

## Multiple Bonding in Heavier Element Compounds Stabilized by Bulky Terphenyl Ligands<sup>†</sup>

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This paper summarizes recent developments involving the preparation and reactivity of molecular species stabilized by terphenyl ligands that feature new bonding environments. Highlights include the synthesis and characterization of dimetallenes and dimetallynes, ArEEAr [E = heavy group 13 (triell) or group 14 (tetrel) element, Ar = terphenyl ligand] and, more recently, the synthesis of a stable chromium(I) dimer, ArCrCrAr, that displays a 5-fold bonding interaction between the chromium centers.

### Introduction

The synthesis of molecular species that have unusual bonding arrangements is a very active research area in inorganic chemistry.<sup>1</sup> In general, curiosity regarding fundamental bonding questions inspires workers in this field to synthesize new and increasingly challenging target molecules. Modern theoretical methods provide parallel and synergistic information on the feasibility of these objectives. One concept that has become the most important for this area has been the use of sterically encumbered ligands to provide kinetic stabilization of highly reactive species.<sup>2</sup> This principle was used effectively by Bradley and co-workers to stabilize low coordination numbers in the realm of transition-metal chemistry. Their approach has influenced important discoveries in many areas including that of metal-mediated catalysis.<sup>3</sup> In the 1970s, Lappert and co-workers applied ligand stabilization techniques to main-group element compounds that resulted in the landmark preparation of the novel tin(II) alkyl dimer {Sn[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>}<sub>2</sub> in 1973.<sup>4</sup> This compound was shown to have a weak Sn–Sn double bond

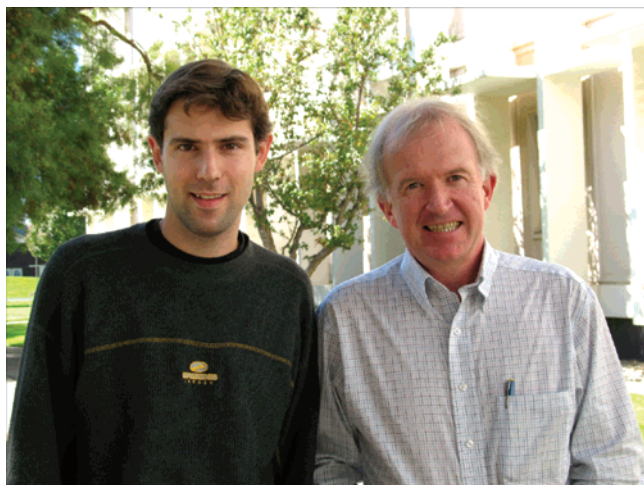
in the solid state and represented the first observation of formal multiple bonding between two heavy main-group elements (period ≥ 3) under ambient conditions. Soon afterward, researchers began exploring the use of hindered aryl ligands in order to facilitate the isolation of new types of stable multiple bonds. Most notably, in 1981 West and co-workers prepared the first stable disilene, Mes<sub>2</sub>Si=SiMes<sub>2</sub>, using bulky mesityl (Mes = C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>) groups.<sup>5</sup> The disilene differed from the tin species in that it did not dissociate into monomers in solution, thus providing the first stable double bond between two heavier main-group elements. Also in 1981, Yoshifuji et al. used the related supermesityl ligand (Mes\* = C<sub>6</sub>H<sub>2</sub>-2,4,6-t-Bu<sub>3</sub>) to prepare the first stable diphosphene, Mes\*P=PMe\*.<sup>6</sup> These compounds played a leading role in the development of inorganic chemistry because they vitiated the pre-existing “double-bond rule”, which had stated that stable multiple bonding was only possible between main-group elements of the second row.<sup>7</sup>

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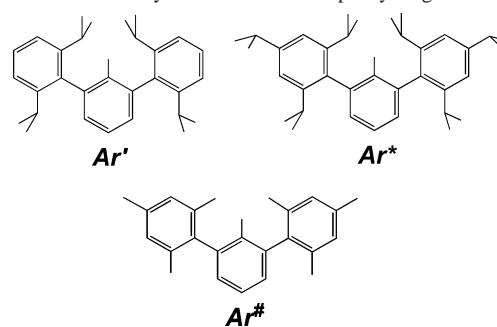


Eric Rivard was born in Gander, Newfoundland, Canada in 1978. He obtained his B.Sc. in Chemistry at the University of New Brunswick, where he conducted undergraduate research with Prof. Jack Passmore in the area of fluorine chemistry. Afterward he moved to the University of Toronto, where he received a Ph.D. degree (2004) under the supervision of Prof. Ian Manners in the domain of inorganic rings, chains, and molecules featuring phosphorus. After a period of NSERC-sponsored postdoctoral study with Prof. Jonas Peters at Caltech, he then moved to the University of California at Davis, where he is now a postdoctoral fellow in the group of Prof. Philip Power. Currently, he is actively investigating the preparation of new inorganic multiple bonds using donor-stabilization strategies and the synthesis of hindered group 14 hydrides and clusters.

Philip Power received a B.A. from Trinity College Dublin in 1974 and a D. Phil. under M. F. Lappert from the University of Sussex in 1977. After postdoctoral studies with R. H. Holm at Stanford University, he joined the faculty at the Department of Chemistry at the University of California at Davis, in 1981, where he is Professor of Chemistry. His main interests lie in the exploratory synthesis of new main-group and transition-metal complexes. A major theme of his work has been the use of sterically crowded ligands to stabilize species with new types of bonding, low coordination numbers, and high reactivity. Early work involved the structural chemistry of organoalkali-metal and organocopper compounds, low-coordinate (2 and 3) transition-metal complexes, multiple-bonded phosphorus and arsenic compounds, and the characterization of persistent or stable main-group element radicals. This developed into a more wide-ranging investigation of multiple-bonded homo- and heteronuclear heavier main-group element compounds as well as their cluster and hydride derivatives. The latter species have led to interest in their applications in hydrogen activation and storage. These investigations necessitated the synthesis and application of several new types of bulky ligands, of which the most prominent have been bulky terphenyls. These greatly expanded the range of known multiple-bonded main-group compounds and more recently have shown their potential to have a large impact on transition-metal chemistry.

Since the mid-1980s, the Power group has actively used both alkyl- and aryl-based ligands to prepare unusual low-coordinate transition-metal and main-group species. A more recent addition to our ligand complement has been the hindered terphenyl ligands of the general form  $-C_6H_3-2,6-Aryl_2$  (Scheme 1). The flanking aryl rings in these ligands generally carry alkyl groups at their ortho and sometimes para positions. These substituents induce an almost perpendicular orientation of the flanking aryls with respect to the

**Scheme 1.** Commonly Used Hindered Terphenyl Ligands



central ring. This generates an overall concave steric pocket that surrounds the ligating *ipso*-carbon and helps protect neighboring reactive centers from degradation processes. As a consequence, terphenyl ligands are especially well suited to the stabilization of low-coordinate bonding environments.<sup>8</sup>

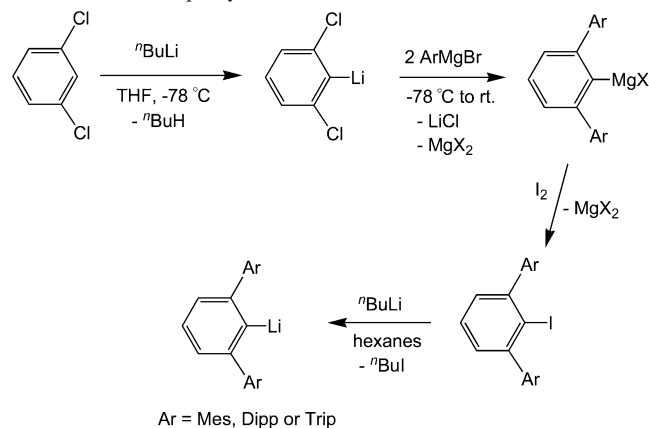
This account focuses on recently (from about the year 2000 to 2006) discovered bonding arrangements involving low-coordinate transition-metal and main-group elements,  $(ArM)_n$  ( $n \leq 2$ ), all supported by terphenyl-based ligands. In addition, selected reactions are discussed in order to highlight some of the chemistry available for these formally unsaturated species.

### Ligand Synthesis

Apart from their steric advantages and resistance to degradation, terphenyl ligands can be easily synthesized from readily available starting materials. Although terphenyl ligands were known as early as 1942,<sup>9a</sup> it was not until 1986, when Hart and co-workers developed a general route to terphenyls via aryl–aryl coupling, that relatively efficient routes to these species became available.<sup>9b</sup> Afterward, a one-pot synthesis of these ligands was developed by Hart and co-workers and this group.<sup>9c,10</sup> We also introduced even bulkier flanking groups such as Dipp ( $C_6H_3-2,6-^iPr_2$ ) and Trip ( $C_6H_2-2,4,6-^iPr_3$ ) to give the larger terphenyl ligands Ar' and Ar\* (Schemes 1 and 2).<sup>10</sup> The terphenyl iodide precursors are now routinely prepared in >100 g scale, and their corresponding terphenyllithium salts can be rapidly generated by treating ArI species with either  $^nBuLi$  or  $^tBuLi$  in hydrocarbon solvents. A number of terphenyllithium derivatives, ArLi,<sup>11</sup> have been structurally characterized and have been used to transfer effectively terphenyl functionality to a wide array of main-group, transition-metal, and lanthanide centers.

In 1996, it was shown that terphenyl ligands could be used to synthesize new triple-bonding motifs with the synthesis of  $Cp(CO)_2Mo \equiv GeAr^\#$ , the first stable species with a triple bond to a heavier group 14 element.<sup>12</sup> We have expanded upon this initial discovery to show that, in general, terphenyl

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**Scheme 2.** One-Pot Route to Terphenyl Iodides and Their Conversion into Terphenyllithium Salts

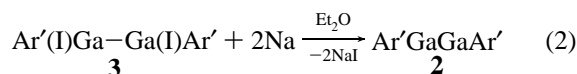
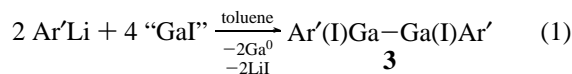
ligands are especially well suited in stabilizing reactive bonding environments, and a number of recent discoveries in this area will be highlighted below.

### Synthesis, Structure, and Reactivity of Group 13 Dimetallenes, Ar'EER' (E = Al–Tl)

The investigation of multiple bonding within group 13 elements is one of the major themes of main-group chemistry.<sup>13</sup> In 1993, the first examples of compounds featuring Al–Al and Ga–Ga linkages with multiple-bond character appeared almost simultaneously in the literature. Pörschke and co-workers reported the synthesis of the monoreduced tetraorganoalane radical  $[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{AlAl}[\text{CH}(\text{SiMe}_3)_2]^\cdot$ , while this group prepared the singly reduced digallane,  $[\text{Trip}_2\text{GaGaTrip}_2]^\cdot$ .<sup>14</sup> Both species were obtained via reduction of the respective neutral dialanes and digallanes  $\text{R}_2\text{EER}_2$  (first isolated by Uhl and co-workers)<sup>14d</sup> with alkali metals and were shown to possess one-electron E–E  $\pi$  bonds by X-ray crystallography and electron paramagnetic resonance (EPR) spectroscopy. Four years later, in 1997, the synthesis and characterization of the digallium species  $\text{Na}_2[\text{Ar}^*\text{GaGaAr}^*]$  (**1**) was published by Robinson and co-workers.<sup>15</sup> This report caused considerable debate (which continues this day) because of the description of the compound as a “digallyne” having a Ga–Ga triple bond. This assignment was made on the basis of a short Ga–Ga distance of 2.319(3) Å and the isoelectronic nature of the  $[\text{Ar}^*\text{GaGaAr}^*]^{2-}$  ion to the (at the time unknown) neutral species  $\text{Ar}^*\text{GeGeAr}^*$ , which is itself an alkyne analogue. Some calculations supported the existence of a Ga–Ga triple bond in **1**;<sup>16</sup> however, others challenged this view.<sup>17,18</sup> The main reasons for doubt included (a) the presence of a trans-bent structure within the  $\text{C}_{\text{ipso}}\text{—Ga—Ga—C}_{\text{ipso}}$  array

[Ga–Ga–C angles: 125.9(2) and 134.0(2)°], which indicated considerable lone-pair character at the gallium centers, (b) the fact that there were significant Na–Ga and Na–aryl interactions, indicating incomplete electron transfer from Na to Ga, which could shorten the Ga–Ga bond in **1**, and (c) the fact that the Ga–Ga interaction was calculated to be quite weak by force-constant calculations.<sup>18c,f</sup> Nagase and Takagi concluded that “the heart of the molecule is a  $\text{Na}_2\text{Ga}_2$  cluster rather than a simple Ga–Ga bond”.<sup>18b</sup> The importance of the  $\text{Na}^+$  ions in stabilizing  $\text{Na}_2[\text{Ar}^*\text{GaGaAr}^*]$  was supported by the reduction of  $\text{Ar}^*\text{GaCl}_2$  with K instead of Na. This afforded the  $\text{K}_2\text{Ga}_4\text{Ar}^*_2$  cluster containing a quasi-aromatic  $[\text{Ga}_4\text{Ar}^*_2]^{2-}$  ring instead of  $[\text{Ar}^*\text{GaGaAr}^*]^{2-}$ .<sup>19a,b</sup> In order to shed further experimental light on this issue, the preparation of a neutral “digallene” derivative  $\text{ArGaGaAr}$  was deemed important because if this species possessed a Ga–Ga double bond, then the assignment of a triple bond in **1** would be supported.

