# **Inorganic Chemistry**

### Reaction of a Germylene, Stannylene, or Plumbylene with Trimethylaluminum and Trimethylgallium: Insertion into Al–C or Ga–C Bonds, a Reversible Metal–Carbon Insertion Equilibrium, and a New Route to Diplumbenes

Jeremy D. Erickson, James C. Fettinger, and Philip P. Power\*

Department of Chemistry, University of California, One Shields Avenue, Davis, California 95616, United States

**S** Supporting Information

**ABSTRACT:** The reaction of the tetrylenes  $Ge(Ar^{M_e})_2$ ,  $Sn(Ar^{M_e})_2$ , and  $Pb(Ar^{M_e})_2$   $[Ar^{M_e})_2 = C_6H_3-2,6-(C_6H_2-2,4,6-(CH_3)_3)_2]$  with the group 13 metal alkyls trimethylaluminum and trimethylgallium afforded  $(Ar^{M_e})_2Ge(Me)AlMe_2$  (1),  $(Ar^{M_e})_2Ge(Me)GaMe_2$  (2), and  $(Ar^{M_e})_2Sn(Me)GaMe_2$  (3) in good yields via insertion reaction routes. In contrast, the reaction of AlMe\_3 with  $Sn(Ar^{M_e})_2$  afforded the [1.1.1] propellane analogue  $Sn_2\{Sn(Me)Ar^{M_e}\}_3$  (5) in low yield, and the reaction of AlMe\_3 or GaMe\_3 with  $Pb(Ar^{M_e})_2$  resulted in the formation of the diplumbene  $\{Pb(Me)Ar^{M_e}\}_2$  (6) and  $AlAr^{M_e}Me_2$  (7) or  $GaAr^{M_e}Me_2$  (8) via metathesis. The reaction



AlAr<sup>Me</sup><sub>6</sub>Me<sub>2</sub> (7) or GaAr<sup>Me</sup><sub>6</sub>Me<sub>2</sub> (8) via metathesis. The reaction of Sn(Ar<sup>Me</sup><sub>6</sub>)<sub>2</sub> with gallium trialkyls was found to be reversible under ambient conditions and analyzed through the reaction of Sn(Ar<sup>Me</sup><sub>6</sub>)<sub>2</sub> with GaEt<sub>3</sub> to form (Ar<sup>Me</sup><sub>6</sub>)<sub>2</sub>Sn(Et)GaEt<sub>2</sub> (4), which displayed a dissociation constant  $K_{diss}$  and  $\Delta G_{diss}$  of 8.09(6) × 10<sup>-3</sup> and 11.8(9) kJ mol<sup>-1</sup> at 296 °C. The new compounds were characterized by X-ray crystallography, NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn, and <sup>207</sup>Pb), IR, and UV–vis spectroscopies.

#### INTRODUCTION

Heavy group 14 metalylenes (:ER<sub>2</sub>, E = Si, Ge, Sn, or Pb; R = bulky monodentate ligands) are Si-Pb analogues of carbenes. However, they possess a longer history as stable species owing mainly to the greater stability of their nonbonded electron pairs. The first example,  $Sn{CH(SiMe_3)_2}_2$ , was synthesized by Lappert and co-workers in 1973,<sup>1</sup> and several hundred stable metalylenes are now known. They have an extensive chemistry and have been shown to undergo a wide variety of reactions, some of which resemble those of carbenes.<sup>2-5</sup> They have played a central role in the development of modern main group chemistry, and more recently, they have attracted interest because of their reactivity toward small molecules such as H<sub>2</sub> and for their catalytic activity.<sup>6,7</sup> Nonetheless, their reactions with other heavier main group organometallic derivatives such as group 13 metal alkyls are poorly studied, and the number of well-characterized species with bonds between the heavier members of group 14 elements germanium, tin, and lead and group 13 metals is relatively low. The majority of the latter have been obtained via simple salt metathesis reactions of group 13 chlorides with lithium salts of organic group 14 molecules, and a number of Ge–Al,<sup>8–11</sup> Ge–Ga,<sup>12–16</sup> and Sn–Ga<sup>17,18</sup> bonded species have been obtained by this route. There also exist group 13-14 Lewis acid-base adducts, in which the group 14

metalylene behaves as a donor to a trivalent group 13 metal compound. Furthermore, anionic N-heterocyclic gallium carbene analogues have been used in the formation of Lewis adducts by acting as both electron pair donors<sup>19,20</sup> and electron pair acceptors<sup>21</sup> in reactions with digermenes and distannenes to give products with Ge–Ga and Sn–Ga bonds. Adduct formation between various stannates and trimethylgallium or -indium has also been observed.<sup>22</sup>

Herein we demonstrate that heavy group 14 metalylenes react with group 13 metal alkyls  $MMe_3$  (M = Al or Ga) to form  $(Ar^{Me_6})_2E(Me)(MMe_2)$  via insertion into the M–C bond. This approach represents a simple and new route to bond types previously obtainable only through salt metathesis and Lewis adduct formation. The products obtained include a germyl– alane and germyl–gallane, as well as a stannyl–gallane. The insertion of  $Sn(Ar^{Me_6})_2$  into GaMe<sub>3</sub> and GaEt<sub>3</sub> was found to be reversible at room temperature. In contrast, the reaction of the plumbylene  $Pb(Ar^{Me_6})_2$  with  $AlMe_3$  or  $GaMe_3$  results in exchange reactions and the formation of the diplumbene  $\{Pb(Me)Ar^{Me_6}\}_2$  and  $(Ar^{Me_6})AlMe_2$  or  $(Ar^{Me_6})GaMe_2$ . Unexpectedly, a 1:1 mixture of the diarylstannylene  $Sn(Ar^{Me_6})_2$ 

Received: November 25, 2014

with trimethylaluminum gave no reaction. However, upon treatment of Sn(Ar<sup>Me<sub>6</sub></sup>)<sub>2</sub> with 2 equiv of AlMe<sub>3</sub> and heating to 85 °C, a reaction occurred to give a rare pentastanna-[1.1.1]propellane Sn<sub>2</sub>{Sn(Me)Ar<sup>Me<sub>6</sub></sup>}<sub>3</sub> in low yield.

#### RESULTS AND DISCUSSION

The behavior of heavy group 14 metalylenes as Lewis acids or bases or their ability to undergo oxidative addition/insertion reactions is characteristic of their chemistry. Insertions into numerous single bonds such as H-H,<sup>23-25</sup> C-C,<sup>26</sup> C-O,<sup>27</sup> O-H,<sup>28,29</sup> P-P,<sup>30</sup> and  $N-H^{5,31}$  have been described in previous publications. Recent investigations involving the reactions<sup>5,24,27,32</sup> of the metalylenes  $Ge(Ar^{Me_6})_2$  and  $Sn(Ar^{Me_6})_2$ with hydrogen, ammonia, or hydrazine provide examples of insertion reactions that may or may not be accompanied by aryl elimination. In reactions with Bronsted acids, however, it was shown that both germylenes and stannylenes insert into O-Hand F-H bonds.<sup>33</sup> In contrast, insertion reactions into metal– carbon bonded species have not been well investigated.

**Synthesis.** Treatment of  $Ge(Ar^{Me})_2$  with trimethylaluminum or trimethylgallium yielded the products 1 and 2 in high yield (Scheme 1). The reaction probably occurs through the

Scheme 1. Reactions of Group 14 Metalylenes with Parent Group 13 Alkyls To Form Products 1, 2, and 3



initial formation of the Lewis acid–base adduct  $(Ar^{M_6})_2$ Ge-MMe<sub>3</sub> (M = Al or Ga) with subsequent insertion of the germanium atom into one of the M–C bonds of the group 13 alkyl. Materials containing group 13–14 bonds exist in the solid state and have been used in such applications as (AlGeIn)N type thin-film light-emitting diodes,<sup>34</sup> semiconductors,<sup>35</sup> and gallium-doped germanium layer superconductors.<sup>36</sup> In molecular species, however, only a handful of stable compounds with heavier group 13–14 element bonds are known, some of which have been structurally characterized (see below, Table 2).

