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Interaction of Multiple Bonded and Unsaturated Heavier Main Group Compounds with Hydrogen, Ammonia, Olefins, and Related Molecules

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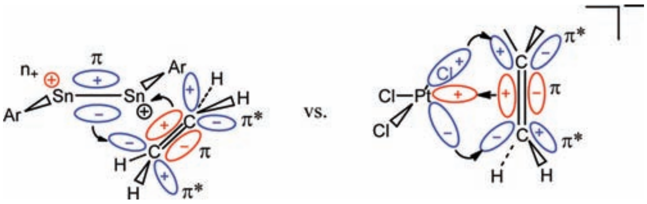
CONSPECTUS



We showed in 2005 that a digermyne, a main group compound with a digermanium core and aromatic substituents, reacted directly with hydrogen at 25 °C and 1 atm to give well-defined hydrogen addition products. This was the first report of a reaction of main group molecules with hydrogen under ambient conditions. Our group and a number of others have since shown that several classes of main group molecules, either alone or in combination, react directly (in some cases reversibly) with hydrogen under mild conditions. Moreover, this reactivity was not limited to hydrogen but also included direct reactions with other important small molecules, including ammonia, boranes, and unactivated olefins such as ethylene. These reactions were largely unanticipated because main group species were generally considered to be too unreactive to effect such transformations.

In this Account, we summarize recent developments in the reactions of the multiple bonded and other open shell derivatives of the heavier main group elements with hydrogen, ammonia, olefins, or related molecules. We focus on results generated primarily in our laboratory, which are placed in the context of parallel findings by other researchers. The close relationship between HOMO−LUMO separations, symmetry considerations, and reactivity of the open shell in main group compounds is emphasized, as is their similarity in reactivity to transition metal organometallic compounds.

The unexpectedly potent reactivity of the heavier main group species arises from the large differences in bonding between the light and heavy elements. Specifically, the energy levels within the heavier element molecules are separated by much smaller gaps as a result of generally lower bond strengths. In addition, the ordering and symmetries of the energy levels are generally different for their light counterparts. Such differences lie at the heart of the new reactions. Moreover, the reactivity of the molecules can often be interpreted qualitatively in terms of simple molecular orbital considerations. More quantitative explanations are accessible from increasingly sophisticated density functional theory (DFT) calculations.

We open with a short description of the background developments that led to this work. These advances involved the synthesis and characterization of numerous new main group molecules involving multiple bonds or unsaturated configurations; they were pursued over the latter part of the last century and the beginning of the new one. The results firmly established that the structures and bonding in the new compounds differed markedly from those of their lighter element congeners. The knowledge gained from this fundamental work provided the framework for an understanding of their structures and bonding, and hence an understanding of the reactivity of the compounds discussed here.

1. Introduction: Heavier Group 14 Element Alkyne Analogues, Related Group 13 Dimetallenes, and Other Low Valent Group 13 and 14 Element Species

The new millennium has seen major developments in multiple bonded heavier main group chemistry.[1] The synthesis and stabilization of heavier group 14 element alkyne analogues REER (E = Si−Pb, R = large organic or silyl substituent)[2] were a significant part of these advances. Beginning with the diplumbyne Ar*PbPbAr* (Ar* = C_6H_3-2,6(C_6H_2-2,4,6-Pr^i_3)$_2$) in 2000,[2d] stable tin,[2b] germanium,[2c] and silicon[2a,e] analogues had been prepared by 2004. This

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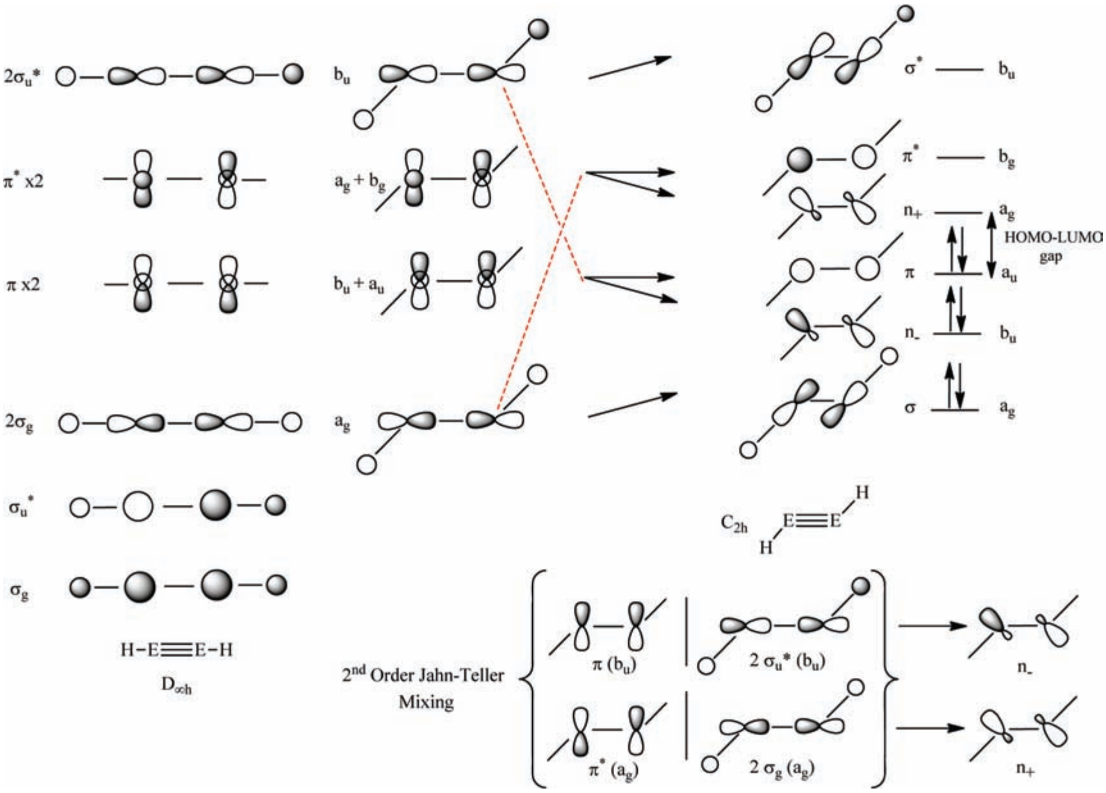
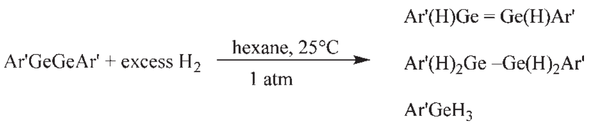


FIGURE 1. Trans-bending second order Jahn–Teller effects in H–E≡E–H (E = Si–Pb) species.

involved reduction of a precursor (monomeric or dimeric organo or silyl substituted element halides) by alkali metals or organoaluminum hydrides. Their synthesis had been foreshadowed by their singly and doubly reduced salts M_nREER (M = Li, Na or K; n = 1 or 2) in 1997[3] and by the germylyne complex (η^5-C_5H_5)$(CO)_2$MoGeC_6H_3-2,6-mesityl$_2$ in 1996.[4] The alkyne analogues have planar, trans-bent core structures with substantial deviation from linearity. The bending increases and the bond order decreases with increasing atomic number so that at lead the Pb–Pb bonding is essentially single. The bending in these compounds has been viewed[5] as a second order Jahn–Teller effect involving certain valence orbitals which are vibronically coupled through a degenerate symmetric bending mode which permits orbital mixing as shown in Figure 1. The bending can also be interpreted in terms of singlet diradical character especially in the case of the germanium and tin compounds where the bond order has been diminished to about two. These compounds are thus "missing" a bond and can be classified as non-Kekule singlet diradical species.[6] Currently, about 20 stable examples have been isolated or structurally characterized.[1,7,8] The tin alkyne analogues can exist as two isomers in the solid state and five of the seven structurally characterized distannynes feature structures with short tin–tin bonds near 2.65 Å and a bending angle near 124°, whereas two (having –SiMe_3 or –GeMe_3 para-substituents on the central aryl ring of the terphenyl) have tin–tin distances near 3.06 Å and a bending angle near 98°.[8] The structures of the latter resemble that of the lead species Ar*PbPbAr* (Pb–Pb–C = 94.26(4)°; Pb–Pb = 3.1881(1) Å) and have single bonds. Two isomeric forms are possible because there is a very small energy difference (ca. 5 kcal mol^{-1}) between them that allows the structures to be affected by packing forces.[6,9] In solution, by electronic spectroscopy, all distannynes are multiple bonded. Only multiple bonded isomers have been observed for the digermynes both in solution and the solid state consistent with calculations that showed that they were the more stable by ca. 15 kcal mol^{-1}.[21] This is too large to allow significant structural changes as a result of packing forces.

