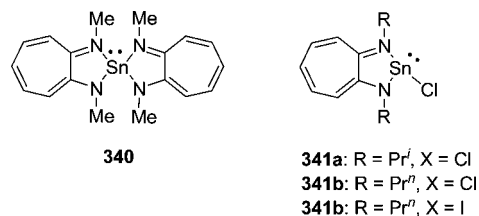


Figure 39. Troponimate Sn(II) complexes.

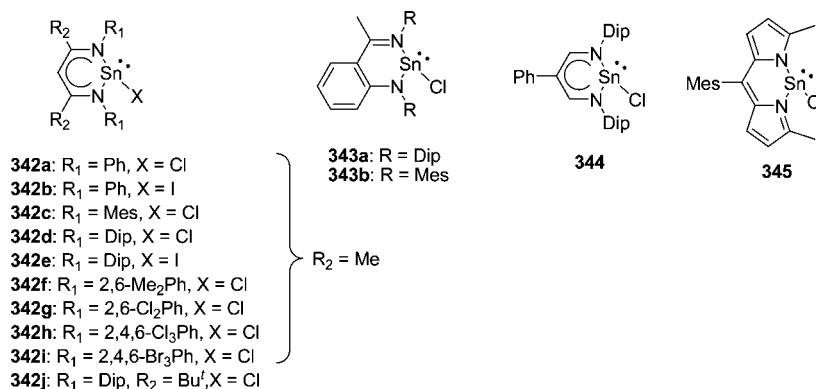


Figure 40. Tin(II) halide six-membered ring systems.

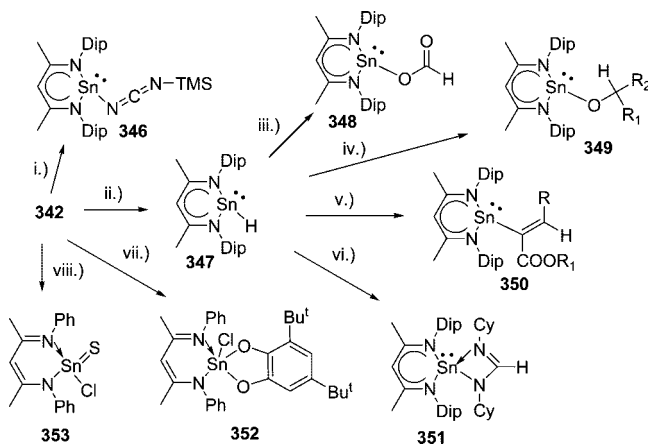


Figure 41. Reactivity of **342** with (i) lithium trimethylsilyldiazomethane, (ii) $\text{AlH}_3 \cdot \text{NMe}_3$, (iii) CO_2 , (iv) ketones, (v) alkynes, (vi) dicyclohexylcarbodiimide, (vii) 3,5-di-*tert*-butyl-orthoquinone, and (viii) sulfur.

tert-butyl groups (**342j**)³⁷⁶ or eliminated with the addition of a phenyl group at the γ -position (**344**) (Figure 40).³⁷⁷ The dipyrromethene derivative **345** has also been reported.³⁷⁸ Such modifications of the backbone have not been reported for the other lighter group 14 elements.