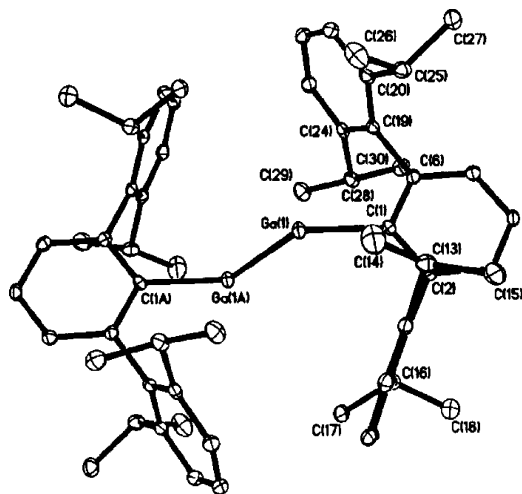
In 2002, we reported the successful preparation of a neutral “digallene”  $\text{Ar}'\text{GaGaAr}'$  [**2**;  $\text{Ar}' = -\text{C}_6\text{H}_3-2,6-(\text{C}_6\text{H}_3-2,6\text{-}^i\text{Pr}_2)_2$ ], which contained a terphenyl ligand closely related to the  $\text{Ar}^*$  ligand in **1**.<sup>20</sup> Compound **2** was prepared in a two-step procedure starting from the readily available gallium(I) precursor, “GaI”,<sup>21</sup> which was initially reacted with  $\text{Ar}'\text{Li}$  in toluene to give the bright-yellow 1,2-diiododigallane  $\text{Ar}'(\text{I})\text{GaGa}(\text{I})\text{Ar}'$  (**3**) in moderate yield (eq 1). In a subsequent step, careful reduction of **3** with sodium metal afforded a deep-green solution from which brick-red crystals of **2** were obtained (eq 2 and Figure 1).



X-ray crystallography revealed the presence of a planar trans-bent C–Ga–Ga–C core in **2** [Ga–Ga–C angle: 123.16(7)°] along with a relatively long Ga–Ga distance of 2.6268(7) Å, which was over 0.3 Å longer than that in the salt **1**. Furthermore, the Ga–Ga distance in **2** was longer than typical Ga–Ga single bonds (2.33–2.54 Å),<sup>22</sup> implying that this bond was quite weak. Indeed, cryoscopy performed on **2** showed that this species exists as a monomer in benzene and may explain the striking color change that was observed

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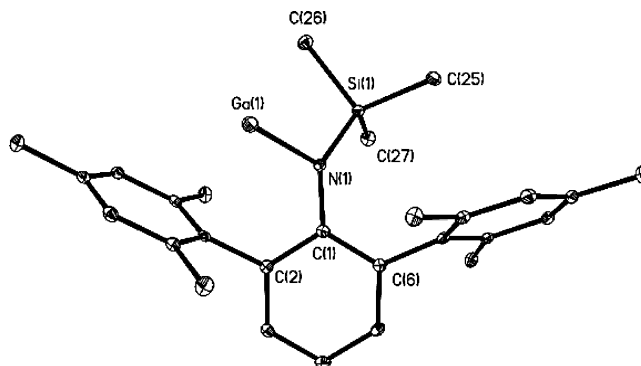
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**Figure 1.** Structure of the trans-bent dimer **2**:<sup>20</sup> Ga–Ga = 2.6268(7) Å; Ga–Ga–C<sub>ipso</sub> = 123.16(7)°.

when **2**, a brick-red solid, is dissolved in hydrocarbons to give intense-green solutions. This behavior parallels that observed within the related tetrahedrane gallanes, (R<sub>3</sub>Ga)<sub>4</sub>, which also have long Ga–Ga bond lengths in the solid state (2.57–2.71 Å) and exist in equilibrium with monomeric structures in hydrocarbon solutions.<sup>23</sup> The dianionic analogue, Na<sub>2</sub>[Ar'GaGaAr'], was also prepared, and this species had metrical parameters very similar to those in **1**, suggesting that steric effects were unlikely to be the main reason for the long Ga–Ga bond observed in **2**. In effect, the presence of a long (and weak) Ga–Ga bond in **2** suggests that the bonding in the “digallyne” **1** is probably closer to a single bond rather than the triple bond originally proposed.

In addition, the more hindered analogue of **2**, GaAr\* [4; Ar\* = –C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-Pr<sub>3</sub>)<sub>2</sub>], was prepared, and this species is also monomeric in solution.<sup>24</sup> Curiously, compound **4** retains its dark-green color in the solid state, suggesting that it could be monomeric in the solid state as well. The possible further weakening or even absence of Ga–Ga bonding in such a species implies that the addition of two electrons to afford Na<sub>2</sub>Ar\*GaGaAr\* does not generate a Ga–Ga triple bond but an approximate single one. Unfortunately, despite numerous attempts, we were unable to obtain crystals of suitable quality for X-ray diffraction experiments. Perhaps in the future the synthesis and characterization of a range of gallium(I) derivatives of modified terphenyl ligands closely related to Ar' or Ar\* will shed further light on the strength of the weak Ga–Ga bonding in these gallium(I) species. The feasibility of obtaining a one-coordinate monomeric gallium(I) species in the solid state was demonstrated by the synthesis of :GaN(SiMe<sub>3</sub>)Ar<sup>#</sup> (**5**; Figure 2).<sup>25</sup> The Ga–N distance in **5** was 1.980(2) Å, and calculations have shown that this compound retains considerable lone-pair character at gallium and that the degree of π bonding between the gallium and nitrogen centers is small (Wiberg

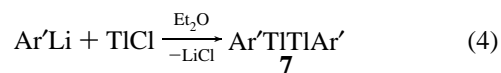
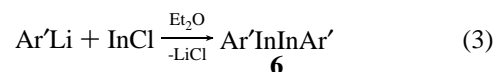


**Figure 2.** Monomeric gallium(I) amide **5**.<sup>25a</sup>

bond order = ca. 1.39). Interestingly, the gallium(I) amide model species :GaNMe<sub>2</sub> was predicted to be more stable than both the bent and linear gallium imine isomers, MeNGaMe, by 34.5 and 36.7 kcal/mol, respectively.<sup>25a</sup>

Because it was shown that the Ar' ligand allowed the isolation of a neutral “dimetallene” of gallium, perhaps other heavy group 13 Ar'EEAr' analogues (i.e., E = Tl, In, and Al) could be similarly prepared. This project was set against the backdrop of a number of key prior results. First, this group and that of Niemeyer had shown that monomeric (one-coordinate) indium and thallium aryls, :EAr\* (E = In and Tl), could be prepared with the bulky terphenyl ligand, Ar\*.<sup>26,27</sup> In addition, the earlier preparation of the dimeric indium and thallium species [E{η<sup>5</sup>-C<sub>5</sub>(CH<sub>2</sub>Ph)<sub>5</sub>}]<sub>2</sub> featuring very long (>3.6 Å) E–E distances by Schumann and co-workers stimulated a great deal of interest (and theoretical study) in the nature of bonding within simple REER species.<sup>28</sup> As in digallenes, R<sub>2</sub>GaGaR, the parent dimetallenes of indium, HInInH, and thallium, HTlTlH, were predicted to adopt trans-bent arrangements with long E–E distances.<sup>29</sup>

Using a strategy parallel to that employed for the synthesis of :InAr\* and :TlAr\*, the slightly less hindered aryllithium salt Ar'Li was reacted with an equimolar amount of InCl and TlCl, respectively (eqs 3 and 4). In both instances,



exceedingly air- and moisture-sensitive deep-red crystalline products were obtained. The thallium derivative displayed further sensitivity to ambient light. X-ray crystallography revealed that both compounds adopted dimeric arrangements (Ar'EEAr'; E = In<sup>30</sup> and Tl,<sup>31</sup> **6** and **7**) with planar trans-bent C–E–E–C cores similar to those in the gallium analogue **2** (Figures 3 and 4). Specifically, an E–E–C angle

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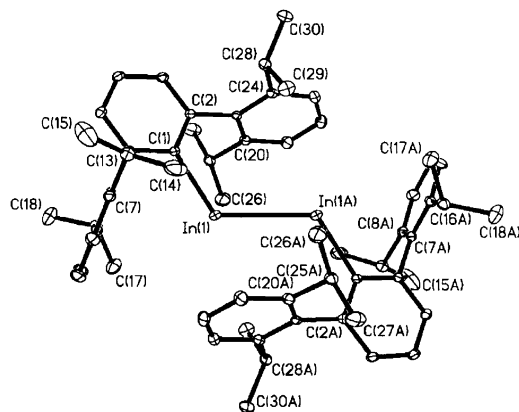
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**Figure 3.** Structure of **6**:<sup>30</sup> In–In = 2.9786(5) Å; In–In–C<sub>ipso</sub> = 121.23(6)°.

of 121.23(6)° was observed for the indium derivative **6**,<sup>30</sup> while in the thallium counterpart **7**, this angle was 119.74–(14)°.<sup>31</sup> The observed In–In distance in **6** was found to be 2.9786(5) Å and is shorter than the value obtained (3.329 Å) from calculations performed on the parent trans-bent diindene, HInInH.<sup>29</sup> Moreover, the In–In distance in **6** is close to values seen within the electron-deficient (InR)<sub>4</sub> tetramers, ca. 3.0 Å,<sup>32</sup> and is considerably longer than currently known distances for In–In single bonds [2.696–(2)–2.938(1) Å].<sup>33</sup> The Tl–Tl distance in **7** [3.0936(8) Å] is considerably shorter than that predicted for the parent dithallene HTlTlH (3.217 Å);<sup>29</sup> however, it is longer than the Tl–Tl single bonds in R<sub>2</sub>Tl–TlR<sub>2</sub> species (2.88–2.97 Å).<sup>34</sup> Therefore, the E–E bonding in **6** and **7** is fairly weak and, interestingly, compound **6** was shown via cryoscopic measurements to have a monomeric structure in solution. The trimeric species (Ar''Tl)<sub>3</sub> (**8**) was also prepared with the aid of the less hindered Ar'' ligand [Ar'' = –C<sub>6</sub>H<sub>3</sub>–2,6–(C<sub>6</sub>H<sub>3</sub>–2,6–Me<sub>2</sub>)<sub>2</sub>] and exhibited lengthened Tl–Tl bond lengths (3.21–3.38 Å), which are comparable to the Tl–Tl interactions observed within the tetrameric species [Tl{C(SiMe<sub>3</sub>)}]<sub>4</sub> (3.32–3.64 Å).<sup>35</sup>

In contrast to the weak E–E bonding predicted (and later observed) for the heavy dimetallenes, REER (E = Ga–Tl), the parent “dialuminene” isomer HAlAlH was predicted to have a considerably stronger E–E bond (ca. 10 kcal/mol).<sup>36</sup> Furthermore, the Al–Al bond length was calculated to be 2.613 Å, which is shorter than the majority of Al–Al single-bond lengths in dialanes R<sub>2</sub>AlAlR<sub>2</sub> (ca. 2.65 Å).<sup>37</sup> Therefore, we sought to prepare a terphenyl-based “dialuminene” of the general form ArAlAlAr.

Reduction of Ar'AlI<sub>2</sub> with sodium in diethyl ether initially yields the aluminum(II) dialuminane Ar'(I)Al–Al(I)Ar' (**9**), which is then converted into the dialuminene Ar'AlAlAr' upon further reduction with sodium. Attempts to grow crystals of this species in toluene led to the [2 + 4] cycloaddition reaction of the putative dialuminene with a molecule of toluene to give **10** as a red solid (Scheme 3 and Figure 5).<sup>38</sup> Consistent with the structure shown below, the Al–Al bond length in **10** [2.5828(7) Å] was only slightly shorter than the distances observed in single-bonded dialanes R<sub>2</sub>AlAlR<sub>2</sub>,<sup>37</sup> while inequivalent C–C and C=C bonds were found within the captured toluene moiety.

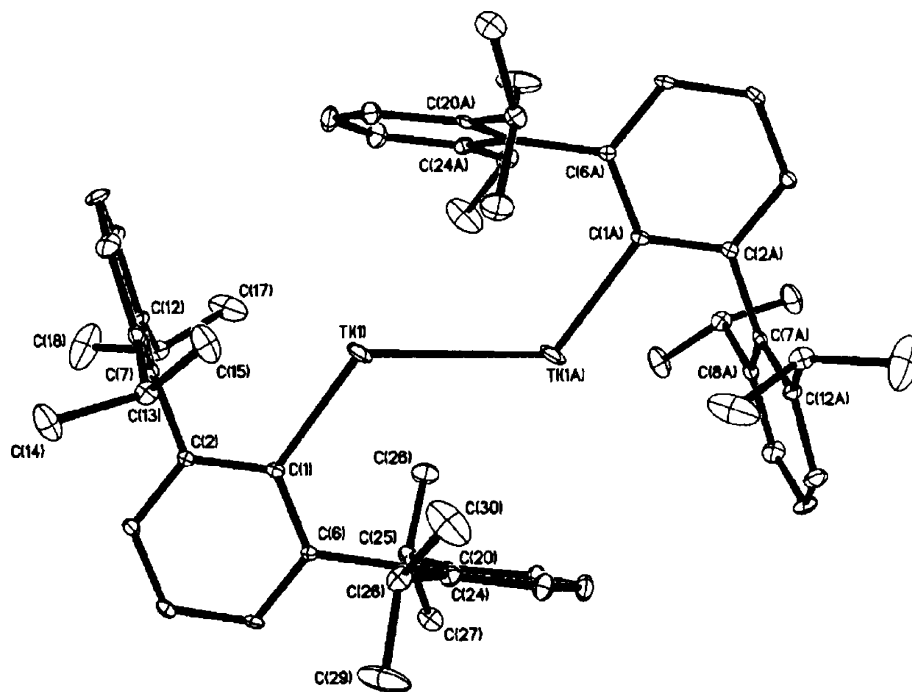
Exposure of the dialuminene Ar'AlAlAr' to an excess of sodium leads to further reduction to afford the sodium salt of the “dialuminyne” dianion, Na<sub>2</sub>[Ar'AlAlAr'] (**11**), in low yield (20%) as dark-red crystals (Figure 6).<sup>39</sup> X-ray crystallography revealed a centrosymmetric Al<sub>2</sub>Na<sub>2</sub> core with Al–Al and Al–Na distances of 2.428(1) and 3.152(1) Å, respectively. Moreover, additional Na–aryl interactions were found between the alkali counterions and the flanking rings of the terphenyl ligand. As in the neutral group 13 dimetallenes, a trans-bent C–Al–Al–C array was present [C(ipso)–Al–Al angle = 131.71(7)°]. For comparison, the recently reported isoelectronic “disilyne” R'SiSiR' (R' = Si[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sup>i</sup>Pr) has a similarly trans-bent geometry with a Si–Si–Si bend angle of 137.44(4)°.<sup>40</sup> Unlike the disilyne R'SiSiR', which has an estimated bond order of 2.6,<sup>40</sup> calculations afford a value of 1.13 for the Al–Al bond order in **11**, while the Ga–Ga bond in the gallium derivative **1** had a slightly higher bond order of 1.39.<sup>39</sup> Of note, the Al–Al distance in **11** is ca. 0.20 Å longer than the recently estimated sum of the triple-bond radii of aluminum (2.22 Å),<sup>41</sup> which supports the lack of significant Al–Al multiple bonding in **11**.