The chemistry of stable compounds with multiple bonds between the heavier group 13 metals is less developed than that of their group 14 neighbors.[1,10,11] Group 13 M(I) metal–metal bonded clusters have been known for over 20 years.[12] The metals have a coordination number ≥ 4 which saturates the metal valence orbitals. Even in the dimers $[M\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$ (M = In or Tl)[13] the ligands are η^5-bound which leaves no valence orbitals available for further interactions. The M–M bonds are weak as evidenced by long (>3.6 Å) M–M distances. Our interest stemmed from attempts to synthesize

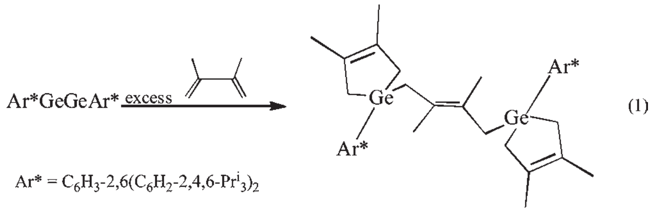
SCHEME 1. Reaction of the Digermyne Ar′GeGeAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$) with H_2 under Ambient Conditions



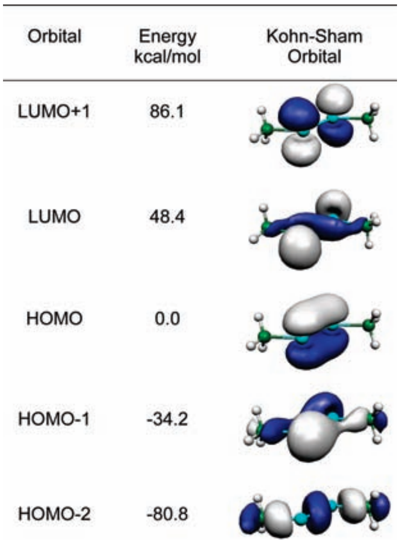
low-coordinate species with multiple bonds between heavy group 13 elements. It was shown that the large Ar* terphenyl substituent stabilized the highly colored, monomeric :InAr* in which the metal had a nonbonded pair and two unoccupied valence p-orbitals. In 2002, it was shown that the slightly less crowding Ar′ ligand (Ar′ = C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$) permitted dimerization to afford the In−In bonded Ar′InInAr′ which had a trans-bent structure and a nominal double bond with an In−In distance of 2.9786(5) Å.[15] It was also shown that its gallium and thallium analogues Ar′GaGaAr′ and Ar′TlTlAr′ had trans-bent, planar, core structures with Ga−Ga and Tl−Tl distances of 2.6268(7) and 3.0936(8) Å.[15] All three dimers were to varying degrees dissociated to monomers in hydrocarbons. The use of extremely large terphenyls such as C_6H-2,6(C_6H_2-2,4,6-Pr^i_3)$_2$-3,5-Pr^i_2 (abbreviated Ar*-3,5-Pr^i_2) was shown to stabilize monomers featuring one-coordinate gallium in the solid state.[16] Attempts to synthesize the dimer Ar′AlAlAr′ led to a reaction with solvent toluene to give a [2 + 4] cycloaddition product.[17a] Apparently, the putative Ar′AlAlAr′ species, which can be reduced to form Na_2Ar′AlAlAr′,[17b] has extremely high reactivity partly as a result of its singlet diradical character.[18] The dimetallenes react[14,15c,19] with a large variety of reagents to give transition metal complexes,[20,14] imides,[21] phosphinidenes,[22] or chalcogenide derivatives.[23]

2. Reactions with Saturated Small Molecules

The low coordination numbers (1 or 2) of group 13 and group 14 dimers, their deep colors, and their singlet diradical character[6,18] suggested high reactivity. An early investigation in 2002 showed that the stable digermyne Ar*GeGeAr* readily underwent a cyclization with 2,3-dimethy1,3-butadiene to give the product depicted in eq 1.[24]



In 2004, Wiberg et al. showed that the quasi-stable disilyne RSi≡SiR (R = SiMe(SiBu^t_3)$_2$) reacted with ethylene and butadiene to give [2 + 2] and [2 + 4] addition products.[2e] Also Sekiguchi et al. have reported that his stable disilyne RSi≡SiR (R = $SiPr^i${CH($SiMe_3$)$_2$}$_2$) reacted stereospecifically with cis and trans but-2-ene.[25]



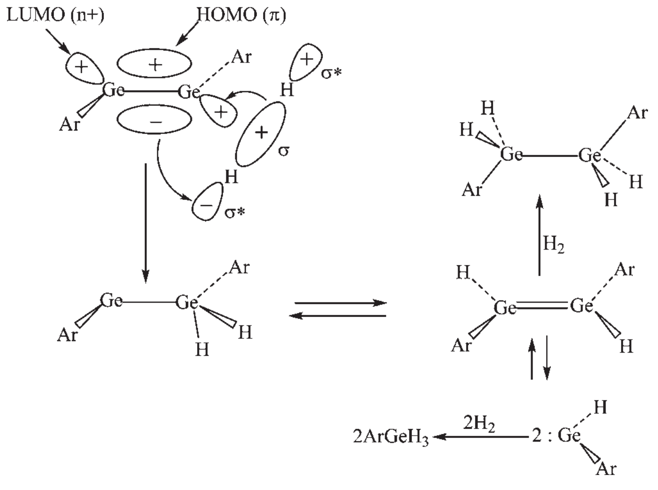
Orbital	Energy kcal/mol	Kohn-Sham Orbital
LUMO+1	86.1	
LUMO	48.4	
HOMO	0.0	
HOMO-1	-34.2	
HOMO-2	-80.8	

FIGURE 2. Illustration of the Kohn−Sham valence orbitals for the model species MeGeGeMe.[28]

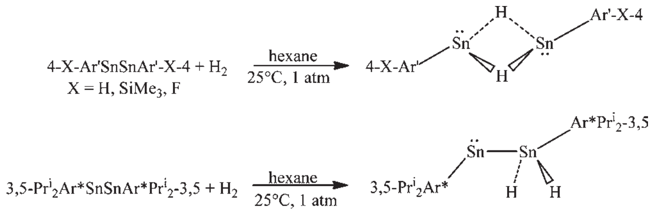
A wide-ranging investigation of the chemical properties of the digermynes and distannynes showed that they were highly reactive. This prompted testing of their reactivity with saturated molecules of which the simplest example is hydrogen.[26] Although no reactions had been reported between any main group molecule and hydrogen under ambient conditions, Himmel and Schnöckel[27] calculated that HGe≡GeH exhibited a heat of hydrogenation (ΔH^{θ}_{R} = ca. −250 kJ mol^{-1}) to give H_2GeGeH_2. This displayed a $\Delta H^{\theta}_{R} = -150$ kJ mol^{-1} when reacted with further equivalent of hydrogen to give H_3GeGeH_3. We discovered that the digermyne Ar′GeGeAr′ reacted readily at 25° and one atm to give a mixture of products as shown in Scheme 1.[26]

The addition of 1, 2, or 3 equiv of H_2 produced different ratios of the products in Scheme 1. With excess H_2, only Ar′(H)$_2$GeGe(H)$_2$Ar′ and Ar′GeH_3, were obtained in an approximately 2:1 ratio. The appearance of the mononuclear germane Ar′GeH_3 in the products indicated cleavage of the Ge−Ge bond which may occur via partial dissociation of the digermene Ar′(H)Ge=Ge(H)Ar′ to germylene, :Ge(H)Ar′, monomers in solution. H_2 may then add to :Ge(H)Ar′ to yield the monogermane Ar′GeH_3. The initial step involves the interaction of H_2 with the frontier orbitals at one of the germanium atoms Ar′GeGeAr′. Some of the calculated valence orbitals for the model species MeGeGeMe are illustrated in Figure 2 where it can be seen that the

SCHEME 2. Activation of H_2 by a Digermyne



SCHEME 3. Reaction of H_2 with Various Distannynes (Ar′-4-X = C_6H_2-2,6(C_6H_3-2,6-Pr^i_2)$_2$-4-X Where X = H (i.e., Ar′), $SiMe_3$, or F) 3,5-Pr^i_2Ar* = C_6H-2,6(C_6H_2-2,4,6-Pr^i_3)$_2$-3,5-Pr^i_2)