By far, the most common reactivity of these species is the substitution of the chloride by a wide range of substituents. Strong organic bases RLi ($R = \text{Me}$,³⁷⁹ Bu^t ,^{321a} and C_6F_5 ³⁸⁰) react with **342d** to give the corresponding substituted compounds. Nitrogen [$\text{LiN}(\text{TMS})_2$,^{320,379} and LiNMe_2 ³⁷⁶] and oxygen (lithium isopropoxide)^{376,381} bases have also been used, as well as sodium azide.^{320,321a,322} Alternatively, the dimethylamino-substituted tin compound can be prepared directly from the protonated Nacnac ligand and $\text{Sn}(\text{NMe}_2)_2$.³⁷⁶ The isopropyl ether is also available by alcoholysis of this amine. Attempts to synthesize the cation by addition of AgOTf lead to the triflate-substituted tin compound, wherein the triflate remains strongly coordinated to the tin center.^{320,321a,378} Reaction of the methyl- or $\text{N}(\text{TMS})_2$ -substituted **342d** with Me_3SnF leads to the fluoride-substituted tin compound.³⁷⁹ The chloride **342d** has also been substituted by the main group potassium germylenide salt **313** mentioned in section 3.2.3 to give a $\text{Ge}(\text{I})\text{—Sn}(\text{I})$ bond³³⁵ and the anionic transition metal complex $\text{K}[\text{FeCp}(\text{CO})_2]$ to give the iron-substituted stannylene.³³⁴ The reaction of tin chloride **342d** and lithium trimethylsilyldiazomethane yielded the unexpected tin(II)-substituted carbodiimide **346** (Figure 41).³⁸² This species was then reacted with $\text{Fe}_2(\text{CO})_9$ to give the $\text{Sn}\text{—Fe}$ complex $\text{Fe}(\text{346})(\text{CO})_4$. A mechanism for this rearrangement is suggested by the authors, but no intermediates could be

observed. A tin(II) center with two Nacnac ligands has been reported, albeit not by a substitution reaction. The reduction of the tin chloride **342d** with KC_8 gave the bis-Nacnac tin(II) compound in very low yield (10%). The second ligand is only attached to the tin center by a single nitrogen because of steric effects.^{321a}

The tin(II) hydride **347** has been a target for some time. The first attempt to synthesize this type of species was by addition of LiAlH_4 to **342d**, which did not lead to the hydride but rather to the exchange of the tin chloride moiety with AlH_2 .^{321a} Further attempts with NaBH_4 , KBH_4 , and KH also failed; however, addition of $\text{AlH}_3 \cdot \text{NMe}_3$ to **342d** gives the desired monomeric tin(II) hydride **347**.³³¹ Hydride **347** is the only such species reported to date. Interestingly, this tin hydride can add across several types of multiple bonds. Bubbling CO_2 gas through a solution of the tin hydride **347** gives the stannylene formate **348** by addition of the $\text{Sn}\text{—H}$ bond across the $\text{C}=\text{O}$ double bond.³⁸⁴ It also adds across the double bonds of several ketones **349** (R_1 and $R_2 = \text{alkyl}$ or aryl), aldehydes **349** ($R_1 = \text{H}$ and $R_2 = \text{alkyl}$ or aryl), and alkynes **350** and the $\text{C}=\text{N}$ double bond of dicyclohexylcarbodiimide **351**.^{383,384} This type of reactivity is also present in the aforementioned germanium(II) hydride (See section 3.2.3). Recently, it was found that some hydride/fluoride exchange occurs when using perfluorophenyl ketones. This exchange also occurs when **347** is dissolved in fluorobenzene; therefore the hydride may be useful in $\text{C}\text{—F}$ bond activation reactions.³⁸⁰

Reactivity of tin(II) chlorides with other organic and inorganic substrates is limited to a single report of **298a** reacting with 3,5-di-*tert*-butyl-orthoquinone to form the pentacoordinate bicyclic tin chloride **352** or elemental sulfur to give the corresponding $\text{Sn}=\text{S}$ species **353** (Figure 41).³²⁰ In both cases, the products were well described but crystal structures are lacking.

There have been several reports of tin(II) chlorides coordinating to transition metals. Tin chlorides react with $\text{Cr}(\text{CO})_5 \cdot \text{THF}$, $\text{W}(\text{CO})_5 \cdot \text{THF}$, and $\text{Fe}_2(\text{CO})_9$ to give the corresponding complexes.^{320,339} The dimethylamino-substituted **342d** also reacts with $\text{Fe}_2(\text{CO})_9$ to give the $\text{Fe}(\text{342d})(\text{CO})_4$ complex. Subsequent reaction with water gives the tin(II) hydroxide transition metal complex.³⁸⁵ This is the only example of a monomeric tin(II) hydroxide. The free hydroxide has, to date, eluded isolation. The tin(II)-substituted carbodiimide also reacts with $\text{Fe}_2(\text{CO})_9$ to form the expected complex.³⁸²

There have been two reports of using the amine- or alkoxy-substituted tin(II) compounds as initiators in the polymerization of lactide.^{376,381} The mechanism and kinetics of this

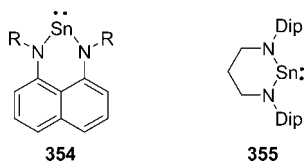


Figure 42. Six-membered stannylenes **354** and **355**.

reaction were studied in depth while comparing the substituent effects.³⁷⁶ Aside from this, there have been no reports of the six-membered tin(II) species discussed herein being used as catalysts or materials.