Repeating the reduction chemistry with the less hindered arylaluminum diiodide, Ar<sup>#</sup>AlI<sub>2</sub>, produced the “cyclotrialuminene” Na<sub>2</sub>[Ar<sup>#</sup>Al]<sub>3</sub> (**12**; Figure 7).<sup>39</sup> This species is formally aromatic (2π electrons), and calculations performed on the isostructural gallium derivative, Na<sub>2</sub>[Ar<sup>#</sup>Ga]<sub>3</sub> (previously reported by Robinson and his group), indicated metalloaromatic character.<sup>13a,42</sup> Calculations on the parent trimer Na<sub>2</sub>(AlMe)<sub>3</sub> reveal significant covalent Na–Al bonding interactions; thus, the Na atoms play an active role in holding the Al<sub>3</sub> core together.<sup>39</sup>

The lightest member of the group 13 dimetallene series, diboronene, HBBH, has been isolated using matrix isolation techniques and shown by both theory and experiment to possess a triplet ground state.<sup>43</sup> It is likely that terphenyl-substituted diboronenes, ArBBAr, would also possess considerable triplet character, and to date, efforts to prepare these species (or their anionic counterparts) have led to ligand degradation processes whereby C–C and C–H bond activa-

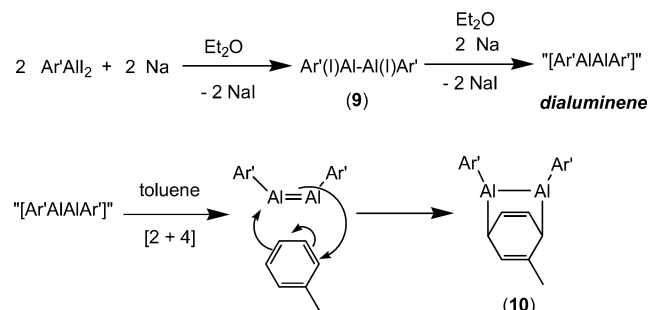
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**Figure 4.** Molecular structure of **7**:<sup>31</sup> Ti–Ti = 3.0936(8) Å; Ti–Ti–C<sub>ipso</sub> = 119.74(14)°.

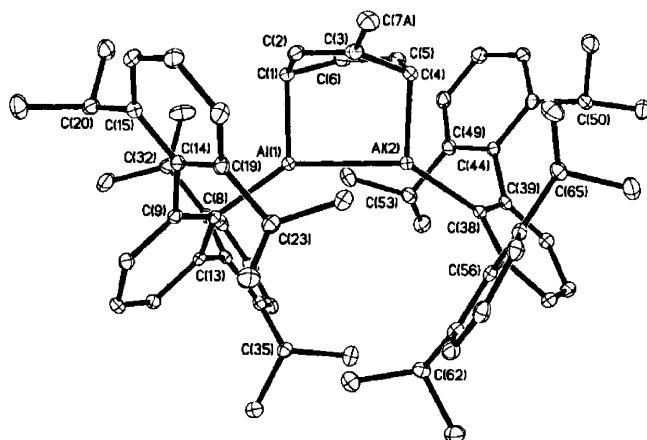
**Scheme 3.** Dialuminene Synthesis and Cycloaddition Chemistry with Toluene



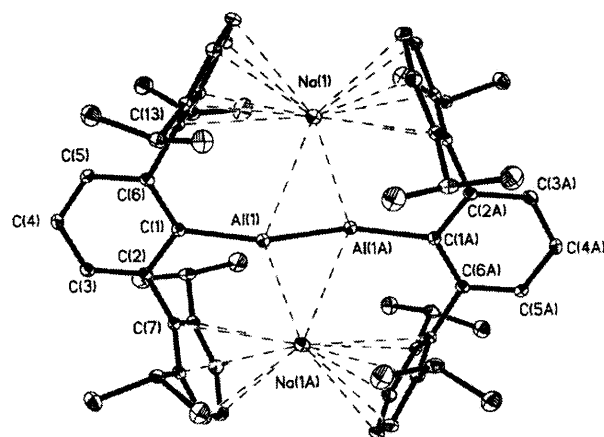
tion is observed.<sup>44</sup> Further ligand modification or the use of Lewis bases may overcome ligand activation to yield stable diboronene adducts.

### Chemistry of Group 13 Dimetallenes, Ar'EEAr' (E = Ga–Tl)

A common property of the group 13 dimetallenes isolated thus far (E = Ga–Tl) is their dissociation into monomeric



**Figure 5.** Cycloadduct **10** obtained by the reaction of transient Ar'AlAlAr' with toluene.<sup>38</sup>



**Figure 6.** Structure of the reduced “aluminyne” salt **11**.<sup>39</sup>

:EAr units in solution and their formal oxidation state of 1+.<sup>45</sup> As a result, the chemistry of the heavy group 13 dimetallenes is strongly influenced by Lewis base character, where the lone pair at the triel (group 13) element can donate electron density to either electron-deficient main-group or transition-metal centers.<sup>45–47</sup> Moreover, the ability of group 13 elements to attain a 3+ oxidation state enables the low-

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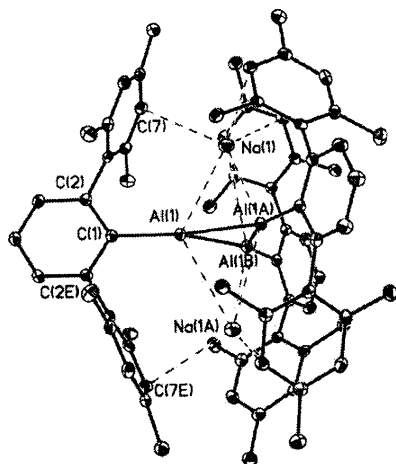
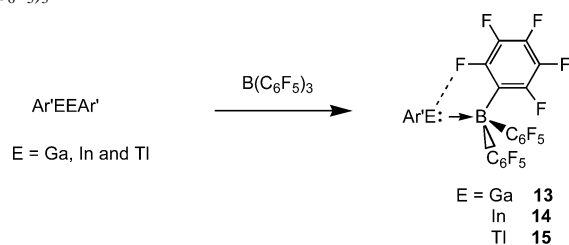


Figure 7. "Cyclotrialluminene" **12**.<sup>39</sup>

Scheme 4. Adduct Formation of :EAR' Fragments with  $B(C_6F_5)_3$ <sup>24,30,31</sup>



valent dimetallenes,  $Ar'EEAr'$ , to participate in a variety of redox processes. As we will see, the construction of new group 13–element multiple bonds can be achieved by taking advantage of the redox flexibility of the :EAR moiety. In addition, because of the increased reluctance of the heaviest member of the group 13 series, thallium, to undergo oxidation (the inert-pair effect), the chemistry of  $Ar'TlIAr'$  often differs considerably from that of its lighter counterparts.

In order to probe the donor ability of the monomeric :EAR' species in solution, the reactivity of the dimetallenes with various Lewis acids was explored. Smooth adduct formation with either the fluorinated borane,  $B(C_6F_5)_3$ , or metal carbonyls,  $Fe(CO)_5$  and  $THF \cdot W(CO)_5$  (Scheme 4), was observed.<sup>24,30,31</sup> These reactions were also accompanied by the bleaching of the initially intensely green ( $Ar'GaGaAr'$ ) or red ( $Ar'InInAr'$  and  $Ar'TlIAr'$ ) solutions to weakly colored reaction products. This drastic color change can be rationalized by noting that the intense colors of the dimetallenes in solution stem from an allowed  $n-p$  transition involving the lone pair and the adjacent vacant  $p$  orbital at the triel center in the monomeric :EAR' fragment. Therefore, upon complexation of the active lone pair in the :EAR' unit, the  $n-p$  transition no longer occurs.

A common feature of compounds **13–15** is the presence of strong dative  $E-B$  bonds and significantly pyramidalized boron centers (Figure 8). Similar structural features have been observed in pioneering work by Cowley and co-workers, who prepared a series of main-group adducts of the general form  $Cp^*E \cdot E'(C_6F_5)_3$  ( $E/E' = B, Al, \text{ and } Ga$ ;  $Cp^* = \eta^5-C_5Me_5$ ).<sup>46</sup> These studies contained rare examples of lighter triel elements, such as boron, in their less-common  $1+$  oxidation state and showed that group 13 elements could act as both electron donors and acceptors within the very same molecule [e.g., in  $Cp^*B \rightarrow B(C_6F_5)_3$ ]. Notably, the Lewis-basic

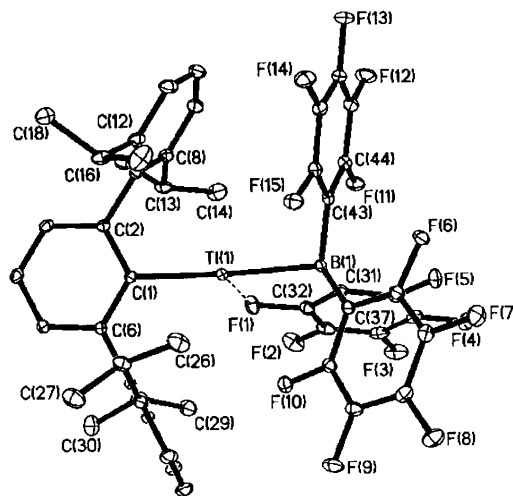
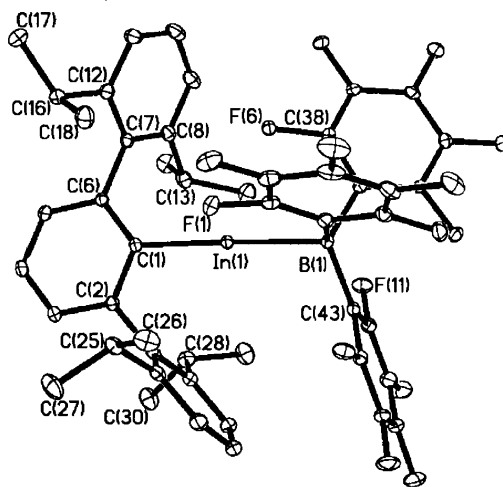
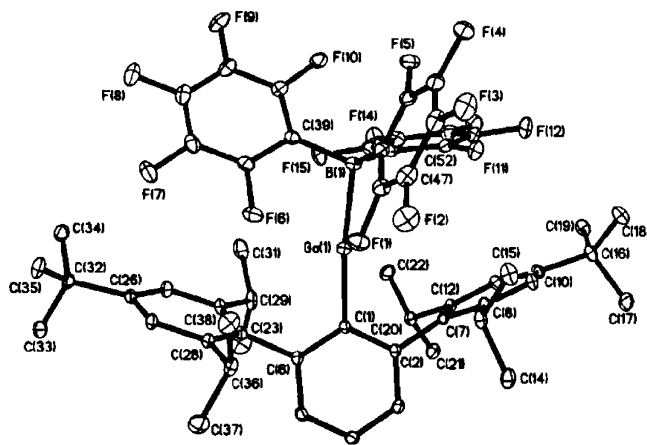
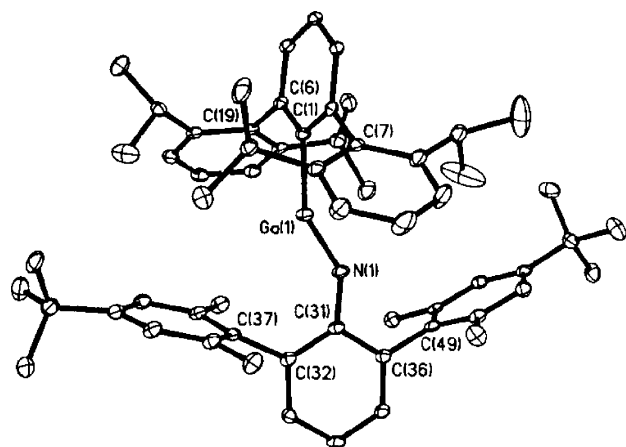


Figure 8. Various aryltriellborane adducts:  $Ar'E \cdot B(C_6F_5)_3$  ( $E = Ga-Tl$ ; **13–15**).<sup>24,30,31</sup>

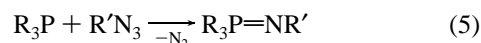
character of the donor centers ( $D_n$ ) in various borane adducts  $D_n \cdot B(C_6F_5)_3$  can be compared by examining the degree of deviation of the borane unit from planarity; the more the aryl rings are bent away from the  $D_n-B$  bonding axis, the stronger the donor. On the basis of this simplified model, the following donor series can be constructed for various :ER fragments (in order of increasing donating ability):  $Cp^*Ga < Cp^*Al < Ar'Ga$  (**2**)  $\approx$   $Ar'Ga$  (**4**)  $< :Ga\{N(Dipp)C(Me)\}_2CH$  (**16**). The increased donor strength of **16** relative to other gallium(I) derivatives is possibly due



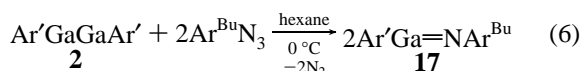
**Figure 9.** Structure of the gallium imide **17**.<sup>49</sup> Ga–N = 1.701(3) Å; Ga–N–C<sub>ortho</sub> = 141.7(3)°; N–Ga–C<sub>ortho</sub> = 148.2(2)°.

to the increased negative charge at gallium induced by the  $\beta$ -diketiminato ligand.<sup>47</sup>

An important reaction in phosphorus chemistry is the oxidation of phosphines by azides, i.e., the Staudinger reaction (eq 5).<sup>48</sup> By direct analogy, we were interested in seeing whether a parallel synthetic route could be used to construct E=N multiple bonds from :EAr' substrates; at the time, such multiple bonds were unknown for E = Al–Tl.