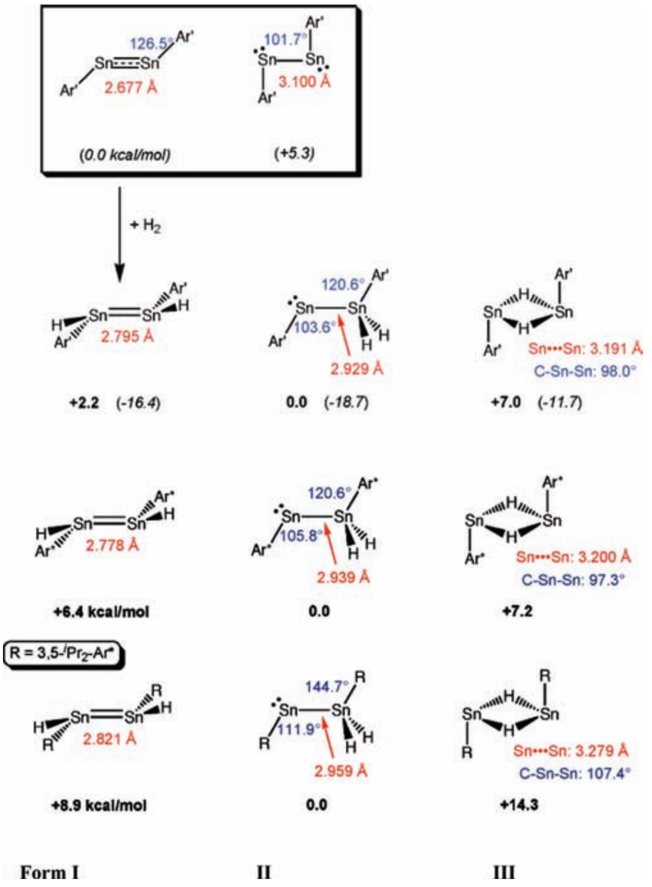


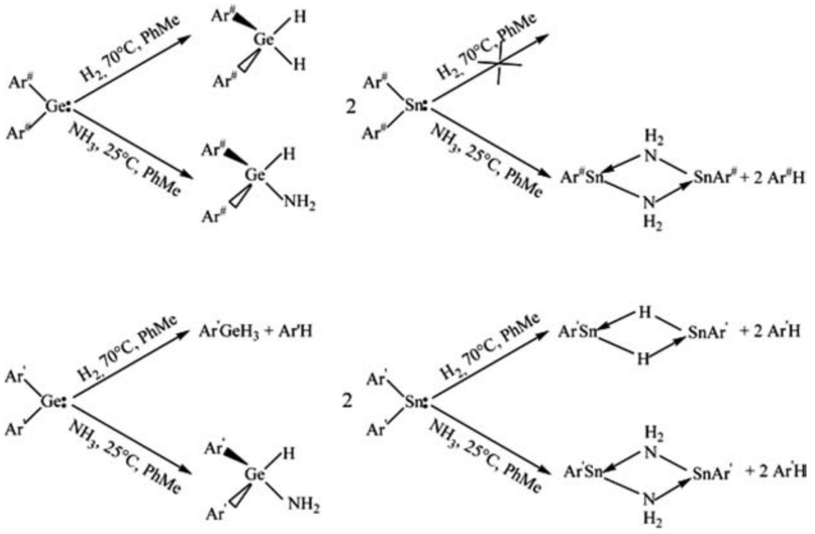
FIGURE 3. Calculated relative energies and selected geometric parameters for various isomer forms of (Ar′SnH)$_2$, (Ar*SnH)$_2$, and [(3,5^{i}Pr$_2$−Ar*)SnH]$_2$ at the B3W91. Numbers in parentheses refer to the stability of the (Ar′SnH) hydrides relative to Ar′SnSnAr′.

HOMO−LUMO energy separation is less than 50 kcal mol^{-1}.[28] A possible reaction sequence is thus shown in Scheme 2 where H_2 is activated synergistically via interaction of its σ and σ^* orbitals with the HOMO (π) and LUMO (n_+) of the digermyne (cf. Figure 1). This scheme gives Ar′GeGe(H)$_2$Ar′ initially which then rearranges to its symmetric isomer, Ar′(H)GeGe(H)Ar′. The unsymmetric Ar′GeGe(H)$_2$Ar′ was stabilized as the adduct Ar′(PMe$_3$)GeGe(H)$_2$Ar′.[29] Calculations[30] on the distannyne/H_2 reaction indicate a similar initial activation pathway in which the unsymmetric Ar′SnSn(H)$_2$Ar′ is generated initially. However, neither a distannene nor a distannane nor a monostannane product was seen. Instead, for most terphenyl substituents, a symmetrically bridged Sn(II) hydride structure of the type ArSn(μ-H)$_2$SnAr was isolated. With very bulky terphenyl groups such as C_6H-2,6(C_6H_3-2,6-Pr^i_2)$_2$-3,5-Pr^i_2 (Ar*-3,5-Pr^i_2), the unsymmetric stannylstannane 3,5-Pr^i_2Ar*SnSn(H)$_2$Ar*-3,5-Pr^i_2 can be obtained (Scheme 3).[31]

More detailed investigations[32] showed that the tin hydrides could also be synthesized by reduction of aryl tin halide precursors with a variety of reducing agents. Calculations (Figure 3) showed that as the bulk of the substituents increased the bridged form (III) and the distannene form (II) became more disfavored. Oddly, only the symmetric Ar′Sn(μ-H)$_2$SnAr′ and Ar*Sn(μ-H)$_2$SnAr* are seen in the crystal phase even though they are calculated to be the least stable (albeit by only ca. 7 kcal mol^{-1}) of the three structural isomers. The apparent inconsistency is probably due to packing forces which can favor the symmetrically bridged isomers. The existence of isomeric forms of the hydrides is unique to the tin species and mirrors earlier findings on related tin compounds with small organic substituents, such as Me or Ph instead of hydrogen, which can also have unsymmetric structures.[33]

In parallel work, Stefan and Bertrand showed that hydrogen could be activated under mild conditions by phosphine boranes (reversibly)[34] and also by carbenes[35] which could also activate ammonia. The unifying theme of these results and ours was that the activation occurred by the use of donor and acceptor orbitals in a synergistic fashion at one or more main group elements (B, C, P, Ge, or Sn). In this sense,

SCHEME 4. Summary of the Reactions of EAr_2 (E = Ge, Sn; Ar = $Ar^\#$ (C_6H_3- 2,6-(C_6H_2-2,4,6-Me_3)$_2$) or Ar′ (C_6H_3- 2,6-(C_6H_3-2,6-$^iPr_2$)$_2$)) with H_2 and NH_3



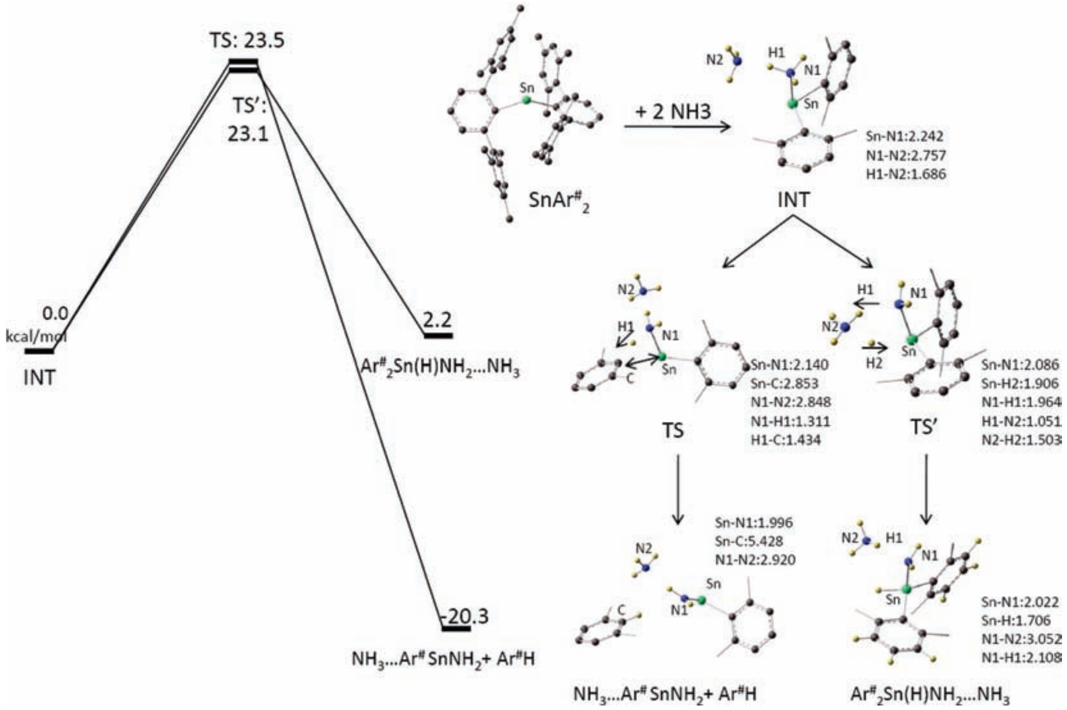


FIGURE 4. Calculated energy and drawings of intermediates and transition states with selected distances (Å) and angles (deg) for the reaction of $SnAr^\#_2$ ($Ar^\#$ = C_6H_3-2,6(C_6H_2-2,4,6−Me_3)$_2$) with NH_3 at the B3PW91 level.

the activation resembles that of H_2 with transition metal complexes where interactions with d-orbitals (rather than s- and p-orbitals) effect activation.