The synthesis of 1 and 2 represent the first synthesis of a germyl–alane and germyl–gallane from germylenes. Compounds 1 and 2 have a four-coordinate germanium and three-coordinate aluminum or gallium atoms as shown by their X-ray crystal structures in Figures 1 and 2 (see below). The bulky terphenyl substituents of the germanium are sufficient to stabilize the three coordination at the group 13 metal. Product 1 is the second structurally characterized germyl–alane of this geometry; an earlier example was reported in 2009 when Nöth and co-workers synthesized tmp<sub>2</sub>AlGe(Me<sub>2</sub>)SiMe<sub>3</sub> (tmp = 2,2,6,6-tetramethylpiperidino) by reaction of LiGe(Me)<sub>2</sub>Si-(tBu)<sub>3</sub> with tmp<sub>2</sub>AlCl.<sup>11</sup>

Reaction of  $Sn(Ar^{Me_6})_2$  with AlMe<sub>3</sub> did not produce a product analogous to 1 but instead gave the pentastanna-[1.1.1]-propellane  $Sn_2\{Sn(Me)Ar^{Me_6}\}_3$ , 5, in low yield. In contrast, the reaction of  $Sn(Ar^{Me_6})_2$  with GaMe<sub>3</sub> produced 3, the tin analogue of 2 (Scheme 1). However, while the reaction



Figure 1. Thermal ellipsoid plot (30% probability) of 1. H atoms are not shown. Selected distances and angles are given in Table 1.



Figure 2. Thermal ellipsoid plot (30% probability) of 2. H atoms are not shown. Selected distances and angles are given in Table 1.

solution initially becomes colorless, it slowly acquired a slight purple color similar to that of the stannylene precursor upon standing. Crystallization from pentane resulted in colorless crystals and a pale purple mother liquor. The crystals were confirmed to be the insertion product **3** by X-ray crystallography (see below, Figure 3). When the colorless crystals of **3** were dissolved in deuterated benzene for NMR spectroscopic



Figure 3. Thermal ellipsoid plot (30% probability) of 3. H atoms are not shown. Selected distances and angles are given in Table 1.

analysis, the solution slowly assumed a purple color resembling that of the diarylstannylene precursor.

Colorless crystals of 3 were dissolved in hexanes, and the solution was dried under reduced pressure. Repetition of this cycle resulted in a progressively darker purple color of the remaining solid. Eventually a pure purple solid was obtained and crystallized from pentane. These purple crystals were confirmed by X-ray crystallography to be Sn(Ar<sup>Me<sub>6</sub></sup>)<sub>2</sub>. In effect, dissolving 3 results in its dissociation to GaMe<sub>3</sub> and Sn(Ar<sup>Me<sub>6</sub></sup>)<sub>2,1</sub> which produces the purple color. This process can be reversed by the addition of excess GaMe<sub>3</sub>. When the resulting colorless solution is evaporated the removal of excess GaMe<sub>3</sub> and subsequent dissolution again regenerates a purple hue. The addition of further GaMe3 regenerates the original colorless solution of 3. This cycle of addition and removal of GaMe<sub>3</sub> was repeated five times with no observable difference between cycles. Reactions of  $Sn(Ar^{Me}_{6})_2$  with the less volatile gallium trialkyl GaEt<sub>3</sub> afforded  $(Ar^{Me_6})_2Sn(Et)GaEt_2$ , 4, for which variable-temperature <sup>1</sup>H NMR spectroscopy permitted a determination of the reaction equilibrium parameters (see below).

While there exist reversible valence equilibrium reactions between heavy main group species, most of these involve monomer–dimer equilibrium of homometallic bridged species dimerization or the formation and breaking of homonuclear E– E bonds such as that observed for heavier element olefin analogues.<sup>37–40</sup> An insertion equilibrium similar to those in Scheme 2 has previously been observed between Ge( $C_6H_3$ -2,6-

## Scheme 2. Dissociation of 3 or 4 Occurs at Room Temperature in Toluene

$(Ar^{Me_6})_2 Sn(R)GaR_2 =$	$= GaR_3 + Sn(Ar^{ivie_6})_2$
R = Me, 3, colorless R = Et, 4, colorless	purple

Mes)<sub>2</sub> or Cl<sub>2</sub>Al(NSiMe<sub>3</sub>)<sub>2</sub>P and P<sub>4</sub> but required UV radiation to rerelease the P<sub>4</sub> cage.<sup>41</sup> Unfortunately, both UV–vis and <sup>1</sup>H NMR variable-temperature experiments were unsuccessful in determining the equilibrium parameters of solutions of **3** between  $-78^{\circ}$  and 85 °C. This is because the reaction mixture, even in a sealed tube, could not be made to regenerate the inserted product **3** once a dissociation equilibrium was established. This can be attributed to the high volatility of GaMe<sub>3</sub> leading to an equilibrium between the solution and the vapor phase. To remedy this problem, the less volatile triethylgallium<sup>42</sup> was tested and also found to undergo a reversible reaction with Sn(Ar<sup>Me<sub>6</sub></sup>)<sub>2</sub>. The equilibrium constant  $K_{\text{diss}}$  and  $\Delta G_{\text{diss}}$  values at 296 K for the dissociation reaction of **4** (Scheme 3) were found to be  $8.09(6) \times 10^{-3}$  and 11.8(9) kJ/ mol, respectively, for an initial concentration of 0.030(3) M of **4** in toluene.

Scheme 3. Novel Synthesis of a Diplumbene (6) and Formation of Corresponding Aryldimethylaluminum (7) and -Gallium (8) Compounds



As noted above, the treatment of  $Sn(Ar^{Me_6})_2$  with  $AlMe_3$ under the same conditions as those employed for the synthesis of 1–3 afforded no reaction. Heating the reactants to reflux in toluene also produced no reaction. However, the addition of a second equivalent of  $AlMe_3$  and continued heating to 85 °C afforded a low yield of a rare example of a pentastanna-[1.1.1]propellane, 5 (see below, Figure 4). Tin–propellane



Figure 4. Thermal ellipsoid plot (30% probability) of 5. H atoms and mesityl substituents are not shown. Selected distances and angles are given in Table 1.

analogues were first synthesized by Sita and co-workers via the thermolysis of the trimer  $Sn_3R_6$  (R = 2,6-diethylphenyl)<sup>43,44</sup> and are of interest for their singlet diradical character.<sup>45,46</sup> Product **5** was observed to be both air and moisture stable.

The reactions of  $Pb(Ar^{Me_6})_2$  with AlMe<sub>3</sub> and GaMe<sub>3</sub> afforded no Pb-Al or Pb-Ga bonded products or indeed any simple oxidative addition products analogous to those seen for 1, 2, 3, and 4. Instead, both reactions yielded the diplumbene, 6, as well as Ar<sup>Me<sub>6</sub></sup> AlMe<sub>2</sub>, 7, or Ar<sup>Me<sub>6</sub></sup> GaMe<sub>2</sub>, 8, coproducts (Scheme 3). These reactions thus represent a new synthetic route to diplumbenes. The few diplumbenes currently known<sup>37-40</sup> have been synthesized by the reaction of  $PbX_2$  (X = Cl, Br) with 2 equiv of a lithium derivative of a bulky alkyl, aryl, or silyl group or by reaction of a halogen-bridging plumbylene dimer with an alkyl Grignard reagent, followed by dimerization. The products 6, 7, and 8 can be accounted for by assuming an initial insertion into the M-C bond of the group 13 alkyl. However, due to lead's tendency to favor a 2+ oxidation state,<sup>47</sup> there is likely an equilibrium between the reactants and the insertion product 5. The overall reaction is in effect a metathesis of methyl and terphenyl groups between aluminum and lead. The resulting plumbylene (Ar<sup>Me6</sup>)PbMe has insufficient bulk to remain monomeric and dimerizes via Pb-Pb bonding, yielding the diplumbene 6 (Scheme 3).

