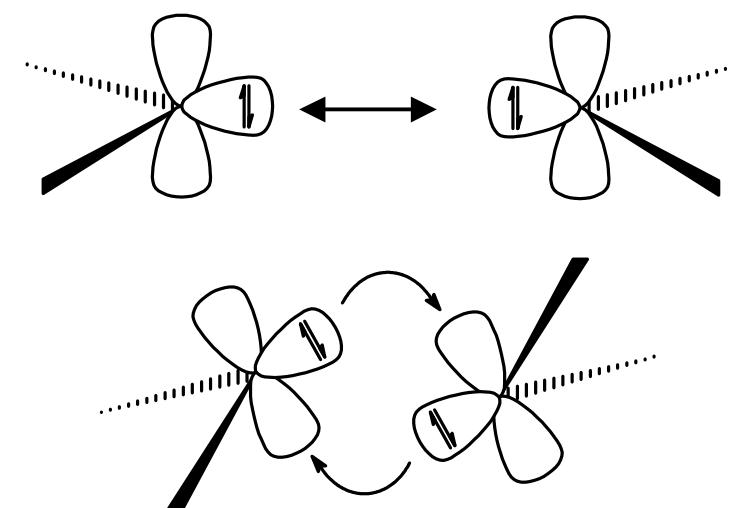
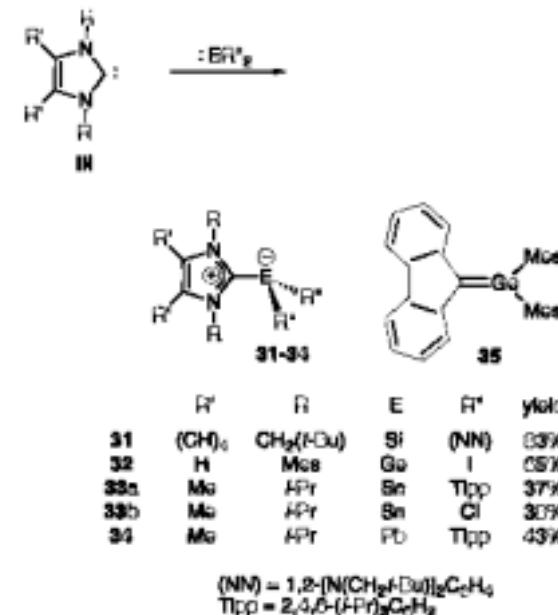




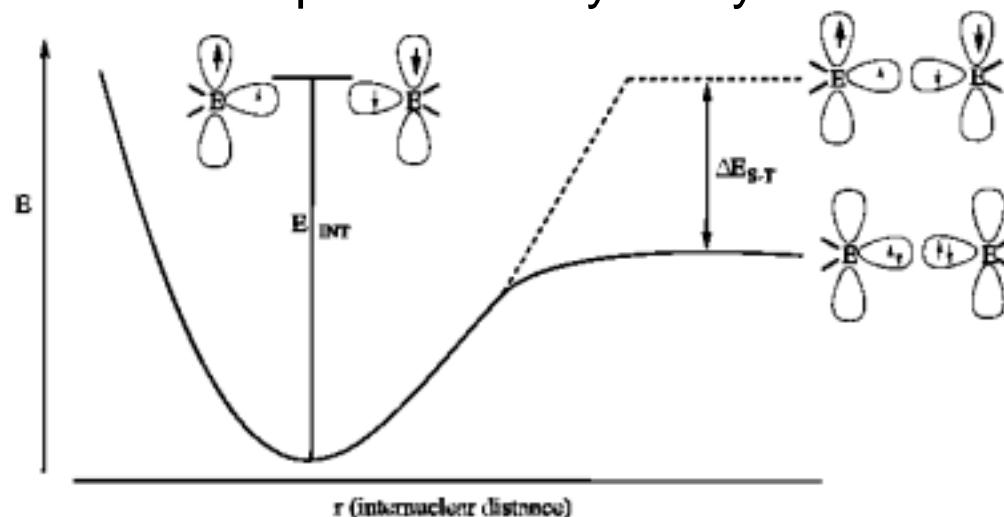
An examination of some of the heavier analogues of carbenic fragments was necessary to understand the nature of the bonding between such fragments. We have already seen that the “dimerization”, “oligomerization” and cycloaddition behaviour of NHC’s was different than that of transient carbenes.

Similarly, the “dimerization” and insertion reaction chemistry of the heavier analogues (and the products derived from those reactions) does not usually resemble that of the transient carbenes. The differences are mostly attributable to the relative stability of the singlet and triplet states for the fragments. The theory that describes the reactivity is known as CGMT after the theoreticians Carter, Goddard, Malrieu and Trinquier.