We also investigated the reactivity of other main group molecules with hydrogen. Divalent germylene, stannylene, and plumbylenes were already available in our laboratory,[36] and their reactions with H_2 or NH_3 afforded considerable variation in behavior as shown in Scheme 4.[37] Treatment of the germylene $GeAr_2^\#$ ($Ar^\#$ = C_6H_3-2,6(C_6H_2-2,4,6−Me_3)$_2$) with H_2 or NH_3 afforded the tetravalent products $Ar_2^\#GeH_2$ and $Ar_2^\#Ge(H)NH_2$ exclusively. For the bulkier Ar′ substituted $GeAr_2'$, treatment with H_2 yielded $Ar'GeH_3$ with Ar′H elimination whereas the reaction with NH_3 yielded $Ar_2'Ge(H)NH_2$ in quantitative yield. In contrast, the reactions of $SnAr_2^\#$ and $SnAr_2'$ with H_2 or NH_3 yielded only divalent products with $Ar^\#H$ or Ar′H elimination. Oddly, no reaction between hydrogen and $SnAr_2^\#$

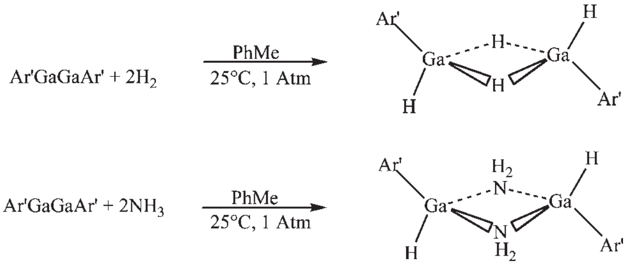
was observed up to 70 °C in toluene. The more crowded $SnAr_2'$ gave the symmetrically bridged $Ar'Sn(\mu\text{-}H)_2SnAr'$ which was identical to that obtained by the reaction of H_2 with Ar′SnSnAr′ described above. Reaction with deuterium afforded $Ar'Sn(\mu\text{-}D)_2SnAr'$ with elimination of Ar′D. The reactions between NH_3 and either $SnAr_2^{\#}$ or $SnAr'_2$ gave the symmetrically bridged parent amido products $Ar^{\#}Sn(\mu\text{-}NH_2)_2SnAr^{\#}$ or $Ar'Sn(\mu\text{-}NH_2)_2SnAr'$ with $Ar^{\#}H$ or Ar′H elimination.

Density functional theory (DFT) calculations of the reactions of H_2 with EAr_2 (E = Ge or Sn) showed that they initially proceed via interaction of the σ orbital of H_2 with the 4p(Ge) or 5p(Sn) orbital with back-donation from the Ge or Sn lone pair orbital to the H_2 σ^* orbital (Figure 4).[38] The subsequent reaction proceeds by an oxidative addition or a concerted pathway. The data showed that the bond strength differences between Ge and Sn, as well as greater nonbonded electron pair stabilization, for tin were in general more important than steric factors in determining the product obtained. The calculations indicated that $Ar^{\#}{}_2GeH_2$ or Ar′GeH were thermodynamically preferred with a further reaction between the latter and H_2 yielding $Ar'GeH_3$. For the reactions of NH_3 with EAr_2 (E = Ge or Sn; Ar = $Ar^{\#}$ and Ar′), the divalent $ArENH_2$ products were also calculated to be the most stable for both Ge or Sn. However, the tetravalent amido species $Ar_2Ge(H)NH_2$ was obtained for kinetic reasons. The reactions with ammonia differed from those with H_2 in that they involved two ammonia molecules in which the lone pair of one NH_3 becomes associated with the empty 4p or 5p orbital while a second NH_3 solvates the complexed NH_3 via an intermolecular N−H−N interaction.

Computations for the reaction of the group 13 species M_2H_2 (M = Al or Ga) with H_2 to give H_2MMH_2 showed that the heats of reaction are negative which tends to support the view that the addition of H_2 to isolable dimetallenes should also be favored.[27] We found that the H_2 reacted (Scheme 5) at ca. 25 °C and 1 atm with toluene solutions of Ar′GaGaAr′ to produce $Ar'(H)Ga(\mu\text{-}H)_2Ga(H)Ar'$ in 62% yield.[38] Structural and spectroscopic data showed that the structure was centrosymmetric with two bridging and a terminally bound hydrogen at each gallium. Attempts to synthesize this dihydride by reduction of $Ar'GaCl_2$ with hydride sources such as $(Bu^tAlH)_2$, NaH, $LiBH_4$, and $LiBHEt_3$ afforded a mixture of products which did not contain the target dihydride species.

Similarly the reaction of Ar′GaGaAr′ with liquid NH_3 at ca. −78 °C afforded a 73% yield of $Ar'(H)Ga(\mu\text{-}NH_2)_2Ga(H)Ar'$ in which gallium has inserted into an N−H bond of ammonia. The galliums are bridged symmetrically by two NH_2 moieties and the hydrogens are terminally bound at each gallium.

SCHEME 5. Reaction of Ar′GaGaAr′ ($Ar' = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}Pr^i{}_2)_2$ with H_2 and NH_3



4. Reactions with Olefins and Related Unsaturated Molecules

The early studies on the ditetrelynes showed that they reacted with several unsaturated molecules including alkynes, nitriles, azides, and N_2O as well as some diolefins.[22,24] Wiberg et al. showed that the quasi-stable disilyne R*Si≡SiR* ($R^* = SiMe(SiBu^t{}_3)_2$) reacted with the parent olefin ethylene below room temperature.[2e] The stable disilyne RSi≡SiR ($R = SiPr^i\{CH(SiMe_3)_2\}_2$) has also been shown to react with some mono-olefins, e.g., cis and trans butenes.[25]

The facile reaction[24] of Ar*GeGeAr* with 2,3-dimethyl-1,3-butadiene suggested that reactions with olefins should be feasible for the less bulky ditetrelynes Ar′GeGeAr′ and Ar′SnSnAr′. We treated a green toluene solution of Ar′SnSnAr′ with ethylene at 25 °C and 1 atm pressure.[39] This produced an immediate color change from green to amber. To our surprise, workup involving the reduction of the solvent volume under reduced pressure (to induce product crystal growth), restored the original green color. Moreover, treatment of the solution with ethylene regenerated the amber color which persisted if the solution was stored under ethylene. Storage of the solution under ethylene at ca. −18 °C yielded crystals of the ethylene adduct as yellow plates. X-ray crystallography showed that the distannyne had complexed two ethylenes as shown in Figure 5. The two CH_2CH_2 units are $\eta^1,\eta^1{:}\mu_2$ bound to the ditin moiety in a *Z* fashion in the two structurally similar, but crystallographically independent, molecules to afford a 1,4-distannabicyclo[2.2.0]butane core structure. It can be seen that the terphenyl ligands are in the *Z* configuration with Sn−Sn−C(ipso) angles of 163.2(1.2)° and tin−tin distances of 2.886(6) Å. The average $Sn{-}CH_2$ bond length is 2.19(2) Å which is indistinguishable from the SnC(Ar′) distance. The C−C bond distance within the CH_2CH_2 units averages 1.54(5) Å which is typical for a C−C single bond. The structure thus has C−C, Sn−C, and Sn−Sn bond lengths in the $\{C(ipso)\}Sn_2(CH_2CH_2)_2$ cores indicated single bonding. Furthermore, the ^1H, ^{13}C, and ^{119}Sn NMR data supported this conclusion. Nonetheless, both complexes

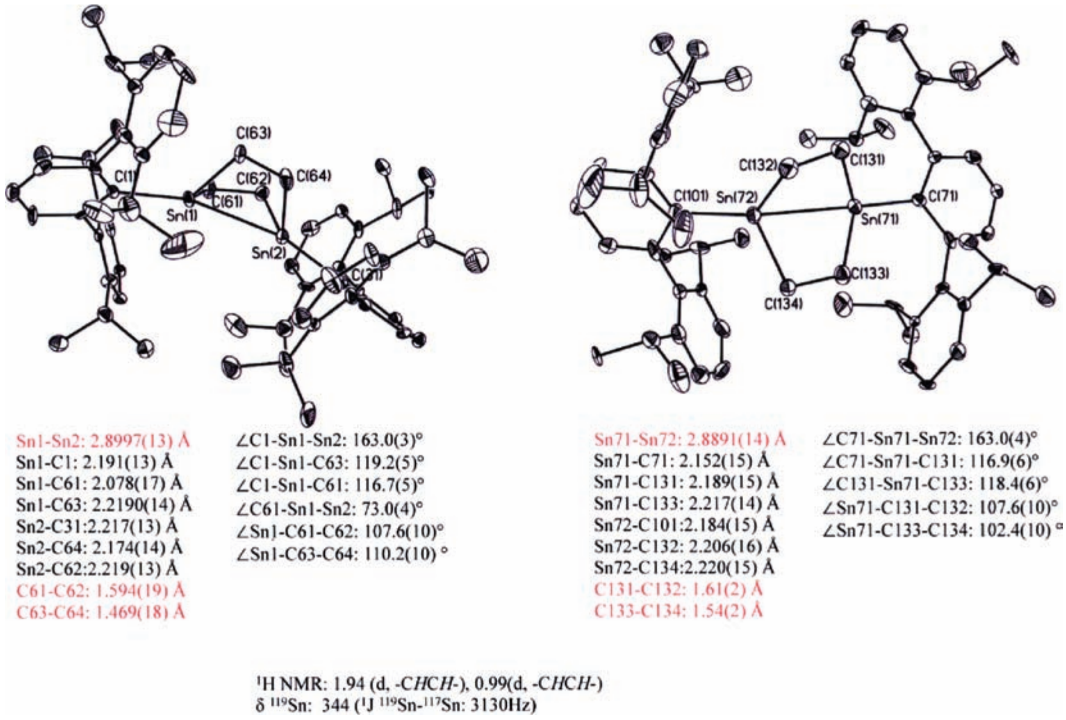
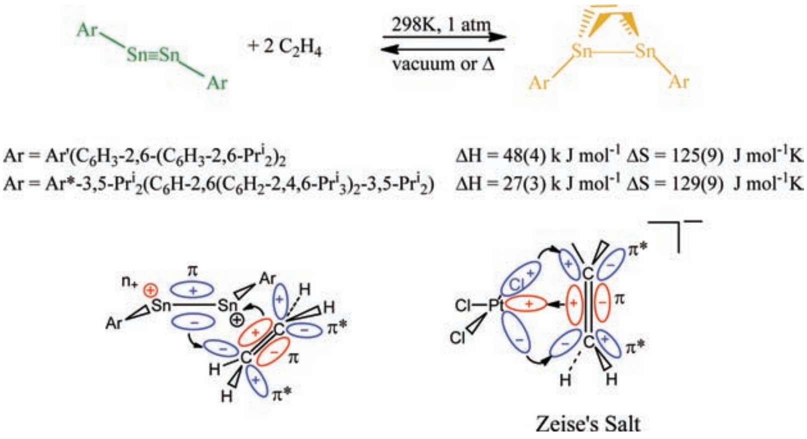