The neutral stannylene Nacnac analogue of **260** and **323** has not been reported. There are two other reported types of neutral six-membered N-heterocyclic stannylenes (Figure 42). The 1,8-diaminonaphthalene derivative **354** has received some interest and can be synthesized by addition of $\text{Sn}[\text{N}(\text{TMS})_2]_2$ to a 1,8-diamine or by addition of SnCl_2 to the dilithium salt.^{386,387} The reactivity of this type of stannylene is limited to coordination complexes with MAr_2 , ($\text{M} = \text{Ge}$ and Sn)^{387b} and its reactivity with SnCl_2 and silylene **212a**.^{387c} Theoretical studies of its reactivity have been published.²⁴² The other six-membered N-heterocyclic stannylene is the saturated unsubstituted system **355**, which is synthesized by addition of SnCl_2 to the dilithium salt.³⁶³ No reactivity of this species has been reported.

3.4. Lead(II) Heterocycles

3.4.1. Four-Membered Ring

There have been only two amidinate and two guanidinate lead(II) compounds reported to date, **356** and **357** (Figure 43). With the smaller amidinate ligand, 2 equiv reacts with PbCl_2 to give the spirocyclic compound **357**, but in the other three cases, only 1 equiv adds to give the expected lead(II) chloride species **356a–c**. All three of these species were found to be loosely associated dimers in the solid state. The only reactivity reported was the serendipitous formation of crystals by the slow exposure of oxygen to **356b**, which gave compound **358**.³⁸⁸

3.4.2. Five-Membered Ring

The five-membered N-heterocyclic plumbylenes reported have either a benzo-fused backbone, **359**, or a saturated backbone, **360** (Figure 44). The unsaturated species has not been synthesized. The first report was the benzo-fused plumbylene **359a**, which was reported only briefly by Lappert et al.²⁰⁴ This species was coordinated by an NHC to form the adduct that was shown to dissociate somewhat upon heating. However, the synthesis or crystal structure of the free species was not fully reported at that time. More recently, the entire series of these species (**359a–d**) were synthesized by addition of $\text{Pb}[\text{N}(\text{TMS})_2]_2$ to the appropriate 1,2-diaminobenzenes.³⁸⁹ The crystal structures of both **359a** and **359d**

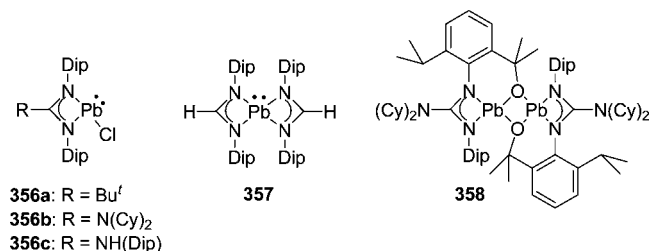


Figure 43. Lead(II) four-membered ring systems.

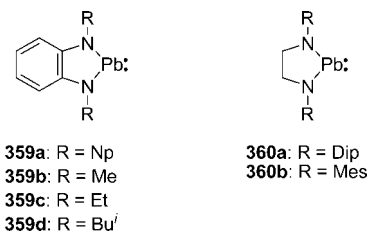


Figure 44. N-heterocyclic plumbylenes.