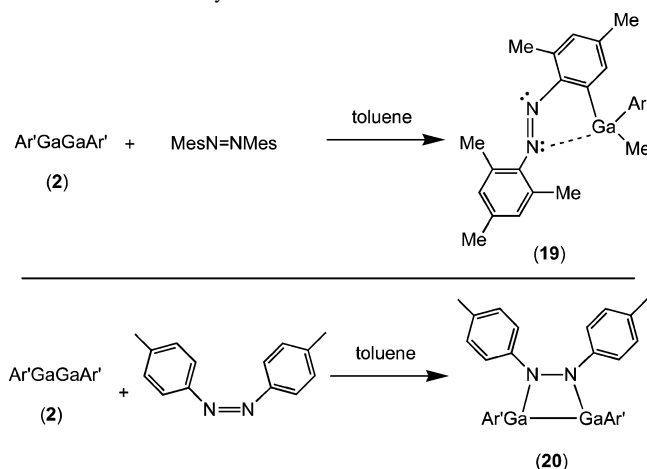
Treatment of **2** with the hindered terphenyl azide Ar<sup>Bu</sup>N<sub>3</sub> [Ar<sup>Bu</sup> = –C<sub>6</sub>H<sub>3</sub>–2,6–(C<sub>6</sub>H<sub>2</sub>–2,6–Me<sub>2</sub>–4'-Bu)<sub>2</sub>] afforded an immediate color change from green to red along with the evolution of dinitrogen (eq 6).



X-ray crystallography revealed the formation of the gallium imide Ar'Ga=NAr<sup>Bu</sup> (**17**) with a short Ga–N bond of 1.701–(3) Å, along with a bent C–Ga–N angle of 148.2(2)° (Figure 9).<sup>49</sup> The short Ga–N distance and the planar C<sub>ortho</sub>–Ga–N–C<sub>ortho</sub> array indicated the presence of a Ga=N multiple bond. The structure of **17** differs greatly from those of iminoboranes, RBNR, which feature linear geometries at boron and nitrogen and extremely short B–N lengths, consistent with B–N triple bonding.<sup>50</sup> Similarly, the indium imide Ar'InNAr<sup>Bu</sup> (**18**) could be prepared from Ar'InInAr' and Ar<sup>Bu</sup>N<sub>3</sub> and possessed a short In–N bond [1.928(3) Å] and bent geometry at indium [142.2(1)°]. The thallium derivative Ar'TlInAr' did not display any reactivity with azides, which is consistent with the increased reluctance of thallium(I) centers to undergo oxidation.

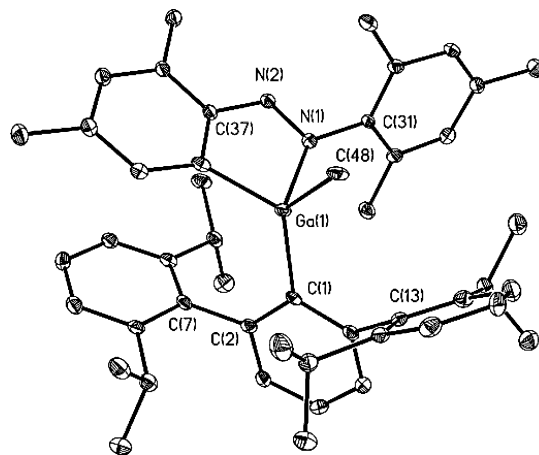
Encouraged by the clean reactivity of dimetallenes with azides, the investigation was expanded to include the reactivity of the “digallene” Ar'GaGaAr' with electron-rich diazenes RN=NR and diazoalkenes R<sub>2</sub>CN<sub>2</sub>. It was found that the reaction path observed depended greatly upon the nature of the diazene used. For example, when diaryldiazenes

**Scheme 5.** Chemistry of Ar'GaGaAr' with Diazenes<sup>25</sup>

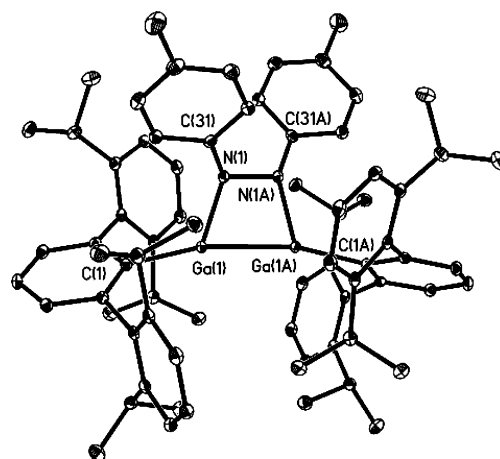


featuring ortho substituents were reacted with **2**, C–C activation transpired to yield the insertion products such as **19** (Scheme 5 and Figure 10). However, when the para-substituted aryldiazene (*p*-tolyl)N=N(*p*-tolyl) was combined with **2**, the trapezoidal 1,2-Ga<sub>2</sub>N<sub>2</sub> heterocycle **20** was obtained as a blue-green solid (Figure 11).<sup>25</sup>

With the objective of preparing a gallaalkene (Ar'Ga=CPh<sub>2</sub>), a solution of **2** was treated with diphenyldiazo-methane, Ph<sub>2</sub>CN<sub>2</sub>. Instead of eliminating dinitrogen to form a species with a Ga–C multiple bond, we observed the



**Figure 10.** Structure of the diazene insertion product (**19**).<sup>25</sup>



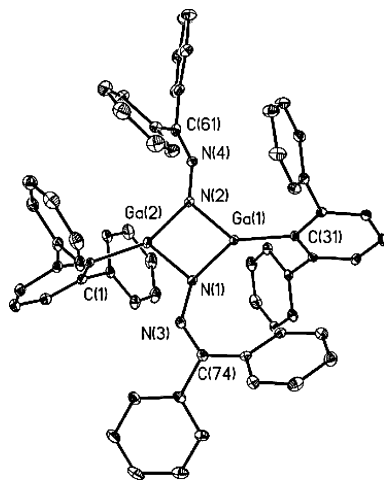
**Figure 11.** Heterocyclic diazene addition product (**20**).<sup>25</sup>

(48) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635.

(49) Wright, R. J.; Phillips, A. D.; Allen, T. L.; Fink, W. H.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 1694.

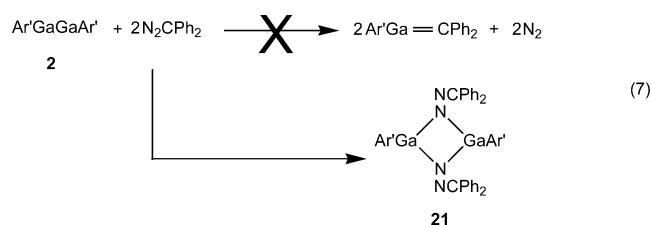
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**Figure 12.** Molecular structure of **21**. The flanking 'Pr groups have been omitted for clarity.<sup>25</sup>

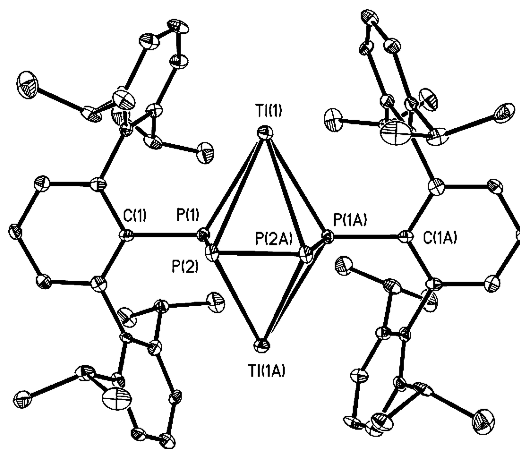
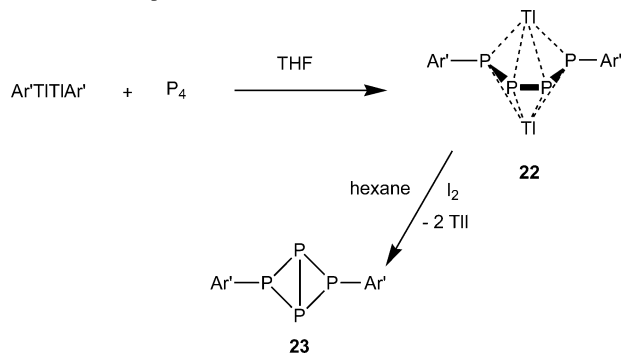
formation of the heterocyclic product **21** featuring a 1,3-Ga<sub>2</sub>N<sub>2</sub> core and intact Ph<sub>2</sub>CN<sub>2</sub> units (eq 7 and Figure 12).<sup>25</sup>



The N–N distances in **21** [1.371(4)–1.400(4) Å] were lengthened by ca. 0.2 Å relative to the parent diazoalkane, while the Ga–N distances were in the range 1.862(3)–1.895(3) Å and are comparable to the Ga–N single bonds of 1.850(2) and 1.870(2) Å within the dimer (Cp\*GaNXyl)<sub>2</sub>.<sup>51</sup> Attempts to extend this chemistry to include the heavier indium and thallium dimetallenes Ar'EEAr' did not yield products analogous to **21**. Instead, dinitrogen evolution was observed, and the formation of Ph<sub>2</sub>C=N–N=CPh<sub>2</sub>, a common decomposition product of diphenyldiazomethane, was isolated.<sup>25</sup>

Currently, the ability of the group 13 dimetallenes to activate small molecules such as H<sub>2</sub>, O<sub>2</sub>, S<sub>8</sub>, and P<sub>4</sub> is being explored. Although much of this work is still at an early stage, we highlight one system that illustrates the possible utility of this strategy. It was recently found that the ‘‘dithalene’’ Ar'TlTlAr' (**7**) reacts smoothly with white phosphorus (P<sub>4</sub>) to give the burgundy colored product Tl<sub>2</sub>[P<sub>4</sub>Ar'<sub>2</sub>] (**22**; Scheme 6).<sup>52</sup> As seen in Figure 13, compound **22** features a

**Scheme 6.** Preparation and Oxidation of **22**<sup>52</sup>



**Figure 13.** Structure of **22**.<sup>52</sup>

formally dianionic and planar [P<sub>4</sub>Ar'<sub>2</sub>]<sup>2-</sup> core with nearly equal P–P bond lengths of 2.136(4) and 2.143(6) Å. These distances are shortened compared to typical P–P single bonds (ca. 2.21 Å)<sup>53</sup> and are longer than the P=P distances found in diphosphenes (1.98–2.05 Å);<sup>54</sup> therefore, it is likely that some P–P multiple-bond character exists within the P<sub>4</sub>Ar'<sub>2</sub> core. Furthermore, the P–P bond order within **22** can be assigned a value of 1.33 if one assumes that this species possesses frontier orbitals similar to those of the dianion of 1,3-butadiene.<sup>52</sup> It is likely that the presence of added Tl–arene interactions helps to preserve the structural integrity of the P<sub>4</sub>Ar'<sub>2</sub> core and thus stabilizes P–P multiple bonding. Treatment of **22** with diiodine led to the rapid expulsion of TlI and the formation of the neutral diaryltetraphosphabicyclobutane Ar'<sub>2</sub>P<sub>4</sub> (**23**). The energy differences between the trans,trans and cis,trans forms of the parent tetraphosphabicyclobutane H<sub>2</sub>P<sub>4</sub> have been calculated to be only 1.2 kcal/mol,<sup>55</sup> and as such, we were able to crystallize both forms of **23** by changing the solvent of crystallization.

### Group 14 Dimetallynes ArMMAr (M = Ge–Pb)

An important focus of the chemistry of the heavier group 14 elements (tetrels: Si–Pb) has been the pursuit of molecules that are structurally related to their lighter carbon analogues.<sup>56</sup> As advances in this field were made, striking differences between the bonding in heavy group 14 and their carbon analogues emerged. These disparities largely stem from a decrease in s/p hybridization as the tetrel group is descended. As the group 14 element becomes heavier, the valence s electrons adopt increasing lone-pair character, which causes significant changes in the bonding and molecular structure. For example, alkenes adopt rigorously

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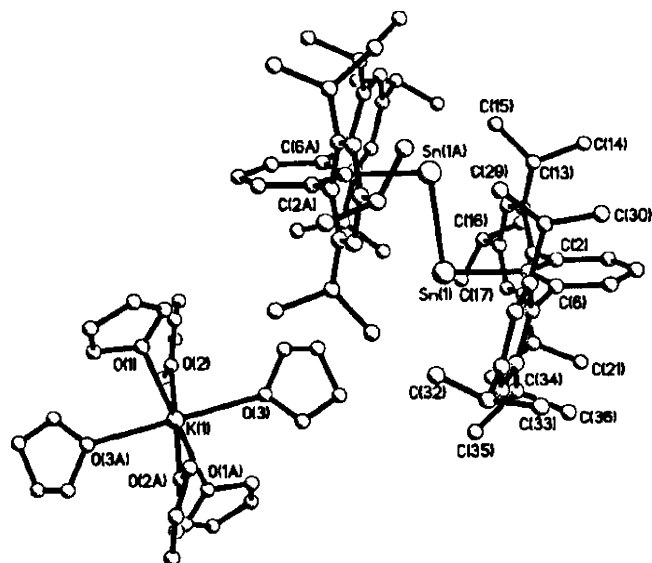


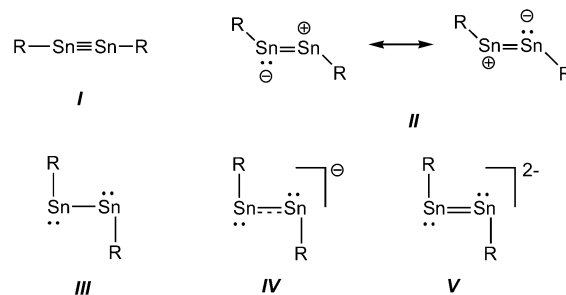
Figure 14. Monoreduced “distannyne” **24**.<sup>58</sup>

planar  $D_{2h}$  geometries; however, as the group is descended, the heavier alkene analogues of silicon, germanium, and lead ( $R_2MMR_2$ ) have increasingly trans pyramidal ( $C_{2h}$ ) geometries and concomitant lengthening of the formal  $M=M$  bond. In the case of tin and lead (and in many instances for germanium), the  $M-M$  bonding becomes so weak that these species dissociate readily in a hydrocarbon solution to yield monomeric species  $R_2M\cdot$ , which are formally related to singlet carbenes  $R_2C\cdot$ .<sup>56</sup>