FIGURE 5. Structure of Ar′SnSnAr′$(C_2H_4)_2$ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$Pr^i_2)_2$ (two molecules per unit cell).

SCHEME 6. Reversible Reactions of Distannynes with Ethylene

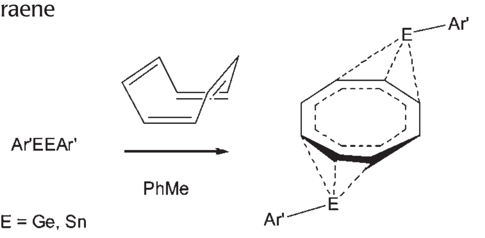


readily dissociate ethylene. A van't Hoff analysis of VT ^{1}H NMR spectra afforded relatively small molar enthalpies of association of -48 and -27 kJ mol^{-1} for the Ar′SnSnAr′$(C_2H_4)_2$ and 3,5-Pr^iAr*SnSnAr*-3,5-$Pr^i_2(C_2H_4)_2$ complexes (Scheme 6). DFT calculations on the model species PhSnSnPh$(C_2H_4)_2$ reproduced the core structural parameters and afforded a more negative ΔH_{assn} of -133 k J mol^{-1} which can be rationalized on the basis of the reduced steric crowding in the model complex. The apparent paradox of weak complexation in the face of slight elongation of the core bonds lengths can be accounted for, at least in part, on the basis of their distorted geometries which suggest considerable internal strain energy. It thus seems that the energy gained in the formation of four Sn–C σ-bonds is in approximate balance with the loss of two ethylene C–C π-bonds plus the increase in strain energy. As a result, the equilibrium in Scheme 6 is strongly affected by the entropic $T\Delta S$ factor so that relatively small physical changes can induce rapid dissociation of the ethylenes. Because of this internal strain, the distannyne–ethylene complexes need just a small outside stimulus (e.g., gentle heating or vacuum) to dissociate and it is noteworthy that propene did not display any olefin complex formation due to the slight increase in steric hindrance. DFT calculations on the Ar′SnSnAr′/ethylene showed that the initial interaction involved one of the tin atoms as illustrated in Scheme 6 which shows a synergic interaction between the n_+(LUMO) and π(HOMO) orbitals of ethylene. The calculations also showed that the subsequent steps (which bear a similarity to those reported by Sekiguchi et al. for the stereospecific interaction of his disilylyne with 1 equiv of a cis or trans but-2-ene)[25] in the formation of the adducts involved essentially zero activation barriers. Investigation of the corresponding reactions of ethylene and norbornadiene with Ar′GeGeAr′ resulted in the isolation of products analogous to those observed for Ar′SnSnAr′ but no dissociation of the olefin was apparent at temperatures below their decomposition points.

More recent investigations have uncovered further reactions with olefins. Treatment of Ar′MMAr′ (M = Ge or Sn) with COT (1,3,5,7-cyclooctatetraene) results in complete cleavage of the M–M multiple bonds to give sandwich complexes as shown in Scheme 7.[40]

In this reaction, the COT rings have been reduced to afford an almost planar $C_8H_8^{2-}$ 10-π aromatic ring for which the spectroscopic and structural properties are consistent with π-electron delocalization. However, the germanium inverse sandwich compound isomerized in solution[40b] to afford a digermanium substituted analogue of the hydrocarbon molecule hypostrophene as illustrated in Scheme 8. VT ^{1}H NMR studies yielded an activation enthalpy near 15 kcal mol^{-1}. Upon heating this above 120 °C, the inverted sandwich structure was regenerated. For the tin system, the inverse sandwich structure alone is observed under analogous conditions.

SCHEME 7. Multiple Bond Cleavage of a Distannyne or Digermyne by Cyclooctatetraene



- Fluxional behavior, single COT resonance:

^{1}H NMR at δ/ppm 5.36 (**Sn**)	5.32 (**Ge**)	free COT 5.79	Li_2COT 5.73
^{13}C NMR at δ/ppm 96.4 (**Sn**)	100.0 (**Ge**)	free COT 132.4	Li_2COT 87.5

The mechanism of this reversible rearrangement remains under computational study (in collaboration with G. Merino), but it is a possibility that the reaction initially involves interaction in a [2 + 2] fashion of the dimetallyne with a double bond from the COT ring as shown in Scheme 9. The heavier ditetrelene double bond of the [2 + 2] product may then dissociate to give a digermylene species and generate the inverse sandwich product in which each EAr′ fragment is complexed on opposite sides of the COT ring as observed in both the tin and germanium (kinetic) products.

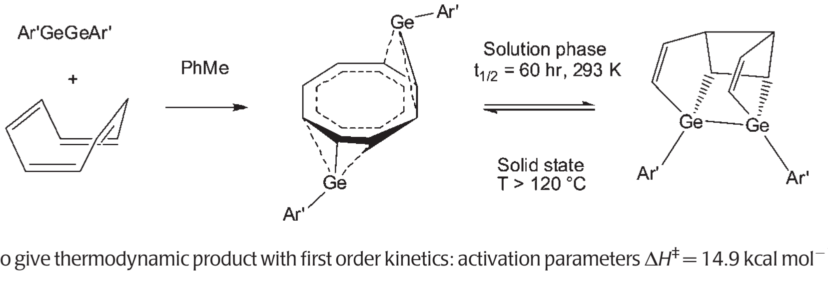
Current work involves the reactions of a wider variety of olefins with unsaturated heavier main group molecules. The latter include the group 13 element dimetallenes such as the earlier mentioned digallene Ar′GaGaAr′, and this species has already been shown to display a higher reactivity with a wider variety of olefins than its group 14 counterpart Ar′EEAr′ (E = Ge or Sn). Currently, the only reactions with unsaturated hydrocarbons that have been reported involve 2,3-dimethyl-1-3-butadiene which affords an unusual 1,6-digalla-2,3,8,9-tetramethylcyclodeca-3,8-diene ring (Scheme 10).[41] In addition, it was shown that Ar′GaGaAr′ reacts with phenyacetylene to afford the unsaturated digallacyclohexadiene which can be readily reduced by potassium to give a delocalized quasi-aromatic digallatabenzene ring.[42]

However, Ar′GaGaAr′ reacts with ethylene, propene, as well as a variety of other olefins both cyclic and noncyclic. Details of these reactions will be reported in the near future.