# Chem 59-651 CGMT Theory of Main Group Multiple Bonds

The CGMT treatment of multiple bonding in this section is taken from the reviews that I have provided to you (Driess, Angew. Chem. Int. Ed., 1996, 35, 828; and Power, Chem. Rev., 1999, 99, 3463), from which you can find the original articles if necessary. Note that many of the ideas from which the theory is derived were postulated by many other researchers much earlier.



**Figure 1.** Generalized schematic illustration of the energy of dissociation of an olefinic double bond into two triplet fragments  $\Delta E_{S-T}$  is the singlet-triplet energy difference which is positive for carbon but negative for Si-Pb.  $\Delta E_{INT}$  = double bond energy.

The general equation used in CGMT can be expressed in the form:

$$E_{\sigma+\pi} = E_{INT} - \sum \Delta E_{s \rightarrow t}$$

Where:  $E_{\sigma+\pi}$  is the actual bond energy;  $E_{INT}$  is the “intrinsic” bond energy; and  $\Delta E_{s \rightarrow t}$  is the singlet-triplet energy difference.



# Chem 59-651 CGMT Theory of Main Group Multiple Bonds

For the combination of 2 identical fragments, the equation will be:

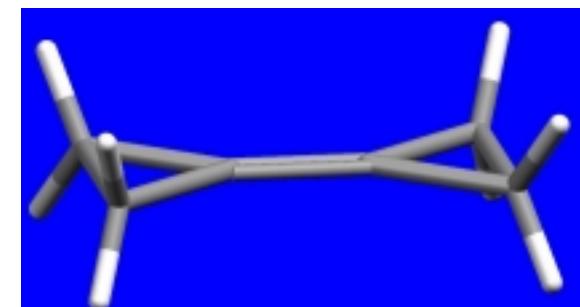
$$E_{\sigma+\pi} = E_{INT} - 2\Delta E_{s \rightarrow t}$$

From the results of numerous calculations and experimental observations, the following conclusions were drawn:

If  $E_{\sigma+\pi} > 2 \sum \Delta E_{s \rightarrow t}$ , then a planar double bond will be observed.

This situation arises in all cases where the triplet fragment is more stable than the singlet fragment (thus  $\Delta E_{s \rightarrow t}$  is negative) and when the strength of  $\sigma$  and  $\pi$  bonds are relatively large. These two criteria explain why the multiple bonds in organic chemistry are generally planar because the organic elements form strong multiple bonds and the fragments often have triplet ground states or small singlet-triplet energies.

For example, the singlet-triplet gap for (cyclopropylidene) is about 13 kcal/mol while the energy of the C=C double bond is around 150 kcal/mol so the inequality is satisfied and the bond should be planar.



 Chem 59-651 CGMT Theory of Main Group Multiple Bonds

If  $E_{\sigma+\pi} < 2 \sum \Delta E_{s \rightarrow t}$ , then a trans-bent double bond will be observed.

This situation arises in cases where the singlet fragment is much more stable than the triplet fragment and when the strength of the  $\sigma$  or, more typically, the  $\pi$  bonds are relatively small. These two criteria explain why the multiple bonds for the heavier elements in the main group are generally not planar. In effect, “normal” multiple bonds will only be observed for the organic elements because it is a special case. **Organic-type multiple bonding is the exception to the rule!** Keep in mind, however, that sterically demanding groups can sometimes enforce planar geometries.

---

For the combination of 2 different fragments, the equation will be:

$$E_{\sigma+\pi} = E_{INT} - \sum \Delta E_{s \rightarrow t}$$

Thus the energy of the singlet-triplet gap for each fragment must be summed. For example, for  $\text{H}_2\text{C}=\text{SiF}_2$ ,  $\sum \Delta E_{s \rightarrow t}$  is obtained by adding  $\Delta E_{s \rightarrow t}$  for  $\text{CH}_2$  (-9 kcal/mol) and  $\text{SiF}_2$  (73 kcal/mol) for a total of 64 kcal/mol. Since the bond energy for an  $\text{Si}=\text{C}$  double bond is around 105 kcal/mol, one would not expect a planar structure since  $105 < 2(64)$ .



# Chem 59-651 CGMT Theory of Main Group Multiple Bonds

Lastly,

If  $E_{\sigma+\pi} < \Sigma \Delta E_{s \rightarrow t}$ , then no bond will be observed and the compounds should remain as monomeric species unless they are forced together.