Despite the ubiquitous nature of alkynes RCCR, the preparation of stable heavier alkyne congeners RMMR ( $M = Si-Pb$ ) was not realized until recently. A major reason for their late preparation is linked to the requirement of a very large R group to provide steric protection of the  $M-M$  bond because now each tetrel element can only support a single substituent.<sup>57</sup>

Early attempts to prepare species of the general form  $ArMMAr$  ( $M = Ge, Sn, \text{ and } Pb$ ) focused on the reduction of organotetrel(II) halides,  $ArMX$ , with various alkali metals. Treatment of the hindered chlorostannane  $Ar^*SnCl$  with 1 equiv of alkali metal exclusively led to the crystallization of the monoreduced distannyne salts  $K(THF)_6[Ar^*SnSnAr^*]$  (**24**) and  $Na(THF)_3[Ar^*SnSnAr^*]$  (**25**) under the conditions employed.<sup>58</sup> Stirring  $Ar^*SnCl$  with an excess of potassium for extended periods afforded the doubly reduced complex  $K_2[Ar^*SnSnAr^*]$  (**26**).<sup>59</sup> The singly reduced species **24** gave an EPR resonance that exhibited coupling to both  $^{117/119}Sn$  isotopes with a small hyperfine splitting of 8–9 G, suggesting the localization of the unpaired electron in a  $\pi$  orbital. The Sn–Sn bond lengths in the monoanions were ca. 2.78–2.81 Å and are similar to the Sn–Sn separation in elemental tin (2.80 Å).<sup>60</sup> In addition, narrow C–Sn–Sn angles of 93.6–98.0° were found (Figure 14), which suggested that the bonding was best represented by form **IV** (the singly reduced

Scheme 7. Possible Bonding Motifs for Neutral and Reduced  $RSnSnR$  Compounds



form of the strongly bent isomer **III**; Scheme 7). The Sn–Sn bond order in **IV** is formally 1.5, and therefore the Sn–Sn bond in **24** is expected to be shorter than that in elemental tin. However, the similarity in bond lengths can be explained by noting that the Sn–Sn  $\sigma$  bond in **24** (and in form **IV**) results mainly from the overlap of p orbitals, and because of their expanded radii, the bond is lengthened.

The doubly reduced  $[Ar^*SnSnAr^*]^{2-}$  unit in **26** exhibited only a slight shortening of the Sn–Sn bond [2.7763(9) Å; Figure 15] and a widening of the Sn–Sn–C angle to 107.50-

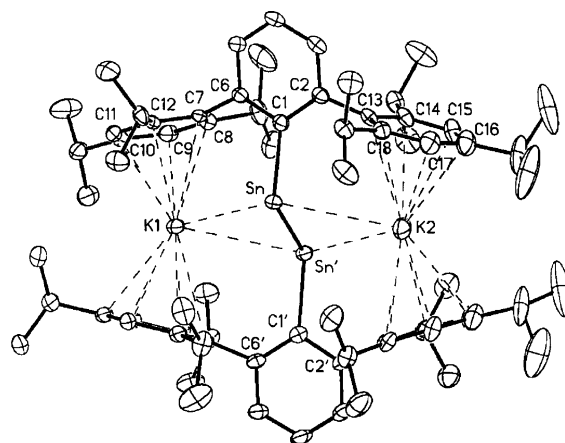
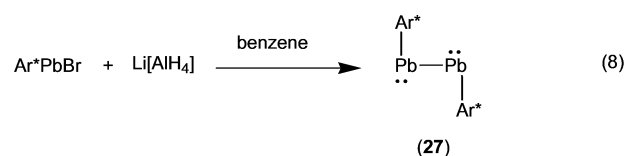


Figure 15. Doubly reduced “distannyne” **26**.<sup>59</sup>

(14)° when compared to their monoreduced analogues **24** and **25**. The marginal shortening of the Sn–Sn bond in the dianions (form **V**) is likely a consequence of increased Coulombic repulsions within these species, which contribute to lengthening of the Sn–Sn distance.

While work was underway to isolate the “digermene” and “distannyne” derivatives,  $ArMMAr$  ( $M = Ge$  and  $Sn$ ) by altering the ligand type and reduction conditions, the heaviest member of this series  $Ar^*PbPbAr^*$  (**27**) was isolated by a different (and unexpected) route.<sup>61</sup> In an attempt to prepare the divalent lead hydride  $Ar^*PbH$ , we treated  $Ar^*Pb(Br)$  with  $Li[AlH_4]$  in benzene. Amber-green dichroic crystals were isolated from this reaction and identified by X-ray crystallography as the diplumbyne  $Ar^*PbPbAr^*$  (10% yield according to eq 8).

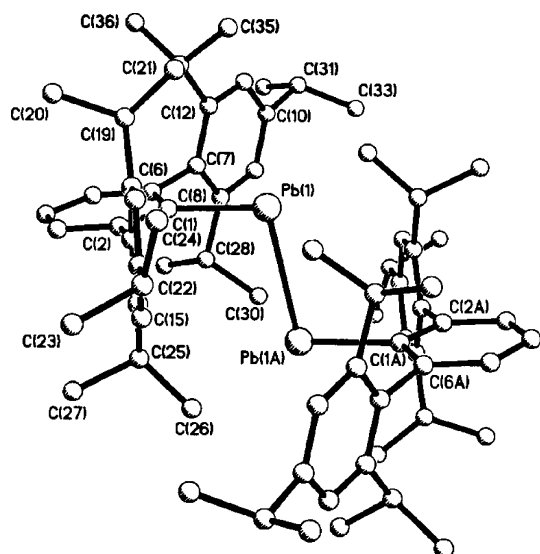


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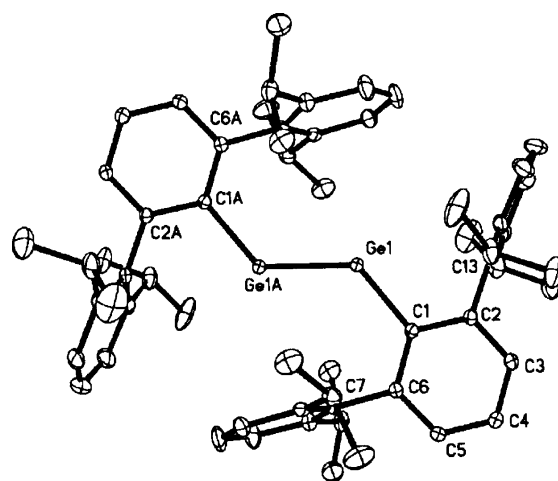
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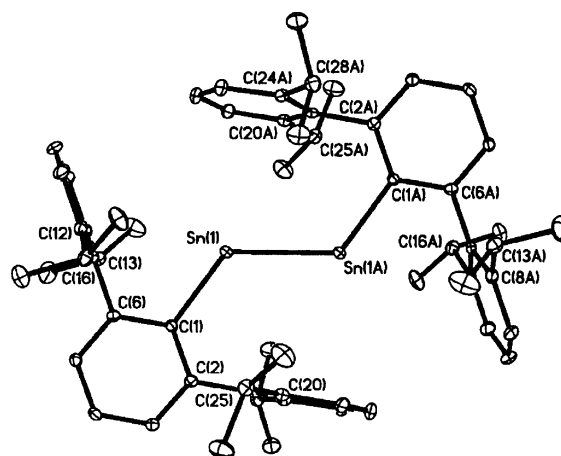
**Figure 16.** Structural representation of **27**.<sup>61</sup> Pb–Pb = 3.1881(1) Å; Pb–Pb–C<sub>ipso</sub> = 94.26(4)°.

This reaction pathway differs from the case of tin, where the dimeric tin(II) hydride [Ar\*Sn( $\mu$ -H)]<sub>2</sub> was obtained.<sup>62</sup> It is possible that the formation of Ar\*PbPbAr\* proceeds via a lead(II) hydride intermediate, Ar\*PbH, which spontaneously eliminates hydrogen to give the lead(I) dimer. It was immediately evident that the bonding in Ar\*PbPbAr\* contrasted greatly with the bonding arrangement in alkynes. For example, a planar trans-bent C–Pb–Pb–C core was seen in **27** with a highly bent Pb–Pb–C angle of 94.26(4)° (Figure 16). Furthermore, the length of the Pb–Pb bond was 3.1881(1) Å and was even longer than the Pb–Pb bond distances found in diplumbanes R<sub>3</sub>Pb–PbR<sub>3</sub> (2.85–2.95 Å).<sup>63</sup> As a result, the bonding in **27** is best described with the diplumbylene canonical form **III** (shown above), with a formal Pb–Pb single bond accompanied by an active lone pair at each lead center with empty p orbitals orthogonal to the C–Pb–Pb–C atom plane. Calculations by Frenking and co-workers of various isomers of HPbPbH showed that a hydrogen substituted structure similar to **27** is not the most stable conformation. Instead, structures with Pb–H–Pb bridges are appreciably more stable [e.g., Pb( $\mu$ -H)<sub>2</sub>Pb].<sup>64</sup> Therefore, the replacement of hydrogen by bulky terphenyl ligands makes a bridging arrangement less favorable and stabilizes the strongly trans-bent conformation in **27**. Computational work on the PhPbPbPh model species showed that a multiple-bonded form featuring a short Pb–Pb distance (2.787 Å) and a wide Pb–Pb–C angle (125.6°) was slightly more stable than the strongly bent single-bonded form.<sup>64</sup>

Soon after the preparation of Ar\*PbPbAr\*, we were able to synthesize and crystallographically characterize the related germanium<sup>65</sup> and tin<sup>66</sup> analogues by using the newly devel-



**Figure 17.** Structure of the trans-bent dimer **28**.<sup>65</sup> Ge–Ge = 2.2850(6) Å; Ge–Ge–C<sub>ipso</sub> = 128.67(2)°.



**Figure 18.** “Distannyne” **29**.<sup>66</sup> Sn–Sn = 2.6675(4) Å; Sn–Sn–C<sub>ipso</sub> = 125.24(7)°.

oped ligand –C<sub>6</sub>H<sub>3</sub>-2,6-Dipp<sub>2</sub>, Ar'. Despite the similarity of Ar' to the previous ligand system Ar\* (related by removal of a para 'Pr group from each flanking aryl ring), use of the Ar' ligand in many instances confers greatly improved crystallinity in comparison to related terphenyl counterparts. Accordingly, treatment of Ar'GeCl and Ar'SnCl with a potassium metal in benzene afforded Ar'GeGeAr' (**28**) and Ar'SnSnAr' (**29**) in moderate yields as deep-orange-red and green solids, respectively.

Digermyne **28** adopted a centrosymmetric structure with a planar trans-bent C<sub>ipso</sub>–Ge–Ge–C<sub>ipso</sub> core with a short Ge–Ge bond of 2.2850(6) Å and a bending angle of 128.67–(2)° at each germanium center (Figure 17). The Ge–Ge distance in **28** was considerably shorter than a typical Ge–Ge single bond (ca. 2.44 Å), consistent with a substantial degree of multiple-bonding character. The distannyne derivative **29** (Figure 18) was shown to possess a structure similar to that of its germanium congener with a short Sn–Sn bond [2.6675(4) Å] and a more trans-bent geometry [C<sub>ipso</sub>–Sn–Sn angle: 125.24(7)°]. The Sn–Sn distance in **29** was significantly (0.1 Å) shorter than the values observed in the reduced analogues **24–26** and shorter than typical Sn–Sn single bonds (ca. 2.81 Å). The bent geometries of both **28** and **29** differ considerably from the linear bonding arrangement found in acetylenes and imply that a reduction in the multiple-bond character (and bond order) occurs

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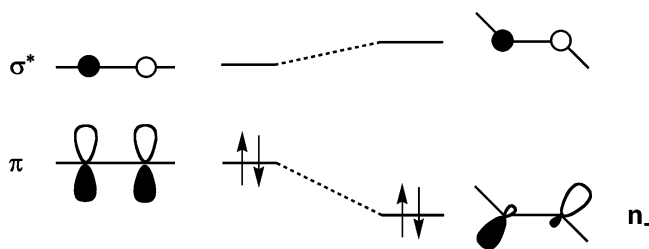
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**Scheme 8.** MO Interaction of the In-Plane  $\pi$  Orbital and the  $\sigma^*$  Orbital in  $C_{2h}$  Symmetry To Generate an  $n_-$  Orbital with Nonbonding Character



upon bending of the C–M–M–C core to give a trans-bent arrangement.<sup>56</sup>

One bonding model that has been employed to explain the preferred trans-bent geometries ( $C_{2h}$ ) within the heavier alkyne analogues involves a second-order Jahn–Teller mixing of M–M  $\sigma^*$  and  $\pi$  levels (and to a lesser degree M–M  $\pi^*$  and  $\sigma$  orbitals). This form of orbital mixing leads to the buildup of lone-pair character at each tetrel (M) center, as is illustrated by the formation of an occupied nonbonding ( $n_-$ ) orbital (Scheme 8) and an unoccupied ( $n_+$ ) orbital. Bonding electron density is effectively shuttled away from a  $\pi$  orbital into a nonbonding-type orbital, resulting in a decrease in the M–M bond order. As the main-group element becomes heavier, the energy levels between the M–M  $\sigma^*$  and  $\pi$  orbitals become closer and orbital mixing becomes more prominent, leading to increasingly large bending angles.<sup>56</sup> As we will see, the bonding situation within the heavy group 14 dimetallynes might even be more complex than originally believed, with the occupation of low-lying excited states (i.e., diradical character) playing a potentially important role.