5. Reactions with Other Unsaturated Molecules

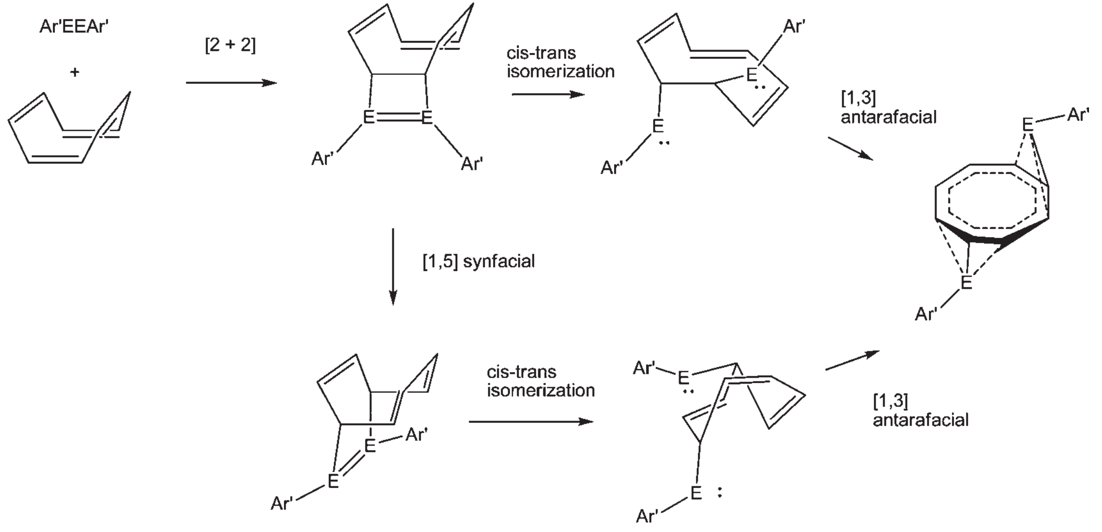
Both the digermyne Ar′GeGeAr′ and distannyne Ar′SnSnAr′ reacted with isocyanides ButNC or MesNC to afford the products as shown in Scheme 11.[20,43]

SCHEME 8. Reversible Isomerization of (Ar′Ge)$_2$(μ_2-η^2:η^2-cot) Occurs with C–C and Ge–Ge Multiple Bond Cleavage[a]

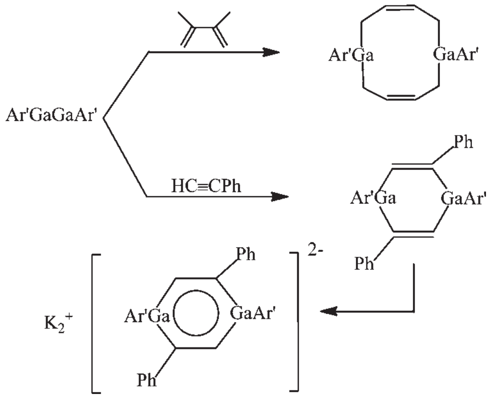


[a] Isomerization occurs in solution to give thermodynamic product with first order kinetics: activation parameters $\Delta H^{\ddagger} = 14.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -6.2$ cal mol^{-1} K^{-1}.

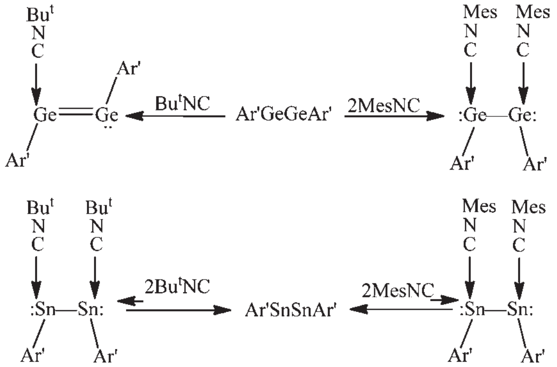
SCHEME 9. Possible Route to Group 14 Element Inverse Sandwich Compounds



SCHEME 10. Reaction of Ar′GaGaAr′ with 2,3-Dimethyl-1,3-butadiene or Phenylacetylene and the Reduction of the Latter Product to Give a Delocalized Digallatabenzene



SCHEME 11. Reactions of Ar′MMAr′ (M = Ge or Sn) with Isonitriles



The reaction of Bu^{t}NC with Ar′GeGeAr′ forms the 1:1 adduct Ar′GeGeAr′(CNBu^t) only. The isocyanide binds to one of the germaniums in the $Ge_2\{C(ipso)\}_2$ core plane and not perpendicular to it as would be expected if it bonded to a π^* orbital. Moreover the Ge–Ge bond distance increases only slightly from 2.2850(6) to 2.3432(9) Å. This finding is entirely consistent with the MO picture shown in Figure 2 where the LUMO to which the isocyanide binds is only slightly bonding and lies in the $Ge_2\{C(ipso)\}_2$ plane. In contrast, use of the essentially two-dimensional MesNC: permitted binding of a second isocyanide which interacts with lowest energy orbital available, the LUMO+1. This produces a large increase (>0.4 Å) in the Ge–Ge bond length to 2.6626(8) Å consistent with the antibonding character of the orbital.

The less crowded distannyne complexed two equiv. of both Bu^{t}NC: and MesNC:.[43] Attempts to synthesize 1:1 complexes were unsuccessful. The 2:1 complexes were unstable to dissociation in toluene at room temperature although they can be isolated and structurally characterized at low temperature. The complexes featured relatively long Sn–Sn bonds of 2.928(2) Å for Ar′SnSnAr′(CNBu^t)$_2$ and 3.0412(3) Å for Ar′SnSnAr′(CNMes)$_2$ consistent with Sn–Sn single bonds. They were isolated as red crystals but when dissolved in hexane at room temperature they gave a green solution that displayed two absorptions at 410 and 597 nm, characteristic of the $\pi \rightarrow n_+$ and $n_- \rightarrow n_+$ transitions of Ar′SnSnAr′. Cooling the solution to ca. −40° restored the red color (absorption at 510–520 nm) and van't Hoff analysis of the VT ^{1}H NMR spectra afforded $\Delta H_{assn} = -25(3)$ and $-127(4)$ kJ mol^{-1} for the Bu^{t}NC and MesNC adducts, with the difference being attributable to the higher steric requirement of the Bu^{t}NC which promotes dissociation. Coordination occurred in the empty 5p orbital perpendicular to the coordination plane. Sekiguchi[44] and co-workers showed that the addition of the nitrile Me_3SiCN to his disilyne RSiSiR ($R = Si\{CH(SiMe_3)_2\}_2Pr^i$) gave the bis(isonitrile) adduct RSiSiR-$(CNSiMe_3)_2$ as a coproduct which probably arises from the existence of the Me_3SiNC in equilibrium with Me_3SiCN.

6. Summary and Future Prospects

The stable multiple bonded and open shell species discussed above possess unique reactivity in many instances. The key to their isolation has been the use of terphenyl ligands which provide the steric hindrance necessary for stability but yet allow access of many small molecules to the reactive centers. The reactions generally take place under ambient conditions and proceed in near quantitative yield. In many cases, the direct reactions, for example, those with hydrogen or ammonia, provide the simplest and highest yielding routes to the respective hydride or amido products. The discovery of reversible olefin and isocyanide complexation as well as various isomerization equlibria involving heavier group 14 element derivatives show that the heavier main group species can engage in dynamic processes. This opens the possibility that these and related main group compounds may have catalytic properties. A conspicuous aspect of the compounds discussed in the Account has been the relatively few results for aluminum,[45] the most abundant main group metal and the most important in the chemical industry. Future developments relevant to the theme of this Account involving this metal may be anticipated.

BIOGRAPHICAL INFORMATION

Philip Power is a Distinguished Professor of Chemistry at the University of California, Davis. 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 type of bonding, low coordination numbers, and high reactivity toward small molecules.

The author is indebted to many talented co-workers named in the references who performed the work described. Fruitful collaborations with Dr. M. Brynda and the groups of Professors M. Head-Gordon, R. Herber, G. Merino, L. Pu, S. Nagase, and H. Tuononen are gratefully acknowledged. The synthesis and characterization of the multiple bonded heavy group 13 and 14 elements was originally supported by the National Science Foundation. The reactivity of main group species toward small molecules has been supported by the Department of Energy, Office of Basic Energy Sciences.

FOOTNOTES

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REFERENCES

1 Fischer, R. C.; Power, P. P. π-Bonding and the Lone Pair Effect in Multiple Bonds Involving Heavier Main Group Elements: Developments in the New Millennium. *Chem. Rev.* **2010**, *110*, 3877–3923.

2 (a) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. A Stable Compound Containing a Silicon-Silicon Triple Bond. *Science* **2004**, *305*, 1755. (b) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. Synthesis and Characterization of a Digermanium Analogue of an Alkyne. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785–1787. (c) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. Synthesis and Characterization of 2,6-$Dipp_2$-$H_3C_6SnSnC_6H_3$-2,6-$Dipp_2$ (Dipp = C_6H_3-2,6-$Pr^i{}_2$): A Tin Analogue of an Alkyne. *J. Am. Chem. Soc.* **2002**, *124*, 5930–5931. (d) Pu, L.; Twamley, B.; Power, P. P. Synthesis and Characterization of 2,6-$Trip_2H_3C_6PbPbC_6H_3$-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-i-Pr_3): A Stable Heavier Group 14 Element Analogue of an Alkyne. *J. Am. Chem. Soc.* **2000**, *122*, 3524–3525. (e) Wiberg showed that the disilyne $(R^*{}_2MeSi)SiSi(SiMeR_2{}^*)$ ($R^* = SiBu^t{}_3$) could be generated in solution and characterized spectroscopically (^{29}Si NMR). See: Wiberg, N.; Niedermayer, W.; Fischer, G.; Nöth, H.; Suter, M. Synthesis Structure and Dehalogenation of the Disilene R(Cl)Si:Si(Cl)R [$R = (tBu_3Si)_2MeSi$]. *Eur. J. Inorg. Chem.* **2002**, 1066–1070. Wiberg, N.; Vasisht, S. K.; Fischer, G.; Mayer, P. A Relatively Stable Disilyne $RSi{\equiv}SiR$ ($R = SiMe(SitBu)_2$). *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823–1828.