This will happen when the strength of the sigma and pi bonding is particularly weak, such as in the case of some Ti(I) compounds:

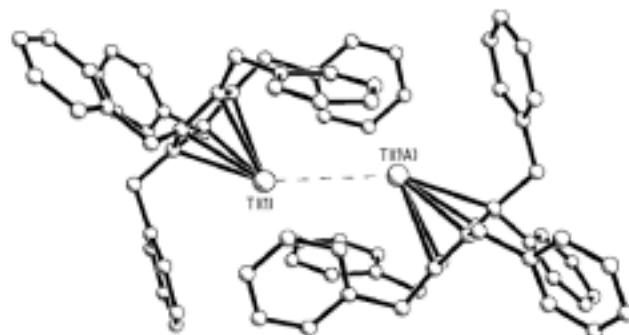
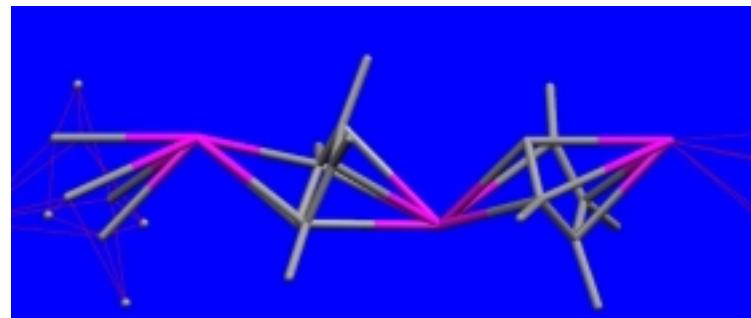


Figure 5. Trans-bent structure of the weakly associated dimer  $[\text{Ti}\{\eta^5\text{-C}_5(\text{CH}_2\text{Ph})_5\}]_2$ .<sup>44b</sup>

$\text{Ti}(\text{C}_5\text{Bz}_5)$  seems to form dimers in the solid state.



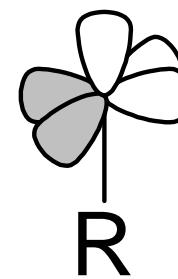
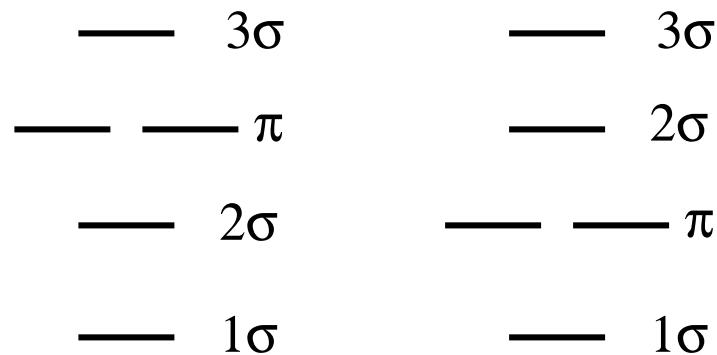
$\text{Ti}(\text{C}_5\text{HMe}_4)$  is an infinite polymer with no Ti-Ti bonding in the solid state.



Although CGMT can tell us whether or not a compound will have a “classical” planar (or linear) or bent multiple bond, it provides no way to predict the exact structure. Furthermore, accurate values for many of the bond energies are not available thus the predictions are often based on calculations.

In practice, one can usually use simple MO/VBT models like the ones that I have shown you to estimate whether or not multiple bonds or related species will have “classical” structures or “distorted” ones. All that is necessary is to determine the multiplicity of the fragment in question and estimate the size of the singlet-triplet splitting.

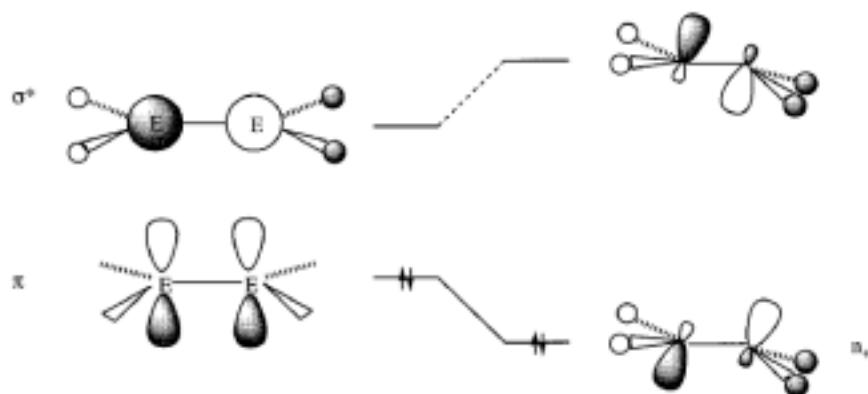
Consider the “di-yl” fragments R-M (M in group 13) and “pnictinidene” R-Pn (Pn in group 15), which are both of approximate  $C_{\infty v}$  symmetry and MO diagrams of the diatomic types:



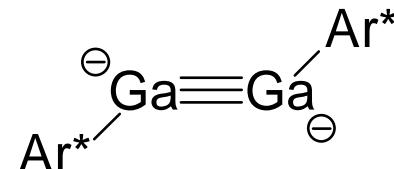
You can figure out the multiplicities by filling in the appropriate number of electrons and figuring out which diagram corresponds to which elements.