It would not be appropriate to leave this section on group 14 dimetallayne analogues without mentioning some further key results from the recent literature. As alluded to in a previous section, the final member of the dimetallayne series, a disilyne  $RSiSiR$ , was structurally characterized in 2004 by the group of Sekiguchi.<sup>40</sup> With the aid of the bulky silyl ligand  $-\text{Si}[\text{CH}(\text{SiMe}_3)_2]_2^t\text{Pr}$ , the thermally stable disilyne  $R'SiSiR'$  (**30**;  $R' = \text{Si}[\text{CH}(\text{SiMe}_3)_2]_2^t\text{Pr}$ ) was prepared by the reduction of the disilane precursor  $R'_2(\text{Br})\text{Si}-\text{Si}(\text{Br})R'_2$  with  $\text{KC}_8$ . The dark-green disilyne **30** exhibited a Si–Si distance of 2.0622(9) Å and a trans-bent geometry with a Si–Si–Si bending angle of 137.44(4)°. The bending angle at silicon was ca. 9° wider than the corresponding angles within the heavier germanium and tin congeners described above and closely match the geometry calculated for the related parent species  $\{[(\text{tBu}_3\text{Si})_2\text{Me}]_2\text{SiSi}[\text{Me}(\text{Si}^t\text{Bu}_3)_2]\}$ .<sup>67</sup> In addition, compound **30** yielded a highly deshielded  $^{29}\text{Si}$  NMR resonance for the silyne silicon center (89.9 ppm). A similar  $^{29}\text{Si}$  NMR resonance was reported earlier by Wiberg and co-workers for the related disilyne featuring the silyl ligand  $-\text{Si}[\text{CH}(\text{SiMe}_3)_2]_2\text{Me}$  (91.5 ppm); however, they have been unable to obtain an X-ray crystal structure of this species to date.<sup>68</sup> More recently, Sekiguchi and co-workers have reported the successful preparation and structural characterization of the singly reduced disilyne radical anion  $[\text{K}(\text{DME})_4][R'SiSiR']$ .<sup>69</sup> This species was obtained via the reduction of **30** with 1 equiv of  $\text{KC}_8$  and contained an

elongated Si–Si distance of 2.1728(14) Å and a more bent structure [internal Si–Si–Si angles = 113.97(6) and 112.84(6)°] consistent with the addition of an electron into a  $\pi^*$  orbital. Although the structural and spectroscopic data for the disilyne support the existence of an Si–Si bond order greater than ca. 2.5, comprehensive theoretical studies by Andreoni and co-workers<sup>70</sup> have indicated a large weakening of the bond (and a lowering of the bond order) upon trans-bending of the structure (see also reference 18f). These views have been disputed however.<sup>71</sup>

Recently, the group of Tokitoh have succeeded in preparing the digermynes  $\text{BbtGeGeBbt}$  using a silyl-rich aryl ligand ( $\text{Bbt} = \text{C}_6\text{H}_2-2,6-\{\text{CH}(\text{SiMe}_3)_2\}_2-4-\text{C}(\text{SiMe}_3)_3$ ).<sup>72</sup> This species crystallized with two molecules in the asymmetric unit with an average Ge–Ge bond length of 2.22 Å and a bent Ge–Ge–C angle of 131° (avg). Compared to the digermynes **28**, Tokitoh's compound displays shorter Ge–Ge bonds and wider average angles at germanium [for **28**: Ge–Ge = 2.2850(6) Å; Ge–Ge–C = 128.27(8)°]. The stronger bonding in  $\text{BbtGeGeBbt}$  was rationalized on the basis of a lower  $\Delta_{\text{D-Q}}$  gap for the  $\text{GeBbt}$  fragment (compared to  $\text{GeAr}'$ ), which leads to a stronger Ge–Ge interaction.<sup>64c,72</sup> The preparation of new “digermynes” derivatives with differing steric and electronic properties will be invaluable in shedding more light on the nature of the bonding interactions within these species.

### Chemistry and Divergent Reactivity of the Group 14 Dimetallynes $\text{Ar}'\text{MMAr}'$ (R = Ge and Sn)

Given the recent preparation of the entire series of heavy alkyne congeners  $\text{RMMR}$  (M = Si–Pb),<sup>40,61,65,66,68,72</sup> there was a strong motivation to explore the reactivity of these species with the ultimate goal of better understanding the bonding within these unique molecules. In this regard, the reactivity of the digermynes  $\text{Ar}'\text{GeGeAr}'$  (**28**) and distannynes  $\text{Ar}'\text{SnSnAr}'$  (**29**) toward a variety of unsaturated molecules was explored, and some key reactions are summarized in Scheme 9.<sup>73</sup>

We began our investigations by examining the reactions of **28** and **29** with diazobenzene,  $\text{PhN}=\text{NPh}$ . In both instances, the M–N–N–M cores had elongated N–N distances of 1.453(5) Å (**31**) and 1.430(3) Å (avg, **32**), consistent with N–N single bonds. In addition, the Ge–N bond length in **31** was 1.879(4) Å and is within the range found in various germanium(II) amides (ca. 1.83–1.89 Å). By comparison, the average Sn–N bond length in **32** was 2.107(2) Å and matched those observed within the tin(II) amide  $\text{Sn}\{\text{N}(\text{SiMe}_3)_2\}_2$  [2.09(1) Å].<sup>74</sup> These data indicated that **31** and **32** can be regarded as formal derivatives of hydrazine where each N atom bears a phenyl group as well as  $\text{Ar}'\text{Ge}$  and  $\text{Ar}'\text{Sn}$  substituents. Furthermore, neither **31** nor **32** reacted further with added diazobenzene, thus

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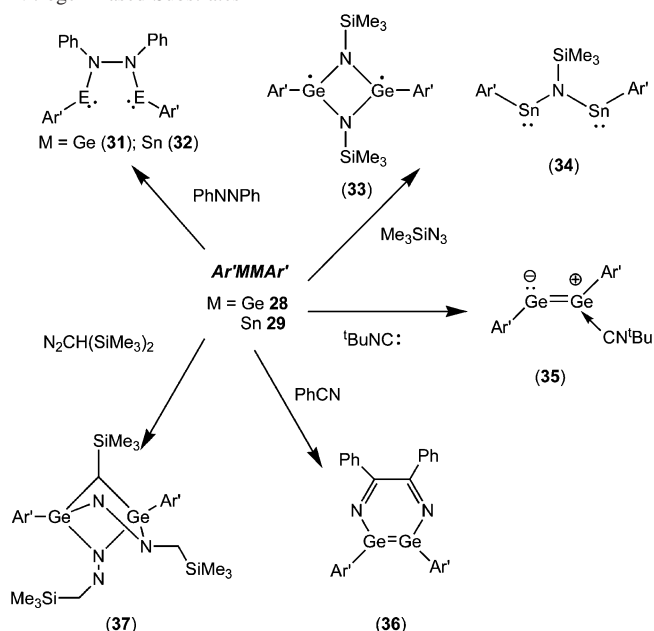
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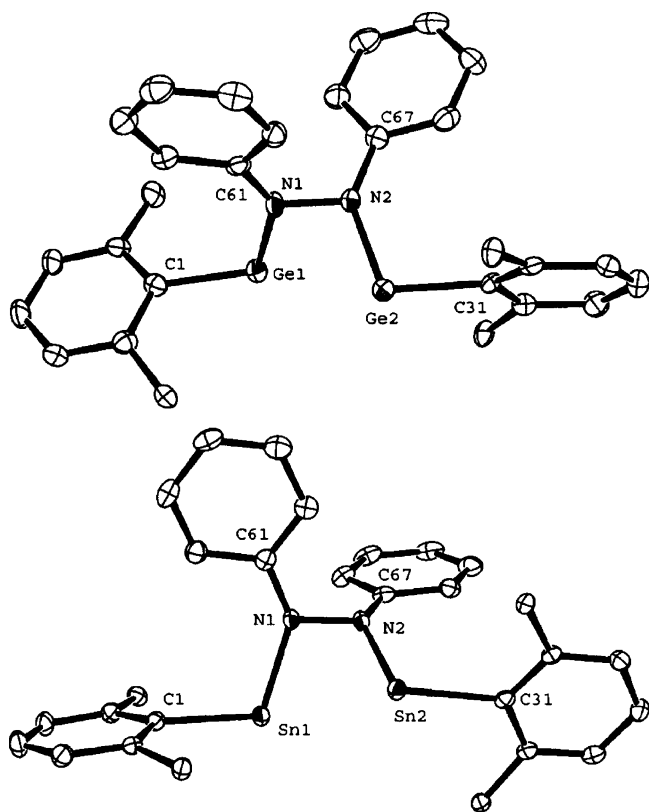
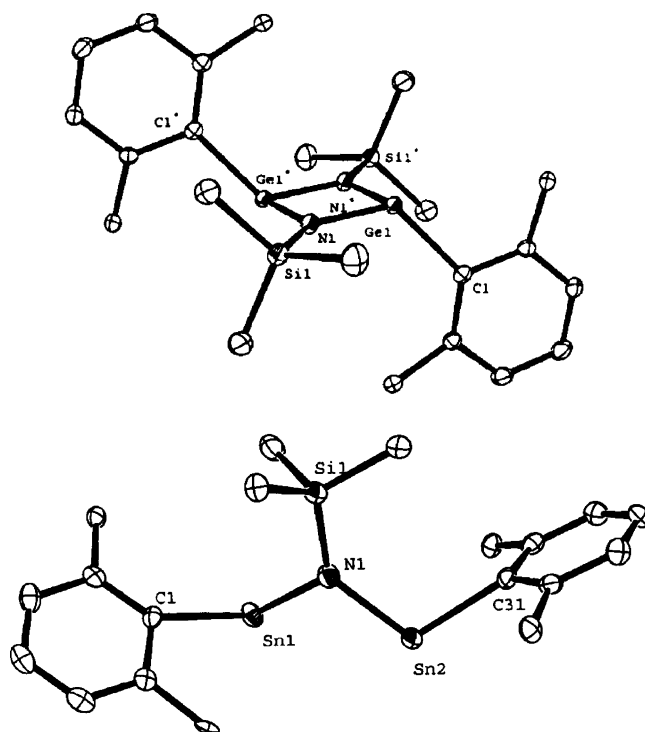
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**Scheme 9.** Reaction Chemistry of **28** and **29** with Unsaturated Nitrogen-Based Substrates<sup>73</sup>

supporting the lack of a reactive M–M bond in these compounds (Figure 19).

When trimethylsilyl azide was added to **28** and **29**, the violet singlet diradicaloid species  $\text{Ar}'\text{Ge}\{\mu\text{-N}(\text{SiMe}_3)\}_2\text{GeAr}'$  (**33**) and the monoamide-linked distannane  $\text{Ar}'\text{Sn}\{\mu\text{-N}(\text{SiMe}_3)\}_2\text{SnAr}'$  (**34**) were obtained.<sup>75</sup> Compound **33** consists of a planar  $\text{Ge}_2\text{N}_2$  ring with planar-coordinated N atoms and significantly pyramidalized germanium centers [ $\Sigma^\circ\text{Ge} = 322.10(7)^\circ$ ]. Consistent with the assignment of a diradicaloid

**Figure 19.** Structure of the hydrazido derivatives **31** and **32**.<sup>75</sup>**Figure 20.** Singlet diradicaloid **33** (upper) and the tin(II) amide **34** (lower).<sup>75</sup>

structure, the Ge–N distances [1.863(2) and 1.874(2) Å] are in the single-bond range, while the Ge–Ge separation (2.755 Å) is about 0.3 Å longer than a normal Ge–Ge single bond (ca. 2.44 Å).<sup>76</sup> Moreover, compound **33** was EPR-silent in the range of 77–300 K and gave normal  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, indicative of a singlet ground state.<sup>75</sup> Similar behavior was noted by Lappert and co-workers in their tin amide diradicaloid,  $\text{ClSn}\{\mu\text{-N}(\text{SiMe}_3)\}_2\text{SnCl}$ , which was synthesized by a different route.<sup>77</sup> Recent computational results have indicated a diradical character as high as 42.2% in the model species  $[2,6\text{-Me}_2\text{C}_6\text{H}_2\text{Ge}(\mu\text{-NSiH}_3)_2\text{GeC}_6\text{H}_3\text{-2,6-Me}_2]$ .<sup>78</sup> The tin species **34** (Figure 20) exhibited similar Sn–N distances [2.055(6) and 2.111(6) Å] as in **32**, along with a trans,trans conformation of the aryl ligands. Of note, the addition of excess  $\text{Me}_3\text{SiN}_3$  to **29** did not yield the tin diradicaloid derivative of **33**.<sup>75</sup>

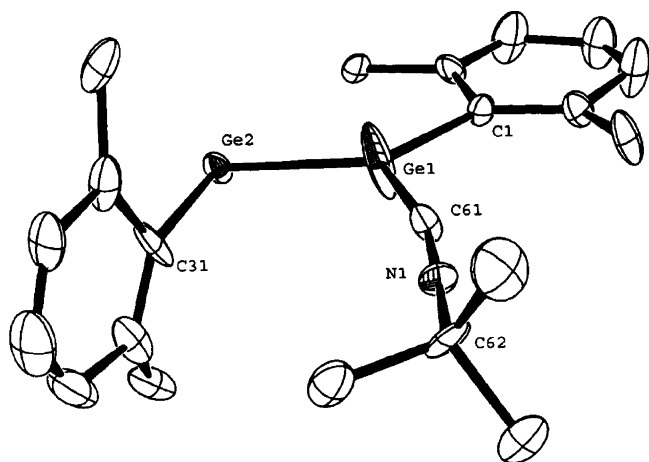
The “digermene” **28** reacted smoothly with  $^t\text{BuNC}$ ,  $\text{PhCN}$ , and  $\text{N}_2\text{CH}(\text{SiMe}_3)$  to yield respectively the 1:1 isonitrile adduct **35**, the  $\text{Ge}_2\text{N}_2\text{C}_2$  heterocycle **36**, and the complicated product **37** (Scheme 9).<sup>72</sup> However, attempts to extend this chemistry to include the tin analogue  $\text{Ar}'\text{SnSnAr}'$  failed because no reactivity was observed with either  $^t\text{BuNC}$  or  $\text{PhCN}$ , and in the case of  $\text{N}_2\text{CH}(\text{SiMe}_3)$ , no clean products could be obtained. The formation of the isonitrile adduct **35** was particularly interesting because it represented an example of a heavier alkyne derivative acting as a Lewis acid. The Ge–Ge bond in the monoadduct **35** was 2.3432(9) Å and ca. 0.06 Å longer than that in the digermene precursor [2.2850(6) Å].<sup>73</sup> However, the Ge–Ge distance in **33** was