The first well-characterized diplumbene, {Pb(Si(SiMe<sub>3</sub>)<sub>3</sub>)R}<sub>2</sub> (R=C<sub>6</sub>H<sub>2</sub>-2,4,6-(CF<sub>3</sub>)<sub>3</sub>), and later the diplumbene {Pb(2,4,6- $tBu_3C_6H_2$ )(CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>-3,5- $tBu_2C_6H_3$ )}<sub>2</sub> were obtained by Klinkhammer via a ligand migration process similar to that of the reaction described for **6–8**, lending further credence to the proposed reaction pathway.<sup>40,48</sup> Furthermore, it is known that diplumbylenes exist in an equilibrium with their dissociated monomers at room temperature.<sup>38,40,48</sup> Compound **6** differs from the related previously reported species {PbMe(Ar<sup>Pr<sup>i</sup></sup>)}<sub>2</sub>

 $(Ar^{Pr_4^i} = C_6H_3 - 2, 6 - \{C_6H_3 - 2, 6 - Pr_2^i\}_2)^{40}$  in that it has a less bulky

Table 1.	Selected	Bond	Distances	(Angstroms)	and	Angles	(deg	rees)	) for	Com	pounds	1-	3 and	l 5–	8
----------	----------	------	-----------	-------------	-----	--------	------	-------	-------	-----	--------	----	-------	------	---

1		2		3		5	
Ge(1)-Al(1)	2.4851(5)	Ge(1)-Ga(1)	2.4443(3)	Sn(1)-Ga(1)	2.6228(2)	Sn(1)-Sn(2)	2.8515(3)
Ge(1) - C(1)	1.9776(15)	Ge(1) - C(1)	1.9741(19)	Sn(1)-C(1)	2.1553(18)	Sn(1)-Sn(1A)	3.4878(5)
Al(1)-C(2)	1.9622(18)	Ga(1)-C(2)	1.983(2)	Ga(1)-C(2)	1.980(2)	Sn(1) - C(1)	2.172(4)
Al(1)-C(3)	1.9528(18)	Ga(1) - C(3)	1.969(2)	Ga(1) - C(3)	1.9639(19)	Sn(1) - C(2)	2.193(3)
C(1)-Ge(1)-Al(1)	102.66(5)	C(1)-Ge(1)-Ga(1)	102.04(6)	C(1) - Sn(1) - Ga(1)	107.67(5)	Sn(1) - Sn(2) - C(2)	120.95(6)
Ge(1) - Al(1) - C(2)	109.23(6)	Ge(1) - Ga(1) - C(2)	111.00(7)	Sn(1)-Ga(1)-C(2)	113.01(7)	Sn(2)-Sn(1)-Sn(2A)	86.502(8)
Ge(1) - Al(1) - C(3)	129.05(6)	Ge(1)-Ga(1)-C(3)	131.65(5)	Sn(1)-Ga(1)-C(3)	126.67(6)	Sn(1)-Sn(2)-Sn(1A)	75.406(10)
C(2) - Al(1) - C(3)	115.50(8)	C(2)-Ga(1)-C(3)	114.68(9)	C(2)-Ga(1)-C(3)	118.16(9)	C(1)-Sn(2)-C(2)	107.40(14)
						C(1)-Sn(2)-Sn(1)	114.84(8)
	6			7		8	
Pb(1)-Pb(1A)		3.2854(5) A	A(1) - C(1)	1.9450(15)	Ga(1)	)-C(1)	1.953(3)
Pb(1)-C(1)		2.272(5) A	A(1) - C(2)	1.9450(15)	Ga(1)	)-C(2)	1.969(2)
Pb(1)-C(2)		2.335(4) A	A(1) - C(3)	1.9698(19)	Ga(1)	)-C(3)	1.970(2)
C(1)-Pb(1)-Pb	(1A)	102.38(13)	C(1) - Al(1) - C(2)	121.18(10)	C(1)-	-Ga(1) - C(2)	122.52(11)
C(2)-Pb(1)- Pb	(1A)	127.70(9)	C(1) - Al(1) - C(3)	119.41(5)	C(1)-	-Ga(1) - C(3)	118.37(9)
C(1) - Pb(1) - C(2)	2)	95.23(16)	C(2) - Al(1) - C(3)	119.41(5)	C(2)-	-Ga(1) - C(3)	119.08(10)

Table 2. Selected Bond Distances (Angstroms) Between Aluminum or Gallium and Germanium or Tin in Molecules Related to  $1-3^a$ 

Ge–Al		Ge-Ga			
1	2.4851(5)	2	2.4443(3)		
$\operatorname{Ge}(\operatorname{AlCl}_2 \cdot \operatorname{OEt}_2)_4^{52}$	2.449(4)				
tmp <sub>2</sub> AlGe(Me <sub>2</sub> )SiMe <sub>3</sub> <sup>11</sup>	2.545(1)	$Ga_2(Ge(I)Ar^{Me_6})_3^{16}$	2.4934(6)		
$Ph_3GeAlMe_2(OEt_2)^{11}$	2.515(1)	$Me_3SiMes_2GeGa\{[N(Ph)CH\}_2\}^{20}$	2.431(1)		
[(Ph <sub>3</sub> Ge) <sub>3</sub> AlH]Li(THF) <sub>3</sub> <sup>11</sup>	2.532(2)	$K{Mes_2GeGa[N(Ph)CH]_2)}^{20}$	2.4600(8)		
$[(Ph_3Ge)_3AlMe]Li(Et_2O)_5^{10}$	2.526(2)	$(Giso)Ge-Ga{N(Ph)CH)_2}^{19}$	2.5157(7)		
		$Ga_4[Ge(SiMe_3)_3]_4^{12}$	2.582(5); 2.468(6)		
Sn-Al		Sn-Ga			
$Cl_3Al(SnNBu^t)_4^{53}$	2.78(1)	3	2.6227(3)		
$Yb{Sn(2-py^R)_3AlMe_3}_2^{22}$	2.8317(10)	$[Me_2Sn{ClGa(DDP)}_2]^{54}$	2.6228(7)		
		$[{Li(THF)Sn(2-py^R)_3}GaEt_3]^{20}$	2.7196(11)		
		$[K(tmeda)][Sn{CH(SiMe_3)_2Ga-\{[N(Ph)CH]_2\}]^{21}$	2.7186(6)		

<sup>*a*</sup>tmp = 2,2,6,6-tetramethylpiperidino, Giso =  $[Pri_2NC{NPh}_2]^-$ , tmeda = tetramethylethylenediamine, py<sup>R</sup> =  $C_3H_3N$ -5-Me, DDP = 2-{(2,6-diisopropylphenyl)amino}-4-{2,6-diisopropylphenyl)imino}-2-pentene

terphenyl ligand as a result of replacement of diisopropylphenyl groups attached to the central aryl ring of the terphenyl ligand by mesityl groups. Yet the Pb–Pb bond in **6** is longer (3.2854(5) vs 3.1601(6) Å), possibly as a result of greater attractive dispersion forces in {PbMe( $Ar^{Pr_4^i}$ )}<sub>2</sub>, similar to those seen in {Pb(Si(SiMe\_3)\_3)R}<sub>2</sub><sup>49</sup> and related species.<sup>50</sup> At room temperature {PbMe( $Ar^{Pr_4^i}$ )}<sub>2</sub> dissociates into two monomeric plumbylenes, as shown by a chemical shift of 8738 ppm in its <sup>207</sup>Pb NMR spectrum. Similarly, although **6** is a dimer in the crystalline state, in solution it is the monomer, as evidenced by its similar <sup>207</sup>Pb NMR chemical shift of 8248 ppm.

**Structures.** The crystal structures for 1, 2, and 3 are shown in Figures 1, 2, and 3, respectively, selected bond lengths and angles are given in Table 1, and selected structural parameters for related compounds are given in Table 2. The structures of 1–3 are very similar in their overall configuration. While the Ge–Al bond length in 1 (2.485(5) Å) is longer than the 2.41 Å predicted by the sum of the covalent radii of aluminum and germanium,<sup>51</sup> it is shorter than most of the related compounds listed in Table 2. Only Ge(AlCl<sub>2</sub>·Et<sub>2</sub>O)<sub>4</sub>, which has tetrahedrally coordinated germanium and aluminum, contains shorter Ge–Al bonds (4.449(4) Å).<sup>52</sup> However, only one other compound, i.e., tmp<sub>2</sub>AlGe(Me<sub>2</sub>)SiMe<sub>3</sub> of Nöth and co-workers, contains a near-planar three-coordinated aluminum, in which aluminum is substituted by two amido substituents and expected to have a smaller effective ionic radius owing to the more electronegative amido substituents. This should result in a shorter Al–Ge bond. It is a possibility that the longer and less electronegative SiMe<sub>3</sub> substituent increases the steric pressure and electron density at germanium such that a longer Ge–Al bond is produced. The Ge–Ga and Sn–Ga bond lengths in **2** and **3** are within the range of known bond lengths for Ge–Ga and Sn–Ga bonded molecular species displayed in Table 2. We note that the Ge–Ga bond (2.4443(3) Å) in **2** is shorter than the Ge–Al bond (2.4851(5) Å) in **1**, and this is consistent with the smaller covalent radius of gallium despite its greater atomic number.<sup>51</sup>

The sum of the interligand angles at the aluminum atom in **1** is  $353.8^{\circ}$ . The metal is displaced 0.367 Å out of the C(2)–C(3)–Ge(1) plane toward a flanking ring of a terphenyl ligand. The distance from the aluminum atom to the plane of the flanking aryl ring is 2.679 Å, suggesting weak coordination, which may cause the aluminum atom's displacement from planar coordination. The weaker aryl interactions with gallium in **2** and **3** are consistent with a more planar gallium coordination. The sums of the angles at the gallium atom for **2** and **3** are 357.6° and 357.9°, the displacement from the

C(2)-C(3)-[Ge(1) or Sn(1)] plane is 0.199 and 0.183 Å, and the distance from the gallium to the flanking aryl ring is 2.829 and 2.854 Å, respectively.