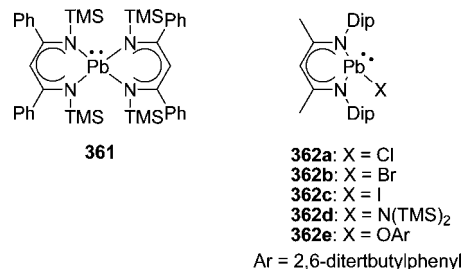


Figure 45. Lead(II) six-membered ring systems.

were obtained, and it was found that they existed as dimers in the solid state with the low-coordinate lead center stabilized by interaction with the aromatic ring of the second plumbylene.

The two saturated plumbylenes **360a** and **360b** (Figure 44) were synthesized from the appropriate diamine and $\text{Pb}[\text{N}(\text{TMS})_2]_2$ or alternatively by addition of PbCl_2 to the dilithium salt. The smaller substituent at nitrogen of **360b** allows a weak interaction between two molecules to form a dimeric species in the solid state wherein one nitrogen coordinates to the lead center.³⁹⁰ There have been no reports of the reactivity of these species.

3.4.3. Six-Membered Ring

A cationic Nacnac lead(II) compound has not been synthesized, but it has been studied by theoretical means.²⁴⁵ There have been several reports of Nacnac lead(II) compounds, the first (**361**) being formed by the reaction of PbI_2 with 2 equiv of the potassium Nacnac salt (Figure 45).³⁹¹ There was no X-ray data reported, but NMR data suggests that the lead center is tetracoordinate. Reaction of PbX_2 ($\text{X} = \text{Cl}$, Br , or I) with the sterically larger Dipp–Nacnac leads to the lead(II) halides **362a–c**.³⁹³

The halide, most often the chloride, can be substituted with a variety of groups usually by direct reaction with alkyl, aryl, alkynyl, amide, and oxide bases.^{393,394} The amino-substituted compound **362d** is also available in one step by reaction of $\text{Pb}[\text{N}(\text{TMS})_2]_2$ with the Nacnac ligand (Figure 45).³⁹² The Pb ether **362e** was similarly synthesized by use of $\text{Pb}(\text{OAr})_2$ ($\text{Ar} = 2,6\text{-(Bu')}_2\text{phenyl}$). The aryloxy group of **362e** can also be substituted by $\text{LiN}(\text{TMS})_2$ or $\text{LiP}(\text{TMS})_2$. Furthermore, the amine group of **362d** can be exchanged to form a lead-substituted phosphasilene **363** by addition of $\text{HP}=\text{Si}(\text{Bu')}_3\text{Si}(2,4,6\text{-triisopropylphenyl})$ (Figure 46).³⁹⁵

There are several reports of these Pb(II) compounds adding across double bonds. The dimethylamine lead(II) species [**362**, $\text{X} = \text{N}(\text{Me})_2$] adds across the $\text{C}=\text{O}$ bond of pyridyl phenyl ketone to give the new alkoxy lead compound **364** (Figure 46).³²⁸ Several alkoxy-substituted compounds [**308**, $\text{X} = \text{OR}$, $\text{R} = \text{Pr}^i$, Bu^i , Bu^n] add across the $\text{C}=\text{O}$ bond of CO_2 to give carbonate derivatives **365**. The isopropoxide

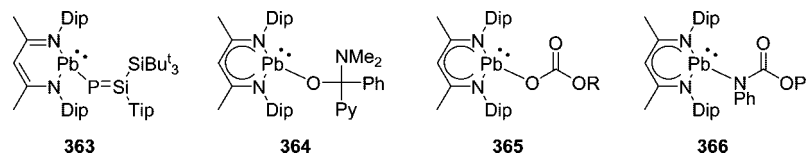


Figure 46. Products from the reaction of **362** with HP=Si(*tert*-Bu₃Si)(2,4,6-triisopropylphenyl) **363**, pyridyl phenyl ketone **364**, CO₂ **365**, and phenylisocyanate **366**.