An alternative, yet equivalent view of the distorted geometries can also be obtained by considering the distortions as a type of Jahn-Teller interaction between the  $\pi$  and the  $\sigma^*$  orbitals. If the orbitals are close enough in energy, which is more likely to occur as you descend the periodic table, they can interact with each other to obtain a lower energy arrangement for the electrons. Note that when this happens, the hypothetical  $\pi$ -type molecular orbital (which would be shared between the two elements) becomes more like a non-bonding “lone pair” orbital, where the electron density becomes more “localized” on the individual atoms.



(See: Lin, JACS, 1998, 120, 12133)



(Robinson, JACS, 1997, 119, 5471; Cotton, JACS, 1998, 120, 1799)

J. Am. Chem. Soc., Vol. 120, No. 8, 1998 1799

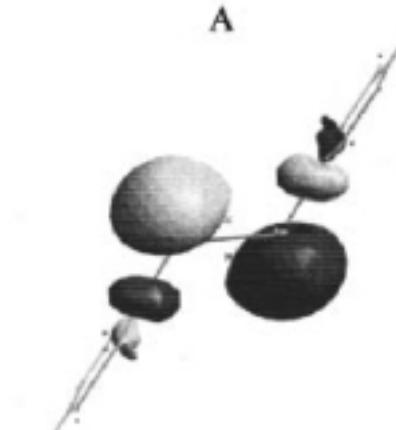
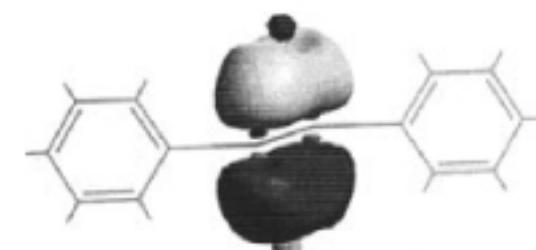


Figure 9. DFT orbital plots for the  $\pi$  bonding orbital (A) and the nonbonding orbital of  $\pi$ -type (B) in  $\text{Na}_2[(\text{C}_6\text{H}_5)_2\text{Ga}=\text{Ga}-(\text{C}_6\text{H}_5)_2]$  corresponding to the calculated structure in Figure 6. Dark and bright portions of the plots represent positive and negative regions of the orbitals, respectively.



# Main Group Multiple Bonds: Synthesis

Multiple bonds between main group elements have been explored in detail for some combinations of elements and barely examined for many others. The most recent major review by Power (*Chem. Rev.*, 1999, 99, 3463) outlines many of the types of molecules that had been made and characterized up to around the start of 1999.

**Table 1. Selected Element Combinations Related to Alkenes from Groups 13–16 that may Feature Double Bonding (Discussed in sections IV.A–L)**

<sup>a</sup> Number of stable compounds that have been structurally characterized. <sup>b</sup> Examples involving bonding to a heavier main group atom only. <sup>c</sup> Not including carbon compounds.



# Chem 59-651 Main Group Multiple Bonds: Synthesis

Compounds containing “triple” bonds to heavier main group elements are much less common than those with double bonds. The primary exception were found in the group 14-15 series such as phosphalkynes ( $\text{R-C}\equiv\text{P}$ ).

Table 2. Selected Element Combinations from Groups 13–16 that may Feature Triple Bonding (Discussed in sections V.A–E)