In the crystal structure of **5** (Figure 4), the five tin atoms are arranged in a trigonal bipyramidal fashion (Figure 4). The axial tins have no organic substituent, whereas the equatorial tins each carry a methyl and a terphenyl ligand. The Sn(1)-Sn(1A) bridgehead distance is 3.4878(5) Å, which is too long for strong bonding. The distance is longer than the corresponding distance in two compounds given in Table 3:  $Sn_5[C_6H_3-2,6-$ 

Table 3. Comparison of Related Sn–Sn Distances in Known Pentastanna[1.1.1]propellanes

	bridgehead—bridgehead distance (Å)	Sn(1)–Sn(2) distance (Å)
5	3.4878(5)	2.8515(3)
$Sn_5[_2C_6H_3-2,6-Et]_6^{43}$	3.367(1)	2.852(1)
$\frac{Sn_5(C_6H_3-2,6-O-iPr_2)_6^{55}}{(C_6H_3-2,6-O-iPr_2)_6^{55}}$	3.42	2.852(1)

Et<sub>2</sub>]<sub>6</sub><sup>44</sup> synthesized by Sita and co-workers and Sn<sub>5</sub>(C<sub>6</sub>H<sub>3</sub>-2,6-{O-iPr}<sub>2</sub>)<sub>6</sub> synthesized by Drost and co-workers.<sup>55</sup> The sum of the covalent radii of two tin atoms is 2.78 Å,<sup>51</sup> and in known pentastannapropellanes single Sn–Sn bonds between equatorial and axial tins are in the range of 2.82–2.87 Å,<sup>43,44,55,55</sup> and the Sn(1)–Sn(2) distance of 1 (2.8515(3) Å) is within these limits (Table 3).



Figure 5. Thermal ellipsoid plot (30% probability) of 6. H atoms are not shown. Selected distances and angles are given in Table 1.

As noted above, the crystal structure of **6** (Figure 5) can be compared to that of the diplumbene {PbMe( $Ar^{Pr_4}$ )}<sub>2</sub> previously synthesized in this laboratory.<sup>40</sup> A comparison of key structural parameters of these two compounds is given in Table 4. The Pb–Pb bond length in **6** is longer than that of {PbMe( $Ar^{Pr_4}$ )}<sub>2</sub> despite the use of a less crowding terphenyl ligand. The shorter Pb–Pb bond length in {PbMe( $Ar^{Pr_4}$ )}<sub>2</sub> may be the result of increased dispersion force attraction owing to the greater number of flanking ring substituents.<sup>49,50</sup>

**Spectroscopy.** As is apparent from Figures 1–3, the AlMe<sub>2</sub> or GaMe<sub>2</sub> moieties lie in cavities formed by flanking mesityl rings from two different terphenyl ligands which inhibit rotation around the Ge–Al, Ge–Ga, and Sn–Ga bond. In the <sup>1</sup>H NMR spectra of compounds 1, 2, and 3, the group 13 metal methyl substituent signals appear near or upfield of 0

Table 4. Comparison of Selected Bond Distances (Angstroms) and Angles (degrees) for  $\{PbMe(Ar^{Pr_4^i})\}_2$  and 6

	{PbMe(Ar	$\{P_{4}^{p_{4}}\}_{2}$ 6	
Pb(1)-Pb(1A)	3.1601	3.2866(5)	)
Pb(1)-C(1)	2.280(	(6) 2.273(6)	
Pb(1)-C(2)	2.318(	(6) 2.329(6)	
C(1) - Pb(1) - C	(2) 91.8(2)	95.3(2)	
C(1)-Pb(1)-Pl	b(1A) 109.35(1	.6) 102.33(17)	
C(2)-Pb(1)-Pl	o(1A) 121.51(1	.4) 127.71(13)	
$\sum Pb(1)^{\circ}$	322.66	325.34	



**Figure 6.** Thermal ellipsoid plots (30% probability) of 7 (left) and 8 (right). H atoms are not shown. Selected distances and angles are given in Table 1.

ppm. For 1 and 2, the two methyl groups are in different environments, as are all mesityl methyl groups. This persists even to a temperature of 55  $^{\circ}$ C, with no change in signal shape. The sharpness of the signals suggests no intermolecular or intramolecular methyl exchange takes place.

Only one signal is observed for the two group 13 metal methyl substituents of 3 at room temperature. The rotational barrier in this species is probably lower because it has the longest group 13-14 bond length as well as the lowest degree of steric crowding. At lower temperatures the signal broadens and splits beginning at 15 °C, becoming fully resolved at -10 °C. The energy barrier for this phenomenon is 55(4) kJ mol<sup>-1</sup> based on the coalescence temperature of 15 °C and final separation of the Ga-Me signals of 180 Hz at -10 °C.<sup>57</sup> A lower temperature produces broadening of the three mesityl methyl signals for 3 at 1.84, 1.93, and 2.17 ppm beginning at -30 °C. At room temperature, when the mesityl methyl signals are fully coalesced, there is a rapid exchange of aryl rings coordinating to the gallium center. At lower temperatures, this movement is slowed, leading to signal broadening. At a low enough temperature, transformation into a multitude of signals as observed in the <sup>1</sup>H spectra of 1 and 2 consistent with restricted rotation is expected, but our instrument lacked the capacity to descend to low enough temperature to resolve these signals.

The <sup>1</sup>H NMR spectroscopy of 4 affords a similar pattern to that of 3, and only one set of signals is observed for identical functionalities of each ligand. A greater degree of signal broadening is observed in 4, but the sharpness of the signals



**Figure 7.** Variable-temperature <sup>1</sup>H NMR of  $(Ar^{Me_6})_2Sn(Et)GaEt_2$  (4). Signals at 1.90 and 1.80 ppm correspond to  $C_6H_2$ -Me groups of the aryl rings of **4**. Quartet at 0.40 ppm is due to the CH<sub>2</sub> group of GaEt<sub>3</sub>. Signal at 1.86 ppm is due to the  $C_6H_2$ -Me groups of Sn $(Ar^{Me_6})_2$ . Remaining signals are identified in the Experimental Section.

increases with increasing temperature, as also observed for **3**. At room temperature in solution, dissociation of **4** into  $Sn(Ar^{Me_6})_2$  and GaEt<sub>3</sub> is observed. Upon increasing temperature (Figure 7), the observed signals for **4** lose intensity until fully disappearing around ca. 360 K. This is accompanied by the appearance of signals for  $Sn(Ar^{Me_6})_2$  and GaEt<sub>3</sub>. This process is reversible, and upon cooling to room temperature, **4** is regenerated. A van't Hoff analysis of the variable-temperature <sup>1</sup>H NMR spectra affords an enthalpy and entropy of association of 52(4) kJ mol<sup>-1</sup> and -134(11) J mol<sup>-1</sup> K<sup>-1</sup> as well as an equilibrium constant of  $8.09(6) \times 10^{-3}$  and  $\Delta G_{diss}$  of 11.8(9) kJ mol<sup>-1</sup> at 0.03 M concentration and 296 °C.

The <sup>1</sup>H NMR spectrum of **5** provides no evidence of paramagnetism. In addition, there is no evidence of an Sn–H absorption in the IR spectrum.<sup>58</sup> This combined with the crystallographic data suggests that **5** exists as a singlet diradical.<sup>45</sup> Compound **5** was most soluble in deuterated benzene and toluene but slowly reacted with these solvents upon standing at room temperature to yield a black precipitate. This limited the time in which samples could be analyzed, making <sup>13</sup>C and <sup>119</sup>Sn NMR spectroscopy exceedingly difficult. Attempts to obtain <sup>13</sup>C NMR and <sup>119</sup>Sn NMR spectra were recorded in deuterated cyclohexane to avoid solvent reactivity, but the solubility of **5** was so low that no signals were ever observed. Product **5** is pale purple in color with a  $\lambda_{max}$  absorption at 560 nm.