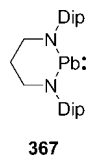


Figure 47.

derivative also adds across the C=N bond of phenylisocyanate, which give the corresponding carbamate derivative **366**.³⁹⁶

The neutral plumbylene derivative of **362** has not been reported. However, plumbylene **367** has been reported to be stable and could be fully characterized (Figure 47).³⁹⁰ In the solid state, the low-coordinate lead center is stabilized by interaction to the aryl group on a second molecule of **367**, creating a dimeric structure. No reactivity of this species has been reported. Calculation on the 1,8-diaminonaphthalene-substituted plumbylene have also been performed, but this species has not been synthesized.²⁴²

4. Conclusions and Outlook

It is clear from the preceding sections that the chemistry of N-heterocyclic systems containing low-valent group 13 element(I) or group 14 element(II) centers has rapidly developed over the past decade, as evidenced by the fact that more than 400 papers have been published in the area in that time. Although these systems are isolobal to each other and to the important N-heterocyclic carbene class of ligands, their chemistries have evolved at different rates and along somewhat different paths. Considering that the first N-heterocyclic group 13 metal(I) system was reported just over 10 years ago, it is not surprising that the body of chemistry devoted to such compounds is significantly smaller than that dedicated to heavier group 14 element N-heterocycles, which have been investigated for considerably longer.

Taking into account the infancy of group 13 N-heterocycle chemistry, much still needs to be done to develop the fundamental aspects of this field. For example, there are currently no known examples of four- or six-membered boron(I) N-heterocycles, four- or five-membered aluminum(I) N-heterocycles, five-membered indium(I) N-heterocycles, or four- or five-membered thallium(I) N-heterocycles. Given the rapid advances in synthetic techniques and ligand development that are occurring in low oxidation state main group chemistry, it is only a matter of time before the stabilization of examples of all such systems will be realized. This will allow the field to flourish in coming decades.

The chemistry of the group 13 element(I) heterocycles that have been developed to date has largely rested on exploring the rich coordination chemistry of these compounds, which can display both nucleophilic and electrophilic properties. This work has led to many fundamental advances in the knowledge of the structure, bonding, and reactivity of metal–metal bonded species. Although this will no doubt continue into the future, these heterocycles have potential uses in a number of other areas, some of which are beginning

to be investigated. For example, considering the huge importance of carbanions to organic chemistry, there are numerous opportunities to examine the synthetic possibilities of boryl anions in organic and inorganic synthesis. Perhaps the biggest challenge here will be the application of nucleophilic boryl anions to catalytic organic transformations, for example, diboration reactions. With respect to heavier group 13 metal(I) heterocycles, the first hints of their potential applicability to a variety of areas have started to come forward. It seems likely that they will find wide use in the stoichiometric (and perhaps catalytic) activation of small molecules (H₂, NH₃, P₄, CO₂, etc.), as specialist reducing agents in the formation of metalloid clusters, alloys, and other binary/ternary materials, low oxidation state/low coordination number p-block compounds, etc.

There are fewer missing compounds in the group 14 element(II) heterocycles, and those that are missing are somewhat hidden by the abundance of related chemistry. However, these gaps remain important targets for fundamental understanding of the group 14 elements. Particularly the free cations of the four-membered amidinate systems are nearly unknown. Additionally, only the “free” Nacnac Ge(II) hydroxide has been reported, while a silicon(II) hydroxide is known merely as a ligand in a Ni(CO)₃ complex. The same is true for the analogous tin species, which is known only as a ligand in an Fe(CO)₄ complex. Such species remain important targets in this domain.

Perhaps the most important target of this chemistry is to broaden the range of applications for these species in which the low-coordinate species play an important role as potential noninnocent ligands in catalysis. The lack of publications about lead(II) species can certainly be partially attributed to the toxicity of this metal, which leads to difficulties in the search for applications. So while lead should continue to garner interest on a fundamental level, the further use of these species may be limited. However, germanium and tin are both important elements, particularly in materials chemistry, and applications may be on the horizon. As noted in the review, there have already been several reports of these element(II) species being used in materials synthesis as single-source molecular precursors or as polymerization catalysts.