3 Olmstead, M. M.; Simons, R. S.; Power, P. P. Synthesis and Characterization of $[Sn_2\{C_6H_3\text{-}2,6(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2\}_2]^-$.: A Singly Reduced Valence Isomer of a “Distannyne. *J. Am. Chem. Soc.* **1997**, *119*, 11705–11706.

4 Simons, R. S.; Power, P. P. $(\eta^5\text{-}C_5H_5)(CO)_2MoGeC_6H_3$-2,6-$Mes_2$: A Transition-Metal Germylyne Complex. *J. Am. Chem. Soc.* **1996**, *118*, 11966–11967.

5 Grev, R. S. Structure and Bonding in the Parent Hydrides and Multiply Bonded Silicon and Germanium Compounds: from MH_n to $R_2M{:}M'R_2$ and $RM{\equiv}M'R$. *Adv. Organomet. Chem.* **1991**, *33*, 125–170.

6 Jung, Y.; Brynda, M.; Power, P. P.; Head-Gordon, M. Ab Initio Quantum Chemistry Calculations on the Electronic Structure of Heavier Alkyne Congeners: Diradical Character and Reactivity. *J. Am. Chem. Soc.* **2006**, *128*, 7185–7192.

7 Sugiyama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. Synthesis and Properties of a New Kinetically Stabilized Digermyne: New Insights for a Germanium Analogue of an Alkyne. *J. Am. Chem. Soc.* **2006**, *128*, 1023.

8 Peng, Y.; Fischer, R. C.; Merrill, W. A.; Fischer, J.; Pu, L.; Ellis, B. D.; Fettinger, J. C.; Herber, R. H.; Power, P. P. Substituent Effects in Ditetrel Alkyne Analogues: Multiple vs Single Bonded Isomers. *Chem. Sci.* **2010**, *1*, 461–468.

9 Takagi, N.; Nagase, S. Tin Analogues of Alkynes Multiply Bonded vs. Singly Bonded Structures. *Organometallics* **2007**, *26*, 469–471.

10 Power, P. P. *Multiple Bonding between Heavier Group 13 Elements. Structure and Bonding*; Atwood, D. A., Roesky, H. W., Eds.; Vol. 103: Group 13 Elements-Research Trends - Book 1; Springer-Verlag: Berlin, Heidelberg, 2002; pp 57—84.

11 Wang, Y. Z.; Robinson, G. H. Organometallics of the Group 13 M-M bond (M = Al, Ga or In) and the Concept of Metalloaromacity. *Organometallics* **2007**, *26*, 2–11.

12 Linti, G.; Schnöckel, H.; Uhl, W.; Wiberg, N. *Clusters of the Heavier Group 13 Elements in Molecular Clusters of the Main Group Elements*; Driess, M., Nöth, M., Eds.; Wiley: New York, 2004; pp 126—168.

13 Schumann, H.; Janiak, C.; Görlitz, F.; Loebel, J.; Dietrich, A. Synthesis and Crystal Structure of Pentabenzylcyclopentadienylindium(I). *J. Organomet. Chem.* **1989**, *363*, 243–251.

14 Haubrich, S. T.; Power, P. P. Monomeric InC_6H_3-2,6-$Trip_2$ (Trip = -C_6H_2-2,4,6-i-Pr_3) and Its Manganese Complex $(\eta^5\text{-}C_5H_5)(CO)_2MnInC_6H_3$-2,6-$Trip_2$: One-Coordinate Indium in the Solid State. *J. Am. Chem. Soc.* **1998**, *120*, 2202–2203.

15 (a) Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. The “Diindene” ArInInAr (Ar = C_6H_3-2,6-$Dipp_2$, Dipp = C_6H_3-2,6-$Pr^i{}_2$). Dimeric versus Monomeric In(I) Aryls: para-Substituent Effects in Terphenyl Ligands. *J. Am. Chem. Soc.* **2002**, *124*, 8538–8539.
(b) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. Synthesis and Characterization of the Neutral “Digallene” Ar'GaGaAr' and Its Reduction to $Na_2Ar'GaGaAr'$ (Ar' = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-$^iPr_2C_6H_3$). *Angew. Chem., Int. Ed.* **2002**, *41*, 2842–2844.
(c) Wright, R. J.; Phillips, A. D.; Hino, S.; Power, P. P. Synthesis and Reactivity of Dimeric Ar′TlTlAr′ and Trimeric $(Ar''Tl)_3$ (Ar′, Ar″ = Bulky Terphenyl Group) Thallium (I) Derivatives: Tl(I)-Tl(I) Bonding in Species Ligated by Monodentate Ligands. *J. Am. Chem. Soc.* **2005**, *127*, 4794–4799.

16 Zhu, Z.; Guo, J. D.; Fischer, R. C.; Ellis, B. D.; Rivard, E.; Merrill, W. A.; Olmstead, M. M.; Pu, L.; Nagase, S.; Power, P. P. Synthesis, Characterization and Real Molecule Calculations for Neutral Organogallium(I) Aryl Dimers and Monomers: Weakness of Gallium-Gallium Bonds in Digallenes and Digallynes. *Chem.—Eur. J.* **2009**, *15*, 5263–5272.

17 (a) Wright, R. J.; Phillips, A. D.; Power, P. P. The [2 + 4] Diels-Alder Cycloadditon Product of a Probable Dialuminene, Ar′AlAlAr′ (Ar′= C_6H_3- 2,6-$Dipp_2$; Dipp = C_6H_3-2,6-$Pr^i{}_2$), with Toluene. *J. Am. Chem. Soc.* **2003**, *125*, 10784–19785. (b) Wright, R. J.; Fettinger, J. C.; Power, P. P. Synthesis and Structure of the “Dialuminyne” $Na_2Ar'AlAlAr'$ and $Na_2(Ar''Al)_3$ (Ar′ = C_6H_3-2,6-$(C_6H_3\text{-}2,6\text{-}Pr^i{}_2)_2$ Ar″ = C_6H_3-2,6-$(C_6H_2\text{-}2,4,6\text{-}Me_3)_2$: Al-Al Bonding in Al_2Na_2 and Al_3Na_2 and Clusters. *Angew. Chem., Int. Ed.* **2006**, *45*, 5953–5956.

18 Moilanen, J.; Power, P. P.; Tuononen, H. M. The Nature of the Bonding in Group 13 Dimetallenes: A Balance between Static and Dynamic Electron Correlation Effects, Singlet Diradical Character. *Inorg. Chem.* **2010**, *49*, 10992–11000.

19 Hardman, N. J.; Power, P. P.; Gorden, J. D.; Macdonald, C. L. B.; Cowley, A. H. Gallium-Boron donor-acceptor bonds. *J. Chem. Soc., Chem. Commun.* **2001**, 1866–1867.

20 Cui, C.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. Reactions of the Heavier Group 14 Element Alkyne Analogues Ar′EEAr′ (Ar = C_6H_3-2,6(C_6H_3-2,6-$\mathrm{Pr^i}_2)_2$; E = Ge, Sn) with Unsaturated Molecules: Probing the Character of the EE Multiple Bonds. *J. Am. Chem. Soc.* **2005**, *127*, 17530–17541.

21 Wright, R. J.; Phillips, A. D.; Allen, T. L.; Fink, W. H.; Power, P. P. Synthesis and Characterization of the Monomeric Imides of Ar′MNAr″ (M = Ga or In; Ar′ or Ar″ = Terphenyl Ligands) with Two-Coordinate Gallium and Indium. *J. Am. Chem. Soc.* **2003**, *125*, 1694–1695.

22 Fox, A. R.; Wright, R. J.; Rivard, E.; Power, P. P. Synthesis and Structure of $\mathrm{Tl_2[Aryl_2P_4]}$: A Thallium Complexed Diarlytetraphosphabutadienide and its Two-Electron Oxidation to a Diaryltetraphosphacyclobutane. *Angew. Chem., Int. Ed.* **2005**, *44*, 7884–7887.

23 Zhu, Z.; Wright, R. J.; Brown, Z. D.; Fox, A. R.; Phillips, A. D.; Richards, A. F.; Olmstead, M. M.; Power, P. P. Chalcogenide/Chalcogenolate Structural Isomers of Organo Group 13 Element Derivatives: Reactions of the Dimetallenes Ar′MMAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$\mathrm{Pr^i}_2)_2$: M = Ga or In) with N_2O or S_8 to give $\mathrm{(Ar'M^{III}E)_2}$ (E = O or S) and the Synthesis and Characterization of $\mathrm{[Ar'EM^I]_2}$ (M = In or Tl; E = O, S). *Organometallics* **2009**, *28*, 2512–2519.

24 Stender, M.; Phillips, A. D.; Power, P. P. Formation of $\mathrm{[Ar^*\overline{Ge\{CH_2C(Me)C(Me)CH_2}\}\text{-}CH_2C(Me)=]_2}$ (Ar* = C_6H_3-2,6-$\mathrm{Trip_2}$; Trip = C_6H_2-2,4,6-i-$\mathrm{Pr_3}$) via reaction of Ar*GeGeAr* with 2,3-dimethyl-1,3-butadiene: evidence for the existence of a germanium analogue of an alkyne. *J. Chem. Soc., Chem. Commun.* **2002**, 1312–1313.