The diplumbene **6** obtained by the route described in Scheme 3 could not be completely purified by recrystallization from the reaction mixture to give NMR spectra that were completely uncontaminated by 7 or **8**. The signals from the reaction mixture of Pb( $Ar^{Me}_{0}$ )<sub>2</sub> and GaMe<sub>3</sub> were assigned by recording a spectrum for 7 synthesized independently by the reaction of Me<sub>2</sub>GaCl with LiAr<sup>Me</sup><sub>6</sub>. This enabled the assignment of the signals of **6** and **8** in a simple manner. The lead–methyl signals are upfield at 0.19 ppm in the <sup>1</sup>H spectrum and at 0.58 ppm in the <sup>13</sup>C spectrum because of the electropositive character of the lead atoms. The <sup>207</sup>Pb signal is observed at 8248 ppm, which lies in a region similar to that of {PbMe(Ar<sup>Pr<sub>4</sub></sup>)}<sub>2</sub> and Pb(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>·4-Pr<sup>i</sup>)ArPr<sup>i</sup><sub>3</sub>, which display <sup>207</sup>Pb signals at 8738 and 8550 ppm, respectively.<sup>40</sup> Product **6** has a red color with a  $\lambda_{max}$  absorption at 466 nm and a shoulder feature at 550 nm, which is similar to the red color of {PbMe(Ar<sup>Pr<sub>4</sub></sup>)}<sub>2</sub> which has a  $\lambda_{max}$  at 468 nm.

The <sup>1</sup>H NMR spectra of 7 and 8 are nearly identical, as would be expected from their similar structure. The only significant differences lie in the methyl group chemical shifts. The aluminum methyl signals of 7 appear at -1.69 and -7.07 ppm in their <sup>1</sup>H and <sup>13</sup>C NMR spectra, while the gallium methyl signals of 8 appear at -0.26 and -0.08, ppm respectively, consistent with the more electropositive character of aluminum in comparison to gallium.<sup>60</sup>

#### EXPERIMENTAL SECTION

**General Experimental Procedures.** Standard Schlenk techniques were used in the synthesis of all products under strictly anhydrous and oxygen-free conditions. All solvents were dried over NaK.  $Ge(Ar^{Me_6})_2$ ,  $Sn(Ar^{Me_6})_2$ , and  $Pb(Ar^{Me_6})_2$  were synthesized according to published methods.<sup>60</sup> AlMe<sub>3</sub> (1.4 M in heptane) and GaMe<sub>3</sub> were used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies were carried out on a Bruker 600 or 500 MHz spectrometer and referenced to residual solvent peaks. <sup>119</sup>Sn and <sup>207</sup>Pb NMR spectroscopies were carried out on a Bruker 500 MHz spectrometer and referenced to SnPh<sub>4</sub> (-128.8 ppm) and PbMe<sub>4</sub> (0 ppm). Melting points were measured in glass capillary tubes sealed under argon using a Mel-Temp II apparatus. Infrared spectroscopy was carried out on a Bruker Tensor 27 IR spectrometer as a Nujol mull. UV–vis data were recorded on an Olis 14 UV/vis/NIR Spectrometer.

 $(Ar^{Me_6})_2$ Ge(Me)AlMe<sub>2</sub> (1). Ge $(Ar^{Me_6})_2$  (0.70 g, 1 mmol) was dissolved in toluene (40 mL) and cooled to ca. -78 °C. A 1.4 M solution of AlMe<sub>3</sub> in heptane (0.79 mL, 1.1 mmol) was diluted with toluene (20 mL) and added dropwise. The mixture was stirred and allowed to warm to room temperature overnight, which resulted in a

color change from purple to colorless. The solvents were removed under reduced pressure, and the resulting white solid was recrystallized from hexanes to give colorless crystals of 1. Yield: 0.481 g, 62%. Mp: 168 °C (decomposition to Ge( $Ar^{Me_6}$ )<sub>2</sub>). <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>61</sub> 25 °C, ppm): -0.76 (s, 3H, Al-Me), -0.45 (s, 3H, Al-Me), -0.12 (s, 3H, Ge-Me), 1.48 (s, 3H, p-Me), 1.64 (s, 3H, p-Me), 1.76 (s, 3H, p-Me), 1.84 (s, 3H, p-Me), 1.91 (s, 3H, o-Me), 1.92 (s, 3H, o-Me), 1.98 (s, 3H, o-Me), 1.99 (s, 3H, o-Me), 2.10 (s, 3H, o-Me), 2.15 (s, 3H, o-Me), 2.23 (s, 3H, o-Me), 2.28 (s, 3H, o-Me), 6.59 (m, 2H, m-C<sub>6</sub>H<sub>2</sub>), 6.67 (m, 1H, m-C<sub>6</sub>H<sub>2</sub>), 6.75 (m, 7H), 6.80 (s, 1H, m-C<sub>6</sub>H<sub>2</sub>), 6.95 (d,  $J_{\rm HH} = 7.5$  Hz, 1H,  $p-C_6H_3$ ), 7.05 (t,  $J_{\rm HH} = 7.5$  Hz, 1H,  $p-C_6H_3$ ), 7.09 (t,  $J_{\rm HH} = 7.5$  Hz, 1H, p-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -3.82, -3.70 (Al-Me), 4.10 (Ge-Me), 20.69, 20.98, 21.56, 22.04, 22.46, 22.81, 22.88, 22.97, 23.66, 23.84 (p- and o-Me); 127.54, 128.29, 128.33, 128.52, 128.99, 129.14, 130.13, 130.25, 130.95, 131.06, 131.56, 132.25, 133.14, 134.78, 135.86, 135.91, 136.07, 136.12, 136.41, 136.56, 136.78, 138.41, 138.84, 139.20, 139.85, 142.12, 142.48, 143.88, 144.87, 145.47, 146.27, 147.35, 148.75, 150.83, 151.57 (Ar). IR: 2900 (br), 1600 (w), 1450 (s), 1370 (s), 1290 (w), 1250 (s), 1075 (br), 1010 (br), 840 (w), 790 (s), 710 (s), 550 (w, br), 350 (w), 275 (w).

(Ar<sup>Me<sub>6</sub></sup>)<sub>2</sub>Ge(Me)GaMe<sub>2</sub> (2). Ge(Ar<sup>Me<sub>6</sub></sup>)<sub>2</sub> (0.70 g, 1 mmol), dissolved in toluene (40 mL) and cooled to ca. -78 °C, was treated dropwise with a solution of GaMe<sub>3</sub> (0.115 g, 1 mmol) in toluene (20 mL). The reaction mixture was stirred and allowed to warm to room temperature overnight, which resulted in a color change from purple to colorless. The solvents were removed under reduced pressure, and the resulting white solid was recrystallized from pentane to give colorless crystals of 2. Yield: 0.588 g, 72%. Mp: 208 °C. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -0.30 (s, 3H, Ge-Me), -0.04 (s, 3H, Ga-Me), -0.01 (s, 3H, Ga-Me), 1.46 (s, 3H, p-Me), 1.65 (s, 3H, p-Me), 1.71 (s, 3H, p-Me), 1.86 (s, 3H, p-Me), 1.90 (s, 3H, o-Me), 1.91 (s, 3H, o-Me), 1.97 (s, 3H, o-Me), 1.98 (s, 3H, o-Me), 2.04 (s, 3H, o-Me), 2.09 (s, 3H, o-Me), 2.24 (s, 3H, o-Me), 2.27 (s, 3H, o-Me), 6.54 (s, 1H, m-C<sub>6</sub>H<sub>2</sub>), 6.61 (d,  $J_{\rm HH} = 7.5$  Hz, 1H, m-C<sub>6</sub>H<sub>3</sub>), 6.65 (d,  $J_{\rm HH} = 7.4$  Hz, 1H, m-C<sub>6</sub>H<sub>3</sub>), 6.67 (s, 1H, m-C<sub>6</sub>H<sub>2</sub>), 6.70 (s, 1H, m-C<sub>6</sub>H<sub>2</sub>), 6.72 (s, 1H, m-C<sub>6</sub>H<sub>2</sub>), 6.74 (m, 3H), 6.78 (s, 1H, m-C<sub>6</sub>H<sub>2</sub>), 6.79 (s, 1H, m-C<sub>6</sub>H<sub>2</sub>), 6.91 (d,  $J_{HH}$  = 7.5 Hz, 1H, m-C<sub>6</sub>H<sub>3</sub>), 7.03 (t,  $J_{HH}$  = 7.5 Hz, 1H, p-C<sub>6</sub>H<sub>3</sub>), 7.08 (t,  $J_{HH}$  = 7.5 Hz, 1H, o-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): 2.80, 3.49, 3.98 (M-Me, M = Ge, Ga), 20.52, 20.75, 21.35, 21.84, 22.18, 22.42, 22.69, 22.75, 23.22, 23.52 (p- and o-Me); 128.13, 128.21, 128.87, 129.02, 129.06, 130.08, 130.12, 130.69, 130.78, 131.11, 131.14, 131.23, 134.79, 135.67, 135.80, 136.12, 136.42, 136.45 136.60, 137.27, 137.48, 139.27, 139.53, 141.82, 142.07, 143.36, 143.38, 144.51, 145.27, 147.71, 148.52, 150.83, 151.13 (Ar). IR: 2900 (br), 1600 (w), 1450 (s)