13-13	13-14	13-15	13-16	14-14	14-15
$\text{D}\equiv\text{D}$	$\text{D}\equiv\text{C}$	$\text{D}\equiv\text{N}$	$\text{D}\equiv\text{O}$	$\text{C}\equiv\text{C}$	$\text{C}\equiv\text{N}$
$\text{D}\equiv\text{Al}$	$\text{D}\equiv\text{Si}$	$\text{D}\equiv\text{P}$	$\text{D}\equiv\text{S}$	$\text{C}\equiv\text{Si}$	$\text{C}\equiv\text{P}$
$\text{D}\equiv\text{Ge}$	$\text{D}\equiv\text{Ge}$	$\text{D}\equiv\text{As}$	$\text{D}\equiv\text{Se}$	$\text{C}\equiv\text{Ge}$	$\text{C}\equiv\text{As}$
$\text{D}\equiv\text{Ir}$	$\text{D}\equiv\text{Sr}$	$\text{D}\equiv\text{S}$	$\text{D}\equiv\text{Te}$	$\text{C}\equiv\text{Sr}$	$\text{C}\equiv\text{Se}$
$\text{D}\equiv\text{Th}$	$\text{D}\equiv\text{Pt}$	$\text{D}\equiv\text{B}$	$\text{Al}\equiv\text{O}$	$\text{C}\equiv\text{Pt}$	$\text{C}\equiv\text{B}$
$\text{Al}\equiv\text{Al}$	$\text{Al}\equiv\text{C}$	$\text{Al}\equiv\text{N}$	$\text{Al}\equiv\text{S}$	$\text{Si}\equiv\text{Si}$	$\text{Si}\equiv\text{N}$
$\text{Al}\equiv\text{Ge}$	$\text{Al}\equiv\text{Si}$	$\text{Al}\equiv\text{P}$	$\text{Al}\equiv\text{Se}$	$\text{Si}\equiv\text{Ge}$	$\text{Si}\equiv\text{P}$
etc.	etc.	etc.	etc.	etc.	etc.
$\text{In}\equiv\text{D}$	$\text{Ti}\equiv\text{Sr}$	$\text{Ti}\equiv\text{S}$	$\text{Ti}\equiv\text{Se}$	$\text{Se}\equiv\text{Pt}$	$\text{Pt}\equiv\text{S}$
$\text{Ti}\equiv\text{Ti}$	$\text{Ti}\equiv\text{Pt}$	$\text{Ti}\equiv\text{B}$	$\text{Ti}\equiv\text{Te}$	$\text{H}\equiv\text{Pt}$	$\text{Pt}\equiv\text{B}$
1 <sup>a</sup>	3 <sup>a</sup>	0 <sup>b</sup>	4	0 <sup>b</sup>	15 <sup>b</sup>

<sup>a</sup> Number of stable compounds that have been structurally characterized. <sup>b</sup> Examples involving bonding to a heavier main group atom only.

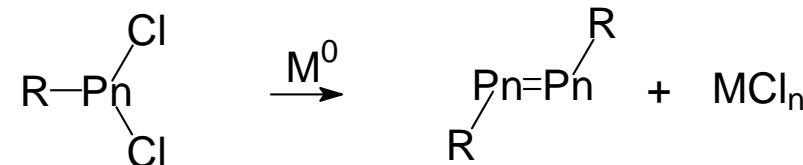


# Chem 59-651 Main Group Multiple Bonds: Synthesis

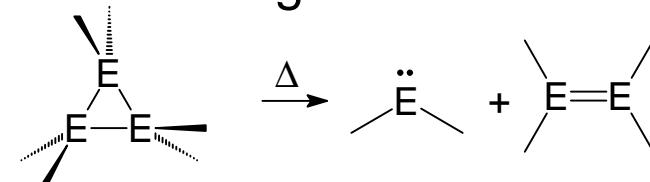
There are too many different synthetic techniques that have been used to make multiple bonds between heavier main group elements so we will examine only a few types of reactions that have been used fairly generally.

The reactions can broadly be classified into the following categories:

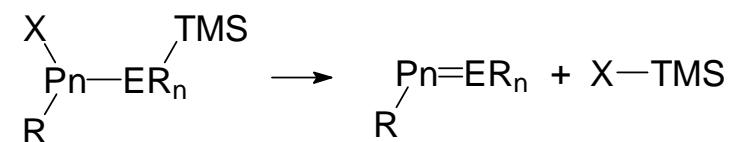
Direct reduction (through the formation of reactive intermediates like the ones that we have examined).



Reduction or decomposition of a precursor containing a bond between the main group elements.



Silyl-halide or silyl-fragment **elimination**.

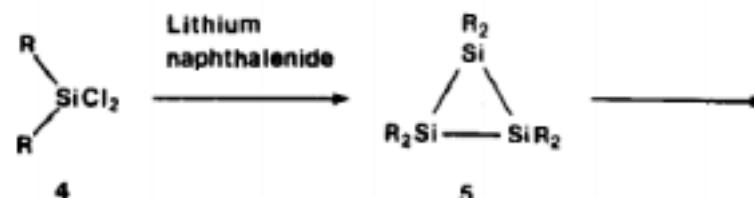


Hydrogen-halide/amide **elimination** (Acid-Base chemistry).



# Chem 59-651 Main Group Multiple Bonds: Synthesis

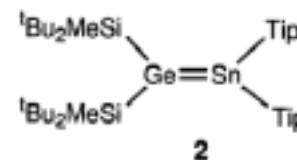
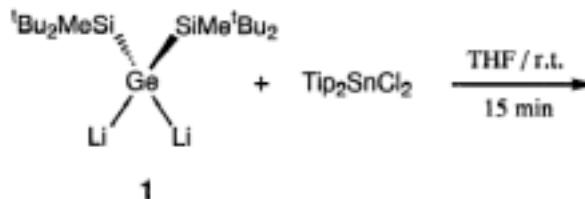
The decomposition of a cyclic compound is one of the classical ways of generating multiple-bonded compounds. The relative stability of the cyclic reagent and multiple bonded products depends on the size of the ring and the bulk of the substituents.