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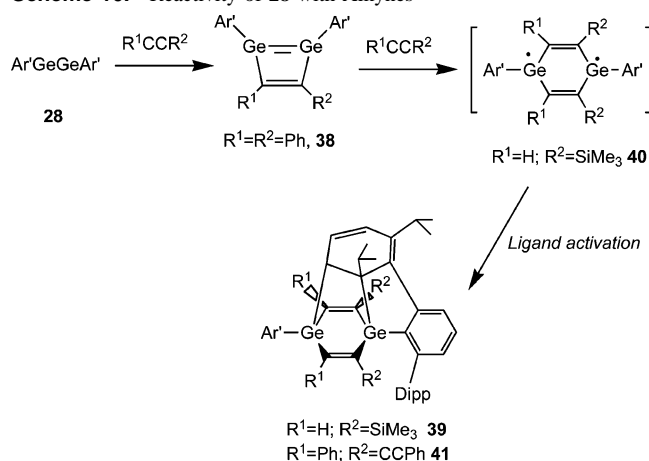
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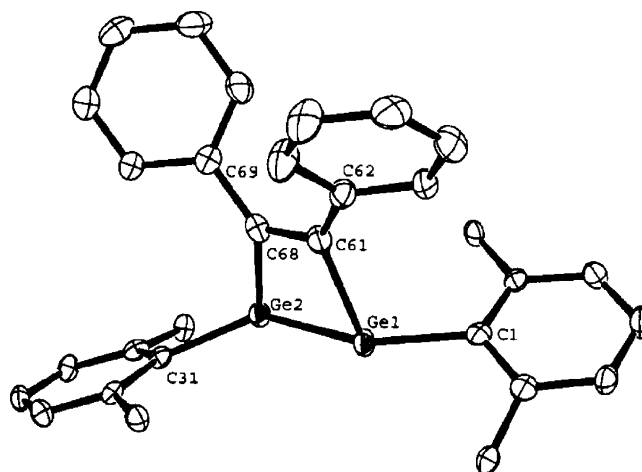
**Figure 21.** Structure of the isonitrile adduct (**35**).<sup>73</sup>

**Scheme 10.** Reactivity of **28** with Alkynes<sup>80</sup>

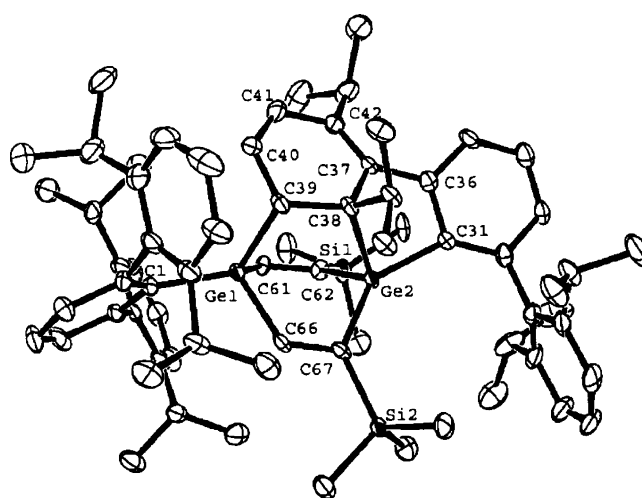


considerably shorter than a typical Ge–Ge single bond (ca. 2.44 Å),<sup>79</sup> thus indicating the retention of significant multiple-bond character (Figure 21). As mentioned previously, the bonding in the digermynes can be represented with the resonating canonical forms **II** (Scheme 7). Therefore, one can view the bonding in **35** as being the Lewis-base-stabilized resonance hybrid with a partial cationic charge at one germanium center, along with substantial lone-pair character at the adjacent Ge atom. We are currently exploring the chemistry of **35** toward various Lewis acids in order to test this bonding hypothesis.

In agreement with the higher reactivity of **28** in comparison with the tin derivative **29**, the digermene displayed clean [2 + 2] reactivity with various alkynes, whereas **29** did not react under similar conditions. For example, the reaction of **28** with PhCCPh gave the stable 1,2-digermacyclobutadiene **38** in high yield as dark-red crystals.<sup>80</sup> In line with the structure depicted in Scheme 10, a C–C double bond was present [1.365(7) Å], while the Ge–Ge distance [2.4708(9) Å] was slightly longer than the known range for “digermenes”, R<sub>2</sub>GeGeR<sub>2</sub> (2.21–2.46 Å).<sup>81</sup> The pyramidal geometry at



**Figure 22.** Molecular structure of **38**. The flanking Dipp groups have been omitted for clarity.<sup>80</sup>



**Figure 23.** Ligand-activated product **39** from the reaction of Ar'GeGeAr' with HCCSiMe<sub>3</sub>.<sup>80</sup>

germanium ( $\Sigma^\circ\text{Ge} = 318.0$  and  $317.3^\circ$ ) coupled with the long Ge–Ge bond lengths indicated that the Ge–Ge interaction in **38** was weak (Figure 22). However, this compound was quite thermally stable (melting point = 178 °C). It is important to bear in mind that the facile [2 + 2] cycloaddition of alkynes to Ar'GeGeAr' is unexpected on the basis of the Woodward–Hofmann rules (the highest occupied molecular orbital of **28** is formally a  $\pi$  orbital); this observation suggests that **28** may possess significant diradical character.

For HCCSiMe<sub>3</sub>, 2 equiv of alkyne was added to **28** to eventually yield a 1,4-digermacyclohexadiene heterocycle **39**.<sup>80</sup> One possible reaction pathway to this product would involve the initial formation of a 1,2-digermacyclobutadiene ring (as with PhCCPh), followed by the addition of a second 1 equiv of alkyne to generate the 1,4-digermabenzene diradicaloid intermediate **40**, which, because of its high reactivity, activates a flanking aryl Dipp ring to give **39**. In order to intercept the diradicaloid intermediate, we reacted **28** with PhC≡C–C≡CPh. However, as with HCCSiMe<sub>3</sub>, 2 equiv of alkyne was consumed to yield an activated product **41** of similar structure to **39** (Scheme 10 and Figure 23).

Recently, we began to explore the reactivity of unsaturated main-group species with dihydrogen. In contrast to the well-studied activation of dihydrogen by transition-metal complexes,<sup>82</sup> similar reactivity for formally closed-shell main-

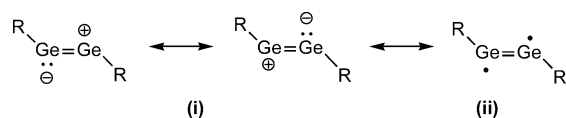
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Scheme 11. Activation of Dihydrogen by **28** at Room Temperature

	Ar'(H)GeGe(H)Ar' ( <b>42</b> )	Ar'H <sub>2</sub> GeGeH <sub>2</sub> Ar' ( <b>43</b> )	Ar'GeH <sub>3</sub> ( <b>44</b> )
1 equiv. H <sub>2</sub>	21 %	10 %	9 %
2 equiv. H <sub>2</sub>	2 %	85 %	13 %
3 equiv. H <sub>2</sub>	0 %	65 %	35 %
room temp.			

Scheme 12. Bonding Scheme for Ar'GeGeAr' Including the Diradicaloid Form **ii**

group compounds has been much rarer.<sup>83</sup> Of note, recent calculations indicate that the parent digermene HGeGeH should react sequentially and exothermically with dihydrogen to eventually yield the digermene H<sub>3</sub>GeGeH<sub>3</sub>. Only the last step in the hydrogenation process (conversion of H<sub>3</sub>GeGeH<sub>3</sub> to GeH<sub>4</sub>) was predicted to be slightly endothermic.<sup>84</sup>

The addition of stoichiometric amounts of dihydrogen (1–3 equiv) to a solution containing **28** at room temperature afforded the product distributions shown in Scheme 11.<sup>85</sup> From the addition of 2 equiv of dihydrogen, we were able to isolate colorless crystals of the digermene Ar'H<sub>2</sub>GeGeH<sub>2</sub>Ar' (**43**) in high yield. Use of lower quantities of dihydrogen yielded appreciable amounts of the monoaddition product (Ar'GeH)<sub>2</sub> (**42**) (by <sup>1</sup>H NMR and IR spectroscopy),<sup>86</sup> whereas the addition of excess dihydrogen to **28** led to the formation of the terphenylgermane Ar'GeH<sub>3</sub> (**44**). All identified germanium hydride intermediates were also characterized by X-ray crystallography.<sup>85</sup> In contrast, Tokitoh's digermene BbtGeGeBbt did not show any observable reactivity toward dihydrogen.<sup>72</sup> At this time, it is difficult to comment as to exact reasons why BbtGeGeBbt does not activate dihydrogen; however, the refinement of current bonding models should help us understand this significant difference in reactivity.

The high reactivity of Ar'GeGeAr' toward alkynes led us to consider the possible contribution of a diradical form (**ii**) as a component of the bonding (and subsequent reactivity) of the dimetallynes RMMR (Scheme 12).

On the basis of available experimental data, all derivatives of RMMR are diamagnetic; therefore, if form **ii** is to be considered, then it must have a singlet ground state. In a recent collaboration with Prof. Head-Gordon and co-workers

at the University of California, Berkeley, calculations were performed on the methyl-substituted species MeMMMe (M = Si–Pb), and some intriguing results were found.<sup>87</sup> With the aid of imperfect-pairing calculations, the digermene MeGeGeMe was shown to possess significant diradical character (13%), whereas the tin and lead analogues had very little (<4%) diradical character in the trans-bent C<sub>2h</sub> form. Notably, the silicon derivative, like the digermene, contained significant diradical character (17%).<sup>87</sup> In all of the MeMMMe derivatives studied, the most stable form was a trans-bent arrangement with a singlet ground state. While the overall geometries and bond lengths of the silicon, germanium, and lead species matched closely the experimentally verified values, the structural parameters for the tin analogue, MeSnSnMe, were significantly different from those found in Ar'SnSnAr' (**29**). For example, the calculated bond length for MeSnSnMe (3.06 Å) was much longer (ca. 0.4 Å) than that observed in **29** [2.6675(4) Å]. Furthermore, the internal C–Sn–Sn angle in MeSnSnMe was calculated to be much narrower (100.0°) than that found in **29** [126.24(7)°]. In addition, detailed calculations by Nagase<sup>88,89</sup> on the hindered distannylene Ar\*SnSnAr\* also suggest that this species is also considerably more bent (C–Sn–Sn angle = 110.0°), with a relatively long Sn–Sn distance of 2.900 Å.<sup>72</sup> The same study predicted that the energy difference between the “multiply bonded” isomer of Ar\*SnSnAr\* and the singly bonded form (analogous to Ar\*PbPbAr\*) with a Sn–Sn–C angle of 99.0° and a Sn–Sn distance of 3.087 Å was only 4.8 kcal/mol. Hence, it appeared that large changes in the structure of the distannynes ArSnSnAr were accompanied by only minor energy changes.

In order to investigate this phenomenon experimentally, a program aimed at modifying the existing Ar' ligand by exclusively changing the substituents at the para position of the central terphenyl ring was initiated. By controlling the electronic and steric nature of the para group, we hoped to induce structural changes within the distannylene core. It was found that the trimethylsilyl-substituted terphenyl ligand, (1-C<sub>6</sub>H<sub>2</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-Pr<sub>2</sub>)<sub>2</sub>)-4-SiMe<sub>3</sub>, Ar'-4-SiMe<sub>3</sub>, when bound to tin, induced dramatic changes to the overall structure of the distannylene isolated. Upon reduction of the tin halide precursor ClSn(Ar'-4-SiMe<sub>3</sub>) with potassium metal, dark-green crystals of the distannylene (4-Me<sub>3</sub>SiAr')SnSn(Ar'-4-SiMe<sub>3</sub>) (**45**) were obtained. X-ray crystallography (Figure 24) indicated that a trans-bent structure was present in the solid state; however, the Sn–Sn bond in **45** was 3.0660(10) Å, which is almost 0.4 Å longer than that in Ar'SnSnAr'

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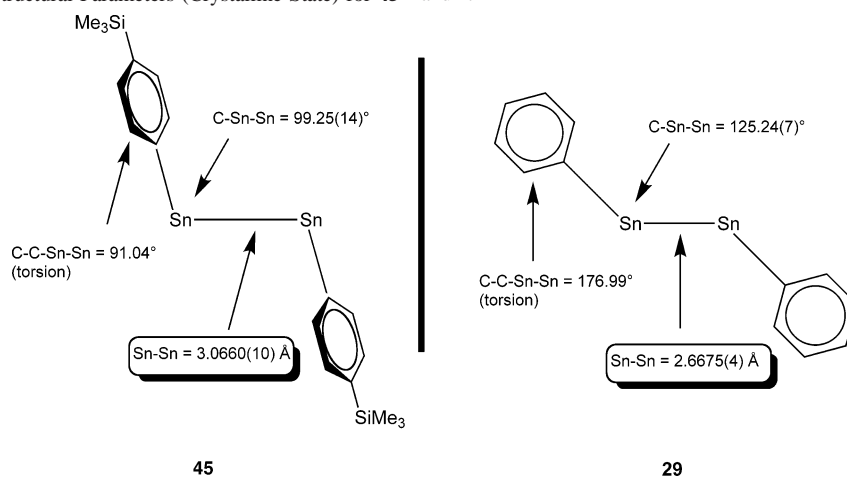
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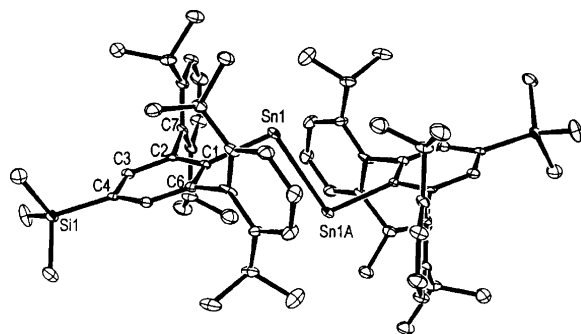
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**Scheme 13.** Differing Structural Parameters (Crystalline State) for **45**<sup>90</sup> and **29**<sup>66</sup>