1360 (s), 1290 (w), 1250 (w), 835 (s), 790 (s), 710 (s), 540 (w). (Ar<sup>Me<sub>6</sub></sup>)<sub>2</sub>Sn(Me)GaMe<sub>2</sub> (3). Sn(Ar<sup>Me<sub>6</sub></sup>)<sub>2</sub> (0.746 g, 1 mmol) was dissolved in toluene (40 mL) and cooled to ca. -78 °C. To this solution, GaMe<sub>3</sub> (0.126 g, 1.1 mmol) in toluene (20 mL) was added dropwise. The resulting mixture was stirred and allowed to warm to room temperature overnight. This resulted in a color change from purple to colorless at low temperature and then a further change to a pale purple at room temperature. The solvents were removed under reduced pressure, and the resulting white solid was recrystallized from pentane, giving a slightly purple solution and colorless crystals of 3. Yield: 0.469 g, 55%. Mp: Turns purple with increasing temperature; melts 156-158 °C. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -0.40 (t, <sup>2</sup>J<sub>HSn</sub> 40.8 Hz, 3H, Sn-Me), -0.04 (s, 6H, Ga-Me), 1.83 (s, 12H, o-Me), 1.92 (s, 12H, o-Me), 2.18 (s, 12H, p-Me), 6.72 (s, 4H, m- $C_6H_2$ ), 6.73 (s, 4H, m- $C_6H_2$ ), 6.76 (d,  $J_{HH} = 7.4$  Hz, 4H, m- $C_6H_3$ ), 7.09 (t,  $J_{\rm HH}$  = 7.5 Hz, 2H, p-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (150 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -4.04 (Sn-Me), 5.12 (Ga-Me), 20.76 (p-Me), 22.20 (o-Me), 22.74 (o-Me), 129.19, 129.55, 129.71, 129.80, 136.38, 136.51, 137.07, 143.55, 146.57, 150.84 (Ar). <sup>119</sup>Sn NMR (186 MHz,  $C_6D_6$ , 25 °C, ppm): -170. IR: 2900 (br), 2700 (w), 1440 (s), 1360 (s), 1290 (w) 1145 (w), 940 (w), 875 (w), 835 (w), 790 (w), 710 (s).

 $(Ar^{Me_6})_2Sn(Et)GaEt_2$  (4).  $Sn(Ar^{Me_6})_2$  (0.345 g, 0.462 mmol) was dissolved in toluene (35 mL) and cooled to ca. -78 °C. To this solution a 4-fold excess of GaEt<sub>3</sub> (0.286 g, 1.82 mmol) in toluene (15 mL) was added dropwise. The resulting mixture was stirred and allowed to warm to room temperature over 1 h, resulting in a pale

purple solution. Toluene and excess GaEt<sub>3</sub> were removed under reduced pressure to afford 4 as a white solid. Crystallization from pentane yielded colorless crystals from a pale purple solution. Yield: 0.3832 g, 91.9%. Mp: White solid gradually turns purple; melts 52–58 °C giving a purple liquid. <sup>1</sup>H NMR (600 MHz, PhMe-*d*<sub>8</sub>, 25 °C, ppm): 0.54 (m, 4H, Ga{CH<sub>2</sub>CH<sub>3</sub>}), 0.83 (t, *J*<sub>HH</sub> = 7.9 Hz, 3H, SnCH<sub>2</sub>CH<sub>3</sub>), 0.88 (t, *J*<sub>HH</sub> = 8.0 Hz, 2H, SnCH<sub>2</sub>CH<sub>3</sub>), 1.15 (t, *J*<sub>HH</sub> = 8.0 Hz, 6H, Ga{CH<sub>2</sub>CH<sub>3</sub>}), 1.81 (s, 12H, C<sub>6</sub>H<sub>2</sub>-Me), 1.90 (s, 12H, C<sub>6</sub>H<sub>2</sub>-Me), 2.18 (s, 12H, C<sub>6</sub>H<sub>2</sub>-Me), 6.68 (s, 4H, m-C<sub>6</sub>H<sub>3</sub>) 6.72 (s, 8H, m-C<sub>6</sub>H<sub>2</sub>), 7.09 (t, *J*<sub>HH</sub> = 7.5 Hz, 2H, *p*-C<sub>6</sub>H<sub>3</sub>). <sup>119</sup>Sn NMR (186 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -146. IR: 2900 (br), 2700 (w), 1450 (s), 1370 (s), 1250 (w) 1145 (w), 795 (m), 710 (m).

**Sn<sub>2</sub>{Sn(Me)Ar<sup>Me</sup>}]**<sub>3</sub> (5). Sn(Ar<sup>Me<sub>6</sub></sup>)<sub>2</sub> (0.746 g, 1 mmol) was dissolved in toluene (40 mL), and to this was added an excess of AlMe<sub>3</sub> (1.4 M in heptane, 1.6 mL, 2.2 mmol) dissolved in 20 mL of toluene dropwise at room temperature. The resulting solution was heated to ca. 85 °C and stirred overnight, yielding a pale red/purple solution. The solvents were removed under reduced pressure, and the resulting dark solid was extracted into hexanes. Dark purple crystals of 5 were produced at -28 °C. Yield: 13 mg. Mp: gradual decomposition above 250 °C, solid did not melt below 300 °C. IR: 2900 (br), 2700 (w), 1440 (s), 1365 (s), 1290 (w), 1250 (w), 1145 (w), 1075 (br), 1010 (br), 935 (w), 870 (w), 830 (w), 790 (s), 710 (s). UV–vis:  $\lambda_{max}$  560 nm.

 $\{Pb(Me)Ar^{Me_6}\}_2 (6). Method A. Pb(Ar^{Me_6})_2 (0.996 g, 1.194 mmol) was dissolved in toluene (40 mL) and cooled to ca. -78 °C. To this solution, AlMe<sub>3</sub> in toluene (15 mL) was added dropwise. The resulting solution was stirred and allowed to warm to room temperature overnight, which resulted in a color change from purple to deep red. A thin dull metal mirror was present on the inside of the flask wall. The solvents were removed under reduced pressure, and the resulting red solid was recrystallized from pentane. This resulted in two different crystal types which were separated by fractional crystallization to yield the deep red diplumbene (6) and the colorless alane (7). Yield: 0.135 g of {Pb(Me)Ar^{Me_6}}_2 + AlAr^{Me_6}Me_2, 12%. Method B. Pb(Ar^{Me_6})_2 (1.050 g, 1.25 mmol) was dissolved in$ 

Method B. Pb( $Ar^{Me_c}$ )<sub>2</sub> (1.050 g, 1.25 mmol) was dissolved in toluene and cooled to ca. -78 °C, and GaMe<sub>3</sub> (0.170 g, 1.5 mmol) in toluene was added dropwise. The resulting solution was stirred and allowed to warm to room temperature overnight, resulting in a color change from purple to deep red. The solvents were removed under reduced pressure, and the resulting red solid was recrystallized from pentane. This resulted in two different crystal types which were separated by fractional crystallization yielding the deep red plumbene (6) and the colorless gallane (8). Yield: 0.999 g of {Pb(Me)Ar<sup>Mec</sup>}<sub>2</sub> + GaAr<sup>Mec</sup>Me<sub>2</sub>, 82%.