4 and 5 : R = 2,6-diethylphenyl  
(Masamune, *Organometallics*, 1984, 3, 333)

1484 *Organometallics*, Vol. 22, No. 7, 2003

Scheme 1



Tip = 2,4,6-trisopropylphenyl

Scheme 2

(Sekiguchi, *Organometallics*, 2003, 22, 1484)

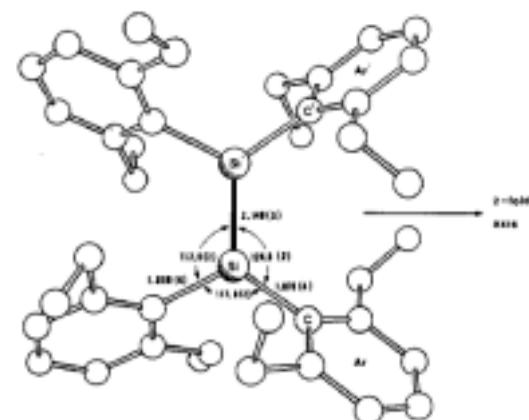


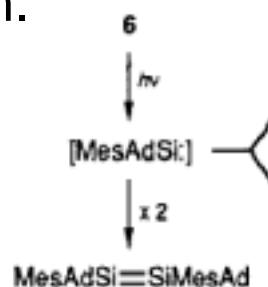
Figure 1. Molecular structure of 3.

Kim Baines at UWO uses this method to generate reactive multiple bonds.

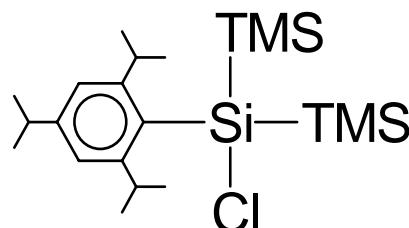


# Chem 59-651 Main Group Multiple Bonds: Synthesis

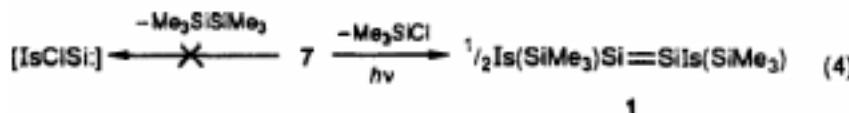
Various elimination reactions are the most common way to synthesize multiple bonded compounds. The reactions are driven by thermodynamically favourable processes (e.g. formation of strong bonds, precipitation, vapourisation etc.) and sometimes require heating or irradiation.



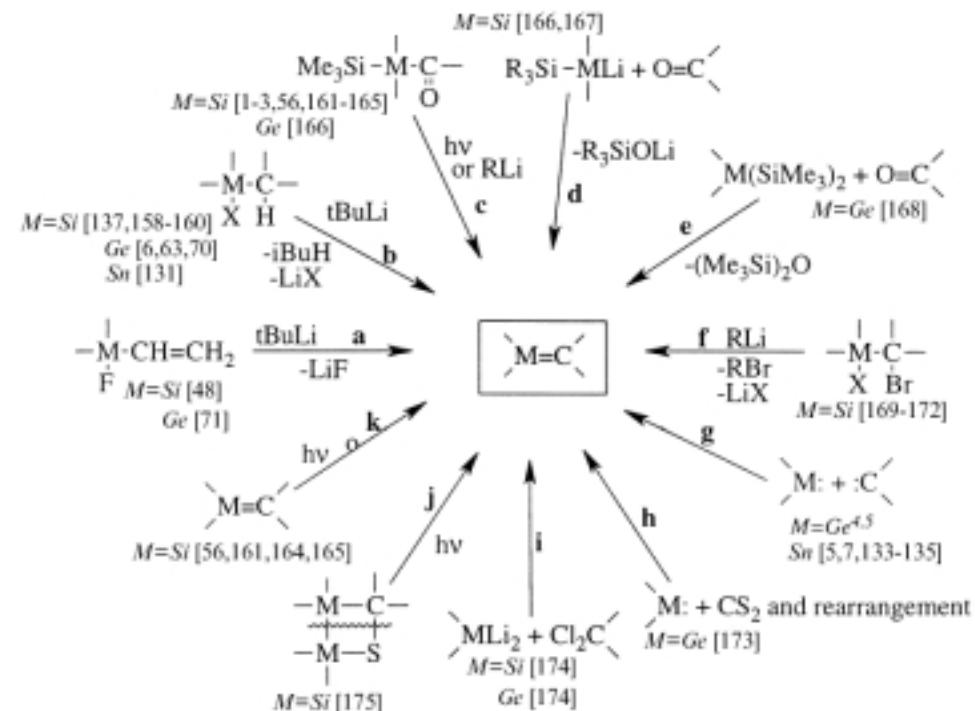
(West, Organometallics, 1989, 8, 2664)