Clearly silicon plays a special role not just in this review but in chemistry in general. As the nearest neighbor to carbon, silicon has been the focus of intense study and been widely compared and contrasted with its organic counterpart. Unfortunately the use of these similarities and differences remains almost strictly fundamental in relation to the silicon(II) species discussed in this review. Exploiting the inherent differences between silicon and carbon, while taking advantage of their similarities, is the largest challenge facing researchers in this field. Carbenes have been widely used as ligands in homogeneous catalysis to great effect because they generally create electron-rich transition metal centers, while silylenes have yet to obtain a foothold in catalysis. The limited reports to date, while encouraging, are too few and

give results that are far from competitive with the most efficient ligands employed in transition metal based homogeneous catalysis. In the past several years, silylene chemistry has somewhat trended away from the Arduendo-type NHC analogues to the four- and six-membered ring systems discussed in this review. This may be due to the ease with which researchers can investigate the fundamentally different properties of silylenes and carbenes without being seemingly limited to and by this pervasive thought that silylenes are not only similar to carbenes but should be used in similar ways. The six-membered Nacnac-based zwitterionic (ylide-like) silylene, which has no analogue in carbene chemistry, takes advantage of the unique properties of silicon and has great potential as a noninnocent ligand for transition metal based homogeneous catalysis. This is just one example of the potential of these species. Undoubtedly, many new applications of all these highly reactive group 13 and 14 heterocycles will become apparent as their fledgling chemistry blossoms in coming years.

5. Addendum

Since acceptance of this manuscript a number of papers have appeared, which should be included in this review. These are briefly summarized here. The reaction of the lithium boryl complex $[(\text{THF})_2\text{Li}\{\text{B}(\text{Ar-DAB})\}]$, **3**, with $[\text{BH}_3(\text{THF})]$ has afforded the boryltrihydroborate complex $[\{(\text{Ar-DAB})\text{BBH}_3\}[\text{Li}(\text{THF})_2]\}_2]$, the further reactivity of which was explored and compared with that of LiBH_4 and an NHC adduct of BH_3 .³⁹⁷ The reactivities of **3** and the corresponding gallyl anion, $[\text{Ga}(\text{Ar-DAB})]^-$, toward the titanium imide complex $[\text{Cp}^*\text{TiCl}(\text{NBu}')(\text{pyridine})]$ have been compared. The boron reagent attacks the coordinated pyridine ligand at its 2-position, while the gallyl anion reacts via salt elimination to give the first example of titanium gallyl complex, $[\text{Cp}^*\text{Ti}\{\text{Ga}(\text{Ar-DAB})\}(\text{NBu}')(\text{pyridine})]$.³⁹⁸ An attempt to prepare a six-membered boron(I) heterocycle via dehydrohalogenation of $[\{\text{HC}(\text{MeCNAr})_2\text{BHCl}\}]$ ($\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2-2,6$) with an N-heterocyclic carbene was not successful and instead led to deprotonation of one ligand methyl group and the formation of a cyclic borane complex.³⁹⁹ The gallyl anion, $[\text{Ga}(\text{Ar-DAB})]^-$, has been used in the preparation of a variety of group 6–9 and 11 metal gallyl complexes via salt elimination reactions. In addition, the reactivity of the known copper gallyl complex, $[\text{Cu}(\text{IPr})\{\text{Ga}(\text{Ar-DAB})\}]$ **118**, toward a variety of unsaturated substrates was explored and found to be very different from that of related copper(I) boryl complexes.⁴⁰⁰ The neutral six-membered gallium(I) heterocycle, $[\text{Ga}(\text{DipNacnac})]$ **129**, has been shown to activate P_4 by insertion of its Ga^{I} center into one P–P bond of that substrate.⁴⁰¹ Moreover, a linear, cationic copper complex of **129**, $[\text{Cu}^{\text{I}}\{\text{Ga}(\text{DipNacnac})\}_2]^+$, has been reported to result from the reduction/coordination reaction of **129** with copper(II) triflate.⁴⁰²