Mp: 190–195 °C. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): 0.19 (s, 6H, Pb–Me), 2.09 (s, 12H, *p*-Me), 2.27 (s, 24H, *o*-Me), 6.75 (s, 8H, *m*-C<sub>6</sub>H<sub>2</sub>), 7.40 (t,  $J_{\rm HH}$  = 7.5 Hz, 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.51 (d,  $J_{\rm HH}$  = 7.5 Hz, 4H, *m*-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): 0.58 (Pb–Me), 21.10 (*p*-Me), 21.34 (*o*-Me), 126.21, 129.03, 134.62, 136.05, 136.85, 137.56, 147.45. <sup>207</sup>Pb NMR (105 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): 8428. IR: 2900 (br), 2700 (w), 1600 (w), 1450 (s), 1370 (s), 1255 (w), 1150 (w), 1015 (w), 840 (m), 790 (m), 715 (m). UV–vis:  $\lambda_{\rm max}$  466 nm.

Products 7 and 8, in addition to being obtained as a mixture with product 6, were synthesized by alternative routes to acquire pure products to facilitate spectroscopic characterization because they could not be completely separated from the mixtures formed with 5. These methods are given alongside the original isolation of a single-crystal product.

**AlAr**<sup>Me<sub>6</sub></sup>**Me**<sub>2</sub> (7). From the product mixture for the synthesis of (Pb  $Ar^{Me_6}$  Me)<sub>2</sub>, 6, via method A, AlMe<sub>2</sub>  $Ar^{Me_6}$ , 7, was separated via fractional crystallization until a single crystal of sufficient purity was obtained for crystallographic study.

For spectroscopic studies, 7 was synthesized via an alternative route as follows. A solution of  $Ar^{Me_6}$  Li (0.350 g, 1.09 mmol) in toluene (30 mL) was added dropwise to Me<sub>2</sub>AlCl (1.1 mL, 1.0 M in heptane) at ca. -78 °C. The resulting mixture was stirred and allowed to warm to room temperature overnight. The solvents were removed under reduced pressure, and the product was extracted with pentane. Crystallization at room temperature afforded 6 as a colorless crystalline solid. Yield: 0.397 g, 98%.

Mp: 123–126 °C. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -0.69 (s, 6H, Al-Me), 2.11 (s, 6H, p-Me), 2.16 (s, 12H, o-Me), 6.84 (s, 4H, m-C<sub>6</sub>H<sub>2</sub>), 7.03 (d,  $J_{\rm HH}$  = 7.6 Hz, 2H, m-C<sub>6</sub>H<sub>3</sub>), 7.34 (t,  $J_{\rm HH}$  = 7.5 Hz, p-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -7.07 (Al-Me), 21.10 (o-Me), 21.13 (p-Me), 125.47, 129.10, 129.38, 136.38, 137.37, 141.34, 148.82 (Ar-H). IR: 2900 (br), 2710 (w), 1600 (m), 1550 (w), 1445 (s), 1355 (s), 1250 (m), 1170 (w), 1070 (m), 1010 (m), 840 (m), 795 (s), 720 (m), 680 (w), 640 (w), 550 (w), 350 (br).

 $GaAr^{Me_6}Me_2$  (8). From the product mixture obtained by the Method B synthesis of (PbAr<sup>Me6</sup>Me)<sub>2</sub>, GaMe<sub>2</sub>Ar<sup>Me6</sup> was separated via fractional crystallization until a single crystal of sufficient purity was obtained for crystallographic study.

For spectroscopic studies, 8 was synthesized via an alternative route. GaMe<sub>3</sub> (0.300 g, 2.61 mmol) in pentane (10 mL) was cooled to ca. -100 °C using an ethanol/liquid nitrogen bath. This solution was treated dropwise with 0.5 equiv of GaCl<sub>3</sub> (0.229 g, 1.3 mmol) in pentane (20 mL). The resulting mixture was stirred and allowed to warm up overnight. The mixture was again cooled to -78 °C and treated dropwise with a slurry of Ar<sup>Me<sub>6</sub></sup>Li (1.24 g, 3.9 mmol) in toluene (25 mL). The mixture was again stirred and allowed to warm to room temperature overnight. The solvents were removed under reduced pressure, and the product was extracted with pentane (25 mL). Concentration to ca. 8 mL resulted in crystallization at room temperature, affording a colorless crystalline solid. Yield: 1.270 g, 74%

Mp: 124−126 °C. <sup>1</sup>Н NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): −0.26 (s, 6H, Ga-Me), 2.11 (s, 6H, p-Me), 2.14 (s, 12H, o-Me), 6.81 (s, 4H,  $m-C_6H_2$ ), 7.03 (d,  $J_{HH}$  = 7.5 Hz, 2H,  $m-C_6H_3$ ), 7.32 (t,  $J_{HH}$  = 7.5 Hz, 1H, p-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, ppm): -0.08 (Ga-Me), 21.01 (o-Me), 21.14 (p-Me), 125.97, 128.86, 128.89, 136.16, 137.16, 140.79, 147.04, 155.23 (Ar-H). IR: 2900 (br), 2720 (s), 1915 (w), 1850 (w), 1790 (w), 1760 (w), 1720 (w), 1695 (w), 1605 (s), 1550 (s), 1445 (br), 1365 (br), 1290 (w), 1250 (w), 1180 (s), 1150 (br), 1090 (w), 1080 (w), 1015 (br), 940 (br), 880 (w), 795 (s), 760 (s), 715 (s), 560 (s), 535 (s).

X-ray Crystallographic Data Collection. Crystals were removed from a Schlenk flask under an N2 stream and immediately immersed in Paratone oil. Single crystals were selected and placed on a plastic loop filament pin and placed on the diffractor under a cold N<sub>2</sub> stream (90 K). All crystallographic calculations were performed on a personal computer (PC) with an Intel i7 3.5 GHz processor and 8 GB extended memory. Data collections were based on a single component, processed with SAINT,<sup>61</sup> and absorption corrections were applied utilizing the program SADABS.<sup>62,63</sup> Structures were determined by direct methods using the program XT, and refinement of the structure was carried out using the program XL.<sup>63</sup> See Supporting Information for further details.

#### CONCLUSIONS

New routes to molecules with rare Ge-Al, Ge-Ga, and Sn-Ga bonds by the reaction of group 14 metalylenes with trimethylaluminum or trimethylgallium have been described. The reaction of  $Sn(Ar^{Me_6})_2$  and  $GaMe_3$  formed an equilibrium mixture of  $Sn(Ar^{Me_6})_2$ , GaMe<sub>3</sub>, and  $(Ar^{Me_6})_2Sn(Me)GaMe_2$ which could not be readily analyzed by <sup>1</sup>H NMR spectroscopy, but the analogous reaction of Sn(Ar<sup>Me<sub>6</sub></sup>)<sub>2</sub> and GaEt<sub>3</sub> was carried out to give 4, which was shown to have an equilibrium constant K and  $\Delta G$  of 8.09(6)  $\times 10^{-3}$  M and 11.8(9) kJ mol<sup>-1</sup> at 296 K. Unexpectedly, a rare singlet diradicaloid pentastanna-[1.1.1]propellane, 5, was obtained while attempting to synthesize a Sn-Al bonded species analogous to 3. It was found that the Pb-Al and Pb-Ga bonded species similar to 1-3 could not be synthesized via the same route owing to the reluctance of lead to become tetravalent. Instead, they reacted via a previously unknown metathesis process to form the new diplumbene 6, along with the corresponding aryldimethyl-group 13 compounds 7 and 8.

#### ASSOCIATED CONTENT

#### Supporting Information

Crystallographic information files for 1-8, thermal ellipsoid plot of the structure of 4, variable- temperature <sup>1</sup>H NMR spectra of 4, data used in van't Hoff analysis of the equilibrium of 4, infrared and NMR spectra for 1-8. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: pppower@ucdavis.edu.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We are grateful to the U.S. Department of Energy, Office of Basic Energy Sciences (FG02-07ER46475) for support of this work.

#### REFERENCES

(1) Davidson, P. J.; Lappert, M. F. J. Chem. Soc., Chem. Commun. 1973, 317.