7



(West, Organometallics, 1992, 11, 3276)



Scheme 1. All routes to stable silenes, germanes and stannenes

(See: Escudie, Coord. Chem. Rev., 1998, 178-180, 565)



# Chem 59-651 Main Group Multiple Bonds: Synthesis

An example of a diphosphene made by Protasiewicz was synthesized by the base-induced dehydrohalogenation (removal of HX) method.

Consider why this method may be more versatile than reduction of a dihalogenated precursor.

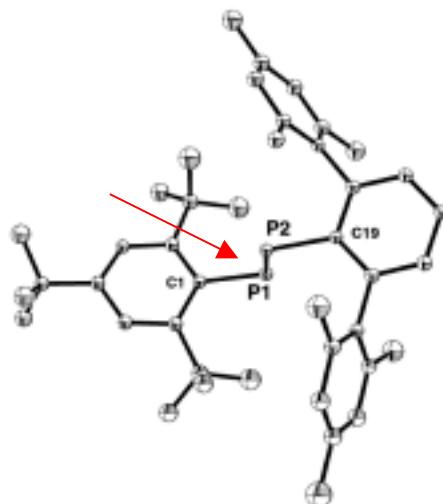
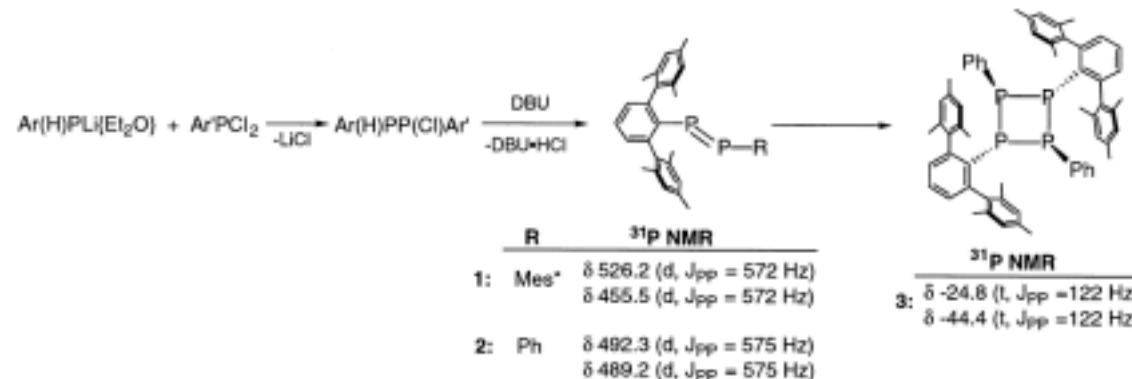


Figure 1. Structure of  $\text{DmpP}=\text{PPh}_3^+$  (1).

Table 2. Selected Bond Distances ( $\text{\AA}$ ) and Angles (deg) for 1 and 3

Compound 1			
P(1)–P(2)	2.0240(13)	P(2)–C(19)	1.846(3)
P(1)–C(1)	1.860(3)		
C(1)–P(1)–P(2)	97.99(11)	C(6)–C(1)–P(1)	120.4(2)
C(19)–P(2)–P(1)	101.19(11)	C(20)–C(19)–P(2)	118.1(2)
C(2)–C(1)–P(1)	120.4(3)	C(24)–C(19)–P(2)	121.7(3)

Compound 3			
P(1)–P(2)	2.228(2)	P(1)–C(1)	1.838(6)
P(1)–P(4)	2.233(2)	P(2)–C(49)	1.852(6)
P(2)–P(3)	2.242(2)	P(3)–C(25)	1.855(6)
P(3)–P(4)	2.252(2)	P(4)–C(55)	1.842(6)
P(2)–P(1)–P(4)	82.84(7)	C(55)–P(4)–P(1)	97.1(2)
P(1)–P(2)–P(3)	78.33(7)	C(55)–P(4)–P(3)	105.1(2)
P(2)–P(3)–P(4)	82.07(7)	C(30)–C(25)–P(3)	121.8(4)
P(1)–P(4)–P(3)	78.02(7)	C(26)–C(25)–P(3)	118.8(4)
C(1)–P(1)–P(2)	109.0(2)	C(54)–C(49)–P(2)	116.5(5)
C(1)–P(1)–P(4)	114.9(2)	C(50)–C(49)–P(2)	125.2(5)
C(49)–P(2)–P(1)	98.7(2)	C(2)–C(1)–P(1)	128.9(5)
C(49)–P(2)–P(3)	105.7(2)	C(6)–C(1)–P(1)	112.5(4)
C(25)–P(3)–P(2)	107.65(19)	C(60)–C(55)–P(4)	125.2(5)
C(25)–P(3)–P(4)	107.44(18)	C(56)–C(55)–P(4)	116.2(5)