25 Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumitomo, M.; Nagase, S. Reactivity of a Disilyne RSi≡SiR (R = $\mathrm{Si^iPr\{CH(SiMe_3)_2\}_2}$ toward π-Bonds: Stereospecific Addition and a New route to an Isolable 1,2-Disilabenzene. *J. Am. Chem. Soc.* **2007**, *129*, 7766–7767.

26 Spikes, G. H.; Fettinger, J. C.; Power, P. P. Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound. *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233.

27 Himmel, M.-J.; Schnöckel, H. Heats of Hydrogenation of Compounds Featuring Main Group Elements and with the Potential for Multiple Bonding. *Chem.—Eur. J.* **2002**, *8*, 2397–2405.

28 Brynda, M.; Power, P. P. Unpublished work.

29 Richards, A. F.; Phillips, A. D.; Olmstead, M. M.; Power, P. P. Isomeric Forms of Divalent Heavier Group 14 Element Hydrides: Characterization of Ar′(H)GeGe(H)Ar′ and $\mathrm{Ar'H_2Ge\text{-}GeAr'\cdot PMe_3}$ (Ar′ = C_6H_3-2,6-$\mathrm{Dipp_2}$; Dipp = C_6H_3-2,6-$\mathrm{Pr^i}_2$). *J. Am. Chem. Soc.* **2003**, *125*, 3204–3205.

30 Peng, Y.; Guo, J. D.; Power, P. P.; Nagase, S. Unpublished work.

31 Peng, Y.; Brynda, M.; Ellis, B. D.; Fettinger, J. C.; Rivard, E.; Power, P. P. Addition of H_2 to distannynes under ambient conditions. *Chem. Commun.* **2008**, 6042–6044.

32 Rivard, E.; Fischer, R. C.; Wolf, R.; Peng, Y.; Merrill, W. A.; Schley, N. D.; Zhu, Z.; Pu, L.; Fettinger, J. C.; Teat, S. J.; Nowik, I.; Herber, R. H.; Takagi, N.; Nagase, S.; Power, P. P. Influence of Steric and Electronic Factors on the Stability of Isomers of Divalent Tin(II) Hydrides: Experimental and Theoretical Studies. *J. Am. Chem. Soc.* **2007**, *129*, 16197–16208.

33 Eichler, B. E.; Power, P. P. Characterization of the Sterically Encumbered Terphenyl-Substituted Species, an Unsymmetric, Group 14 Element, Methylmethylene, Valence Isomer of an Alkene, Its Related Lithium Derivative 2,6-$\mathrm{Trip_2H_3C_6(Me)_2Sn\text{-}Sn(Li)(Me)C_6H_3}$-2,6-$\mathrm{Trip_2}$, and the Monomer Sn(t-Bu)C_6H_3-2,6-$\mathrm{Trip_2}$ (Trip = C_6H_2-2,4,6-i-$\mathrm{Pr_3}$). *Inorg. Chem.* **2000**, *39*, 5444–5449.

34 (a) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. Reversible Metal-free Hydrogen Activation. *Science* **2006**, *314*, 1124–1128. (b) Stephan, D. W. Activation of Dihydrogen by Non-Metal Systems. *Chem. Commun.* **2010**, *46*, 8526–8533.

35 (a) Frey, G. D.; Lavallo, B.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. Facile Splitting of Hydrogen and Ammonia by Nucleophilic Activation at a Single Carbon Center. *Science* **2007**, *316*, 439. (b) Bertrand, G. Stable Singlet Carbenes as Mimics for Transition Metal Centers. *Chem. Sci.* **2011**, 2389–2399.

36 Simons, R. S.; Pu, L.; Olmstead, M. M.; Power, P. P. Synthesis and Characterization of the Monomeric Diaryls $\mathrm{M\{C_6H_3\text{-}2,6\text{-}Mes_2\}_2}$ (M = Ge, Sn, or Pb; Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$—) and Dimeric Aryl-Metal Chlorides $\mathrm{[M(Cl)\{C_6H_3\text{-}2,6\text{-}Mes_2\}]_2}$ (M = Ge or Sn). *Organometallics* **1997**, *16*, 1920–1925.

37 (a) Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. Diarylstannylene Activation of Hydrogen or Ammonia with Arene Elimination. *J. Am. Chem. Soc.* **2008**, *130*, 12268–12269. (b) Peng, Y.; Guo, J.-D.; Ellis, B. D.; Zhu, Z.; Fettinger, J. C.; Nagase, S.; Power, P. P. Reaction of Hydrogen or Ammonia with Unsaturated Germanium or Tin Molecules under Ambient Conditions: Oxidative Addition versus Arene Elimination. *J. Am. Chem. Soc.* **2009**, *131*, 16272–16282.

38 Zhu, Z.; Wang, X.; Peng, Y.; Lei, H.; Fettinger, J. C.; Rivard, E.; Power, P. P. Addition of Hydrogen or Ammonia to a Low Valent Group 13 Metal Species at 25°C and 1 atm. *Angew. Chem., Int. Ed.* **2009**, *48*, 2031–2033.

39 Peng, Y.; Ellis, B. D.; Wang, X.; Fettinger, J. C.; Power, P. P. Reversible σ-Complexation of Ethylene by Main Group Molecules under Ambient Conditions. *Science* **2009**, *325*, 1668–1670.

40 (a) Summerscales, O. T.; Wang, X.; Power, P. P. Cleavage of the Sn-Sn Multiple Bond in a Distannyne by Cyclooctatetraene: Formation of the π-Bound Inverse Sandwich Complex $\mathrm{(Ar'Sn)_2}(\mu^2\text{-}\eta^2{:}\eta^3\text{-COT})$ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-$\mathrm{^iPr_2)_2}$). *Angew. Chem., Int. Ed.* **2010**, 4788–4790. (b) Summerscales, O. T.; Power, P. P. Unusual Electrocyclic Rearrangements with Group 14 Element Compounds: Formation and Isomerization of a π-Aromatic Digermyl Complex with Carbon-Carbon and Germanium-Germanium Multiple Bond Cleavage. *J. Am. Chem. Soc.* **2011**, *133*, 180–182.

41 Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. Structures, Bonding, and Reaction Chemistry of the Neutral Organogallium(I) Compounds $\mathrm{(GaAr)_n}$ (n = 1 or 2) (Ar = Terphenyl or Related Ligand): An Experimental Investigation of Ga—Ga Multiple Bonding. *J. Am. Chem. Soc.* **2003**, *125*, 2667–2679.

42 Zhu, Z.; Wang, X.; Olmstead, M. M.; Power, P. P. Synthesis and Characterization of $\mathrm{[Ar'GaC(Ph)CH]_2}$ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-$\mathrm{Pr^i}_2)_2$) and $\mathrm{K_2[Ar'GaC(Ph)CH]_2\cdot OEt_2}$: from Digallacyclohexadiene to Digallatabenzene. *Angew. Chem., Int. Ed.* **2009**, *48*, 2027–2030.

43 (a) Spikes, G. H.; Power, P. P. Lewis Base Induced Tuning of the Ge-Ge Bond Order in a "Digermyne". *Chem. Commun.* **2007**, 85–87. (b) Peng, Y.; Wang, X.; Fettinger, J. C.; Power, P. P. Reversible Complexation of Isocyanides by the Distannyne Ar′SnSnAr′ (Ar′ = C_6H_3-2, 6 (C_6H_3-2, 6-$\mathrm{^iPr_2)_2}$). *Chem. Commun.* **2010**, 943–945.

44 Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. Reactivity of the Disilyne RSi≡SiR (R = $\mathrm{SiPr^i\{CH(SiMes)_2\}_2}$) toward Silylcyanide: Two Pathways to Form the Bis-Adduct $\mathrm{[RSiSi(CNSiMe_3)_2]}$ with Some Silaketrimine Character and a 1,4-diaza-3,3-disilabenzene Analogue. *J. Am. Chem. Soc.* **2008**, *130*, 16848–16849.

45 Schnöckel and co-workers have shown that AlCl generated at low temperature reacts with olefins and alkynes to form interesting cyclic and cage products. See: (a) Schnöckel, H.; Leimkuhler, M.; Lotz, R.; Mattes, R. Dimeric 1,4-Dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene, a Compound with Aluminum-Olefin π-Bonds. *Angew. Chem., Int. Ed.* **1986**, *25*, 921–922. (b) Dohmeier, C.; Mattes, R.; Schnöckel, H. Synthesis and Molecular Structure of the Cyclic Hexamer of 2,3-dimethylbutene Aluminium Monochloride. *Chem. Commun.* **1990**, 358–359. (c) Üffing, C.; Ecker, A.; Köppe, R.; Merzweiler, K.; Schnöckel, H. Two Isomers with an $\mathrm{Al_4C_8}$ Framework. *Chem.—Eur. J.* **1998**, *4*, 2142–2147.