Recently, the first bis-silylene oxide $([\text{PhC}(\text{Bu}'\text{N})_2\text{Si}-\text{O}-\text{Si}(\text{NBu}')_2\text{CPh}])$ has been reported.⁴⁰³ It also functions as a bidentate ligand by reaction with $\text{Ni}(\text{COD})_2$, which gives the $(\eta^2\text{-L})\text{Ni}(\text{COD})$ complex. Four-membered chlorosilylene **200** and bis-silylene **206** react with 1 and 2 equiv of benzil, respectively, to give the corresponding siladioxolene analogues with penta-coordinate silicon centers.⁴⁰⁴ A possible mechanism for these cyclization reactions is discussed. Two theoretical studies involving five-membered silylenes of type **210** have recently appeared.⁴⁰⁵ In both cases, the effects of adding other heteroelements to the ring system were inves-

tigated. Three new silylenes of type **210** have been reported where $\text{R} = \text{Xyl} = 2,6\text{-dimethylphenyl}$,⁴⁰⁶ *tert*-amyl, and *tert*-octyl.⁴⁰⁷ The Xyl-substituted version was reported as part of an electrochemical and theoretical study also involving **210a**, **210c**, **211a**, **211d**, and **211e**. Cyclic voltametry was performed on all of these species, and the results were compared with theoretical studies.⁴⁰⁶ The *tert*-amyl and *tert*-octyl were part of a study also involving **210a–c** and **211a** wherein the radicals of these species formed by muonium addition were investigated by μSR spectroscopy. Attempts to synthesize phosphonyl radical adducts of **210a** and **211a** by addition of $[(\text{Pr}^i)_2(\text{O})\text{P}]_2\text{Hg}$ to the free silylenes resulted not in radicals but in various Hg adducts, whose formation was attributed to a radical mechanism.⁴⁰⁸ However, radical adducts were formed with germynes **298a** and **299a** and could be studied by EPR spectroscopy. These radicals were also investigated theoretically. Attempts to synthesize a Grubbs-type ruthenium silylene **210a** complex resulted in the formation of the novel $\text{Ru}(\text{210a})(\text{PCy}_3)_2(\text{H})(\text{Cl})$ by addition of the free silylene to either $\text{Ru}(\text{CHPh})(\text{PCy}_3)_2(\text{Cl})_2$ or $\text{Ru}(\text{PCy}_3)_2(\text{H}_2)(\text{H})(\text{Cl})$.⁴⁰⁹ The mechanism of the first reaction could not be elucidated. The corresponding NHC complex was also synthesized and compared with the silylene species. A new iridium complex has been synthesized by the insertion of **260** into the Ir–H bond of IrCp^*H_4 .⁴¹⁰ This Si–H complex is not indefinitely stable but could be characterized or trapped by addition of $\text{B}(\text{C}_6\text{F}_5)_3$, which reacts with the anionic methylene group of the ligand. If not trapped, the complex undergoes migration of a hydride ligand to the methylene group to form a new complex that could also be characterized. A new synthetic methodology for the preparation of the dichloro precursors of silylene **210b** and germylene **298c,d** has been reported.⁴¹¹ This report also contains the alternative preparation of **298d** by dehydrogenation of the dihydrogermane precursor using a frustrated Lewis pair. Additional reactivity of $(\text{DipNacnac})\text{Ge}-\text{H}$ has been reported.⁴¹² Reaction with N_2O yields the previously reported germanium(II) hydroxide. Addition of TMSN_3 gives $(\text{DipNacnac})\text{Ge}-\text{N}_3$ and $(\text{DipNacnac})\text{Ge}-(\text{NHTMS})_2$. Two trifluoromethylketones react to give the $(\text{DipNacnac})\text{Ge}-\text{OR}$ species resulting from addition of the Ge–H bond across the C=O bond. The Ge–H bond also adds across two different alkynes. Finally, $(\text{DipNacnac})\text{Ge}-\text{Me}$ reacts with TMS diazomethane to give $(\text{DipNacnac})\text{Ge}-(\text{Me})(\text{NH}-\text{N}=\text{CHTMS})$. The tin compound $(\text{DipNacnac})\text{Sn}-\text{NMe}_2$ reacts with ketones in a fashion similar to the hydride **347** and yields tin alkoxides similar to **349** (where H is replaced by NMe_2).⁴¹³ Two terminal alkynes also react with this species to eliminate HNMe_2 and give the corresponding $(\text{DipNacnac})\text{Sn}-\text{alkyne}$ compound.

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