- (2) Ya. Lee, V.; Sekiguchi, A. Organometallic Compounds of Low-Coordinate Si, Ge, Sn, and Pb: From Phantom Species to Stable Compounds; John Wiley & Sons: Chichester, 2010.
- (3) Power, P. P. Acc. Chem. Res. 2011, 44, 627-637.
- (4) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. Chem. Rev. 2009, 109, 3479-3511.
- (5) Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. J. Am. Chem. Soc. 2008, 130, 12268.
- (6) Power, P. P. Nature 2010, 463, 171-177.
- (7) Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. J. Am. Chem. Soc. 2014, 136, 3028-3031.
- (8) Rösch, L.; Erb, W. Angew. Chem., Int. Ed. 1978, 8, 631-632.
- (9) Wingleth, D. C.; Norman, A. D. Inorg. Chim. Acta 1986, 114, 191-196.
- (10) Habereder, T.; Knabel, K.; Nöth, H. Eur. J. Inorg. Chem. 2001, 5, 1127-1129.
- (11) Habereder, T.; Nöth, H.; Suter, M. Z. Naturforsch. 2009, 64b, 1387 - 1396.
- (12) Amberger, E.; Stoeger, W.; Hönigschmid. J. Organomet. Chem. 1969, 18, 77-81.
- (13) Schwan, F.; Mallela, S. P.; Geanangel, R. A. J. Chem. Soc., Dalton Trans. 1996, 4183-4187.
- (14) Linti, G.; Rodig, A. Chem. Commun. 2000, 127-128.
- (15) Linti, G.; Rodig, A.; Köstler, W. Z. Anorg. Allg. Chem. 2001, 627, 1465-1476 2001.
- (16) Richards, A. F.; Brynda, M.; Power, P. P. Organometallics 2004, 23. 4009-4011.
- (17) Weibel, A. T.; Oliver, J. P. J. Am. Chem. Soc. 1972, 94, 8590-8592.
- (18) Weibel, A. T.; Oliver, J. P. J. Organomet. Chem. 1974, 74, 155-166.
- (19) Green, S. P.; Jones, C.; Lippert, K.-A.; Mills, D. P.; Stasch, A. Inorg. Chem. 2006, 45, 7242-7251.
- (20) Rupar, P. A.; Jennings, M. C.; Baines, K. M. Can. J. Chem. 2007, 84, 141-147.
- (21) Jones, C.; Rose, R. P.; Stasch, A. Dalton Trans. 2008, 2871-2871.
- (22) Zeckert, K. Dalton Trans. 2012, 41, 14101-14106.
- (23) Wang, Y.; Ma, J. J. Organomet. Chem. 2009, 694, 2567.

<sup>(24)</sup> Peng, Y.; Guo, J. D.; Ellis, B. D.; Zhu, Z. L.; Fettinger, J. C.; Power, P. P. J. Am. Chem. Soc. 2009, 131, 16272-16282.

(25) Protchenko, A. V.; Birjkumar, K. H.; Dange, D.; Schwarz, A. D.; Vidovic, D.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. J. Am. Chem. Soc. **2012**, 134, 6500–6503.

- (26) Lips, F.; Fettinger, J. C.; Mansikkamäki, A.; Tuononen, H. M.; Power, P. P. J. Am. Chem. Soc. 2014, 136, 634–637.
- (27) Wang, X. P.; Zhu, Z. L.; Peng, Y.; Lei, H.; Fettinger, J. C.; Power, P. P. J. Am. Chem. Soc. 2009, 131, 6912.

(28) Lappert, M. F.; Miles, S. J. J. Organomet. Chem. 1981, 212, C4.
(29) Schager, F.; Goddard, R.; Seevogel, K.; Pörschke, K.-R. Organometallics 1998, 17, 1546-1551.

(30) Mahmoud, A-K. M.; Peter, H. B.; Lappert, M. F.; Nixon, J. F.; Uiterwood, P. Dalton Trans. 2008, 21, 2825–2831.

(31) Martin, D.; Soleilhavoup, M.; Bertrand, G. Chem. Sci. 2011, 2, 369–376.

(32) Brown, Z. D.; Guo, J.-D.; Nagase, S.; Power, P. P. Organometallics **2012**, 31, 3768–3772.

(33) Brown, Z. D.; Erickson, J. D.; Fettinger, J. C.; Power, P. P. Organometallics 2013, 32, 617–622.

(34) Goßler, C.; Kunzer, M.; Baum, M.; Wiemer, M.; Moser, R.; Passow, T.; Köhler, K.; Schwarz, U. T.; Wagner. *J. Microsyst. Technol.* **2013**, *19*, 655–659.

(35) Horigami, O.; Luhman, T.; Pande, C. S.; Suenaga, M. Appl. Phys. Lett. 1976, 28, 738-740.

(36) Fiedler, J.; Heera, V.; Skrotzki, R.; Herrmannsdörfer, T.; Voelskow, M.; Mücklich, A.; Facsko, S.; Reuther, H.; Perego, M.; Heinig, K.-H.; Schimdt, B.; Skorupa, W.; Gobsch, G.; Helm, M. *Phys. Rev.* **2012**, *B* 85, 134530–1–134530–10.

(37) Klinkhammer, K. W.; Fässler, T. F.; Grützmacher, H. Angew. Chem., Int. Ed. **1998**, 37, 124–126.

(38) Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M. Angew. Chem., Int. Ed. **1999**, 38, 187–189.

(39) Stürmann, M.; Saak, W.; Weidenbruch, M.; Klinkhammer, K. W. *Eur. J. Inorg. Chem.* **1999**, 579.

(40) (a) Phillips, A. D.; Hino, S.; Power, P. P. J. Am. Chem. Soc. 2003, 125, 7520-7521. (b) Hino, S.; Olmstead, M.; Phillips, A. D.; Wright,

R. J.; Power, P. P. Inorg. Chem. 2004, 43, 7346–7352.

(41) Dube, J. W.; Graham, C. M. E.; Macdonald, C. L. B.; Brown, Z. D.; Power, P. P.; Ragogna, P. J. *Chem.—Eur. J.* **2014**, *20*, 6739–6744.

(42) Shatunov, V. V.; Korlyukov, A. A.; Lebedev, A. V.; Sheludyakov, V. D.; Kozyrkin, B. I.; Orlov, V. Y. J. Organomet. Chem. 2011, 696, 2238-2251.

(43) Sita, L. R.; Bickerstaff, R. D. J. Am. Chem. Soc. 1989, 111, 6454–6456.

(44) Sita, L. R.; Kinoshita, I. J. Am. Chem. Soc. 1992, 114, 7024–7029.

(45) Nied, D.; Breher, F. Chem. Soc. Rev. 2011, 40, 3455-3466.

(46) Abu, M. Chem. Rev. 2013, 113, 7011-7088.

(47) Fischer, R. C.; Power, P. P. Chem. Rev. 2010, 110, 3877-3923.

(48) Stürmann, M.; Weidenbruch, M.; Klinkhammer, K. W.; Lissner, F.; Marsmann, H. Organometallics **1998**, *17*, 4425–4428.

(49) Arp, H.; Baungartner, J.; Marschner, C.; Zark, P.; Müller, T. J. Am. Chem. Soc. 2012, 134, 6409-6415.

(50) Rekken, B. D.; Brown, T. M.; Fettinger, J. C.; Lips, F.; Tuononen, H. M.; Herber, R. H.; Power, P. P. J. Am. Chem. Soc. 2013, 135, 10134–10148.

(51) Pyykkö, P.; Atsumi, M. Chem.-Eur. J. 2009, 15, 12770-12779.

(52) Purath, A.; Dohmeier, C.; Baum, E.; Köppe, R.; Schnöckel, H. Z. Anorg. Allg. Chem. 1999, 625, 2144–2148.

(53) Veith, M.; Frank, W. Angew. Chem., Int. Ed. 1985, 24, 223–224.
(54) Kempter, A.; Gemel, C.; Fisher, R. A. Inorg. Chem. 2008, 16, 7279–7285.

(55) Drost, C.; Hildebrand, M.; Lönnecke, P. Main Group Met. Chem. 2002, 25, 93.

(56) Davies, A. G. *Organotin Chemistry*, 2nd ed.; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, 2004; pp 306–307.

(57) Chen, W.; Twum, E. B.; Li, L.; Wright, B. D.; Rinaldi, P. L.; Pang, Y. J. Org. Chem. 2011, 77, 285–290.

(58) Hayashi, K.; Iyoda, J.; Shiihara, I. J. Organomet. Chem. 1967, 10, 81–94.

(59) Allen, L. C. J. Am. Chem. Soc. 1989, 111, 9003–9014.

(60) Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. Organometallics 1997, 16, 1920–1925.

- (61) SAINT (Version 8.32); Bruker AXS Inc.: Madison, WI, 2002.
- (62) Blessing, R. H. Acta Crystallogr. 1995, A51, 33-38.

(63) Sheldrick, G. M. SADABS, Siemens Area Detector Absorption

- Correction; Universität Göttingen: Göttingen, Germany, 2008.
- (64) Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112-122.