(Scheme 13).<sup>90</sup> Moreover, the C–Sn–Sn angle in **45** [99.25(14)°] decreased by ca. 26° as compared to the value of 125.24(7)° found in Ar'SnSnAr'.<sup>66</sup> Another major difference between the structures of the two distannyne lies in the relative orientation of the central aryl rings of the terphenyl ligands. In Ar'SnSnAr', these central rings are coplanar to C<sub>ipso</sub>–Sn–Sn–C<sub>ipso</sub> unit, whereas in the silyl derivative, the rings are canted to an approximately perpendicular arrangement (torsion angle = 91.04°). Notably, the UV–vis spectra of Ar'SnSnAr', Ar'SnSnAr', and (4-Me<sub>3</sub>SiAr')SnSn(Ar'-4-SiMe<sub>3</sub>) show only minor changes upon ligand modification, suggesting that similar structures are found for all three species in solution.<sup>90b</sup> Computational work by Nagase and co-workers suggests that the distannyne retain multiple-bonded rather than single-bonded structures in solution.<sup>89</sup> Very recently, we have prepared the related tin hydride, [(4-Me<sub>3</sub>SiAr')Sn(μ-H)]<sub>2</sub>, which has much different spectroscopic features from **45**, thus ruling out the possibility that then bent distannyne **45** was actually a tin hydride.<sup>91</sup> Density functional theory calculations on the model species EC<sub>6</sub>H<sub>4</sub>-4-X (E = Ge or Sn; X = H, SiMe<sub>3</sub>, F, and Cl) indicate that the Δ<sub>D-Q</sub> energy difference between H- and SiMe<sub>3</sub>-substituted fragments is <0.5 kcal/mol. This appears to confirm the possibility that packing forces could cause the structural changes.<sup>92</sup> At present, it is unclear to what degree crystal packing forces play in dictating the overall structure of the distannyne in the solid state. The preparation of a family of distannyne each featuring selectively modified terphenyl ligands might help us better understand the factors that govern the geometry (and possibly the reactivity) of heavy group 14 dimetallynes.

**Figure 24.** Structure of the highly bent distannyne **45**.<sup>90</sup>

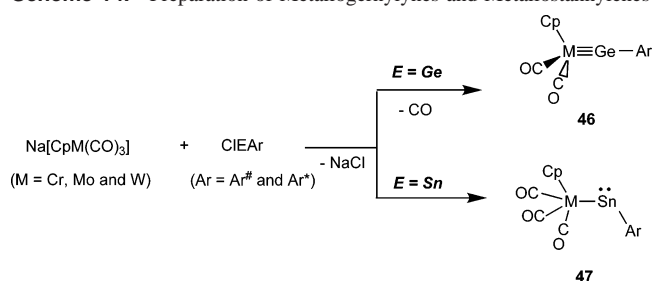
### Low-Coordinate Transition-Metal Chemistry

Concurrent with the development of new ligand archetypes, a number of transition-metal complexes have emerged that exhibit novel coordination geometries and reactivity. As a result, ligand design remains a key component in modern synthetic inorganic chemistry.<sup>93</sup> Motivated by prior results in the p-block elements, we wished to prepare transition-metal complexes stabilized by hindered terphenyl ligands with the ultimate goal of uncovering new bonding arrangements and/or unusual reactivity.

As mentioned at the beginning of this paper, terphenyl ligands had already been used successfully to prepare various germylyne transition-metal complexes of the form Cp(CO)<sub>2</sub>M≡GeAr (**46**; M = Cr, Mo, and W; Ar = Ar<sup>#</sup> or Ar\*),<sup>12,94</sup> These species were prepared from the reaction of Na[MCP(CO)<sub>3</sub>] with ClGeAr and generated NaCl and CO byproducts (Scheme 14). The isolated germylynes, **46**, displayed nearly linear M–Ge–C(Ar) angles and very short M–Ge bonds consistent with a significant degree of multiple-bond character.<sup>95</sup> In the case of tin, a similar salt elimination reaction transpired; however, CO elimination did not occur,

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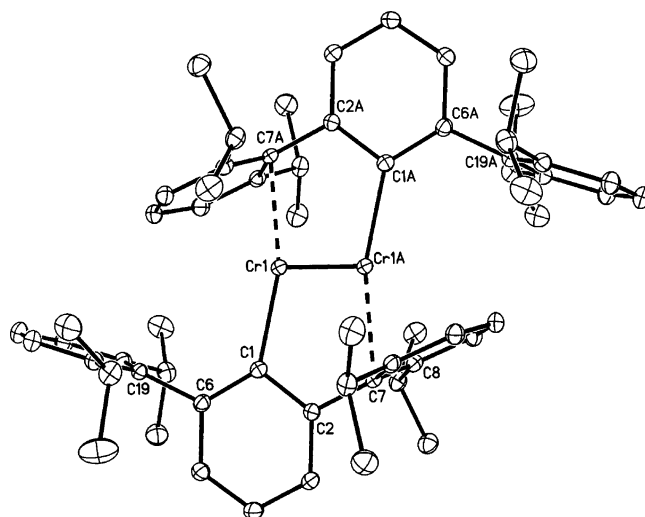
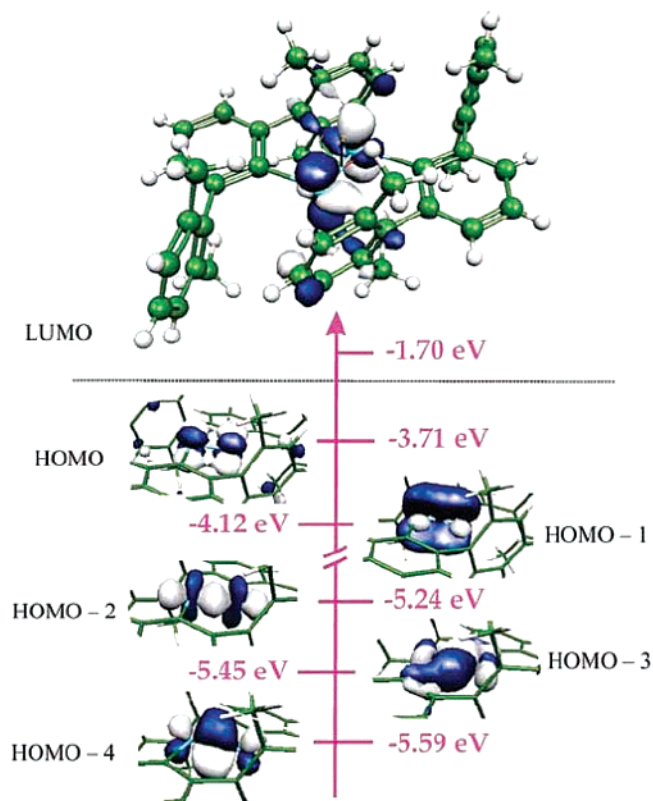


**Scheme 14.** Preparation of Metallogermylynes and Metallostannylenes

and the bent metallostannylenes  $\text{Cp}(\text{CO})_3\text{M}-\text{Sn}-\text{Ar}^*$  (**47**;  $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ) were obtained.<sup>96</sup> The group of Filippou also used hindered ligands to isolate a series of linear (and multiple-bonded) metallogermylynes, -stannylenes, and -plumbylynes of the general composition  $[\text{X}(\text{L})_n\text{M}\equiv\text{ER}]$  (**48**;  $\text{X} = \text{halide}$ ;  $\text{L} = \text{phosphine ligands}$ ;  $\text{M} = \text{Mo or W}$ ;  $\text{E} = \text{Ge}, \text{Sn}, \text{and/or Pb}$ ;  $\text{R} = \text{Cp}^*$  and  $\text{Ar}^*$ ).<sup>97</sup>

Currently, the reduction of terphenyl-substituted transition-metal metal halides,  $\text{Ar}'\text{MX}$  ( $\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{and Co}$ ;  $\text{X} = \text{halide}$ ),<sup>98</sup> is being investigated in order to synthesize low-valent complexes of the form  $\text{Ar}'\text{MMAr}'$ . The presence of formally monodentate  $\text{Ar}'$  ligands in  $\text{Ar}'\text{MMAr}'$  allows for the possibility of formal  $\text{M}-\text{M}$  bond orders greater than 4 because the number of valence orbitals available for  $\text{M}-\text{M}$  bonding can be increased to five with the use of a single large monodentate ligand. Treatment of the blue chromium(II) complex  $[\text{Ar}'\text{CrCl}]_2$  with a slight excess of  $\text{KC}_8$  afforded dark-red, pyrophoric crystals of the chromium(I) dimer  $\text{Ar}'\text{CrCrAr}'$  (**49**).<sup>99</sup> X-ray crystallography (Figure 25) revealed that a very short  $\text{Cr}-\text{Cr}$  bond was present [1.8351(4) Å] along with a planar trans-bent  $\text{C}_{\text{ipso}}-\text{Cr}-\text{Cr}-\text{C}_{\text{ipso}}$  core [ $\text{C}-\text{Cr}-\text{Cr}$  angle:  $108.78(3)^\circ$ ]. Furthermore, a  $\text{C}\cdots\text{Cr}$  interaction of 2.2943(9) Å was found between each chromium center and the *ipso*-carbon of a flanking Dipp ring of an adjacent ligating terphenyl group. Calculations show that this interaction is weak and that it is significantly longer than the  $\text{Cr}-\text{C}_{\text{ipso}}$  bond length of 2.1310(10) Å. It is also noteworthy that calculations by Weinhold and Landis predicted a trans-bent structure for the model species  $\text{HMMH}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ).<sup>100</sup>

The short  $\text{Cr}-\text{Cr}$  distance in **49** strongly suggested the presence of considerable multiple-bond character between these metal centers. Much of our understanding in the field of  $\text{M}-\text{M}$  multiple bonding stems from the seminal work of Cotton and co-workers,<sup>101</sup> who first described the  $\text{Re}-\text{Re}$  interaction within the  $[\text{Re}_2\text{Cl}_8]^{2-}$  ion as having a quadruple bond resulting from the mutual overlap of  $\sigma$ ,  $2\pi$ , and  $\delta$

**Figure 25.** Structure of the chromium(I) dimer **49**.<sup>99</sup>  $\text{Cr}-\text{Cr} = 1.8351(4)$  Å;  $\text{Cr}-\text{Cr}-\text{C}_{\text{ipso}} = 108.78(3)^\circ$ .**Scheme 15.** Calculated Frontier MOs for **49**<sup>99</sup>

symmetric d orbitals.<sup>102</sup> In fact, the  $\text{Cr}-\text{Cr}$  interaction in **49** is within 0.01 Å of the  $\text{Cr}-\text{Cr}$  distance in Cotton's quadruply bonded chromium(II) dimer  $\text{Cr}_2\{\text{C}_6\text{H}_3-2\text{-OME-5-Me}\}_4$  [1.828(2) Å].<sup>103</sup>

The observation of a very short  $\text{Cr}-\text{Cr}$  bond in **49** prompted the exploration of the bonding in this molecule using theoretical methods. These studies revealed that a 5-fold bonding interaction was present between two  $d^5$  chromium(I) centers. A simplified molecular orbital (MO) diagram can be used to explain the nature of the 5-fold  $\text{Cr}-\text{Cr}$  interaction (Scheme 15) with the assumption of local  $C_{2h}$  symmetry at chromium. In this simplified model, the metal-ligand interactions are assumed to involve mainly s orbitals on chromium, leading to two metal-ligand MOs:

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one is bonding with respect to the metal–metal bond, while the other is antibonding. This leaves five d orbitals on each chromium center available for bonding interactions (involving 10 valence electrons): one  $\sigma$  ( $d_z^2$  overlap;  $A_g$  symmetry), two  $\pi$  ( $d_{yz}$  and  $d_{xz}$ ;  $B_u$ ), and two  $\delta$  ( $d_{x^2-y^2}$  and  $d_{xy}$ ;  $B_g$ ). The actual bonding situation is more complex because mixing between orbitals of the same symmetry (e.g., s and  $d_z^2$  orbitals) can occur. Recent theoretical studies on the parent species PhCrCrPh and HCrCrH have replicated the short Cr–Cr bond length and overall trans-bent geometry observed in **49**.<sup>100,104</sup> These results suggest that, although the stability of the chromium(I) dimer  $Ar'CrCrAr'$  can be linked to the presence of a bulky  $Ar'$  ligand, the bent geometry of the compound is inherent to dimeric species of the general form RCrCrR and is not a direct consequence of having terphenyl-based ligands. Bond-order calculations on the model species PhCrCrPh afford a bond order of 3.62.<sup>104</sup> This is considerably lower than the formal bond order of 5 in the quintuple-bonded species. The lower bond order is due to mixing of antibonding excited states into the ground state. This mixing is often found in multiple-bonded transition-metal species,<sup>101</sup> and calculations on  $[Re_2Cl_8]^{2-}$  show that the bond order is 3.2 even though the Re atoms are linked by four orbital overlaps to afford a formal quadruple bond.<sup>105</sup> Currently, we are exploring the preparation of related transition-metal and group 12 dimers,  $ArMMAr$ , and are examining the reactivity of the electron-rich Cr–Cr manifold in **49**.

### Conclusions and Future Directions

The development of new hindered terphenyl ligands (Ar) has led to the preparation of a number of main-group and transition-metal species of the general form  $ArMMAr$ . Depending on the nature of the element present, versatile

M–M bonding environments ranging from very weak (e.g., in group 13 elements) to strong (in chromium) can be observed. Future reactivity studies should help shed more light on the bonding within these species and will likely lead to more unexpected results.

Although not explicitly mentioned in this paper, the use of aryl-based ligands in the context of p-block and transition-metal cluster chemistry is underway.<sup>106</sup> We are also exploring the use of exogenous donor molecules to stabilize highly reactive unsaturated molecules previously unattainable with hindered ligands alone.<sup>107</sup>

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