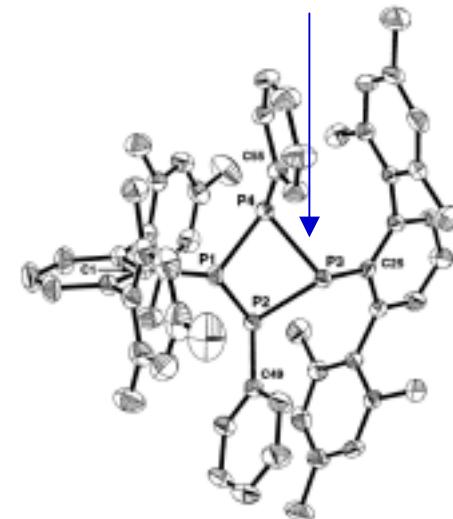
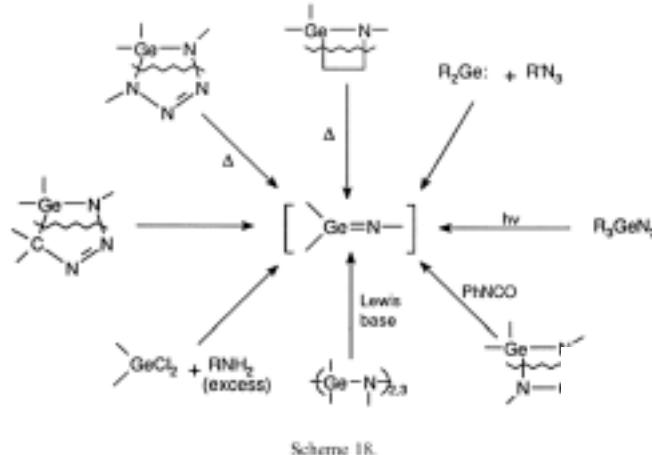


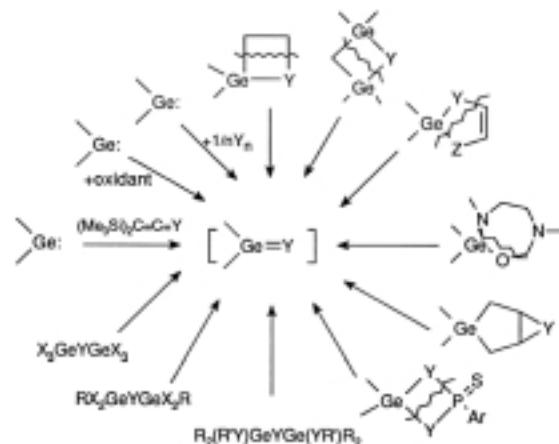
Figure 2. Structure of  $[\text{DmpP}=\text{PPh}_3]_2$  (3).



An interesting way of making multiple bonded species that works in a few cases is the oxidation of a reasonable precursor molecule that contains the main group element in a relatively low oxidation state. This method has been used primarily to make imides and chalcogenide multiple bonds.

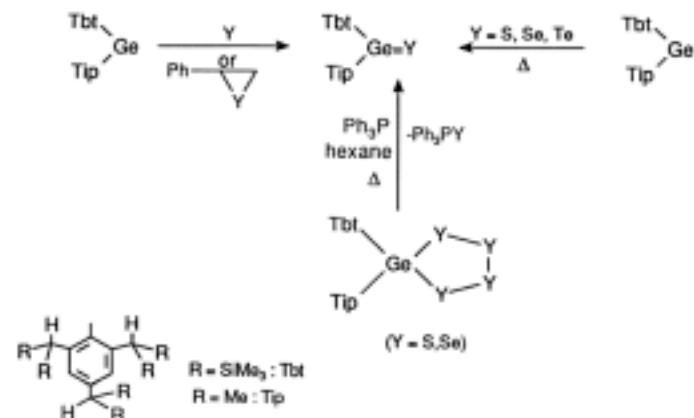


Scheme 18.



Scheme 19.

(See: Barrau, Coord. Chem. Rev., 1998, 178-180, 593 for appropriate references)



Scheme 33.

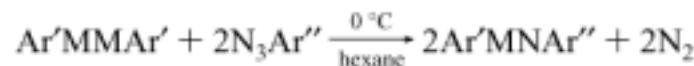
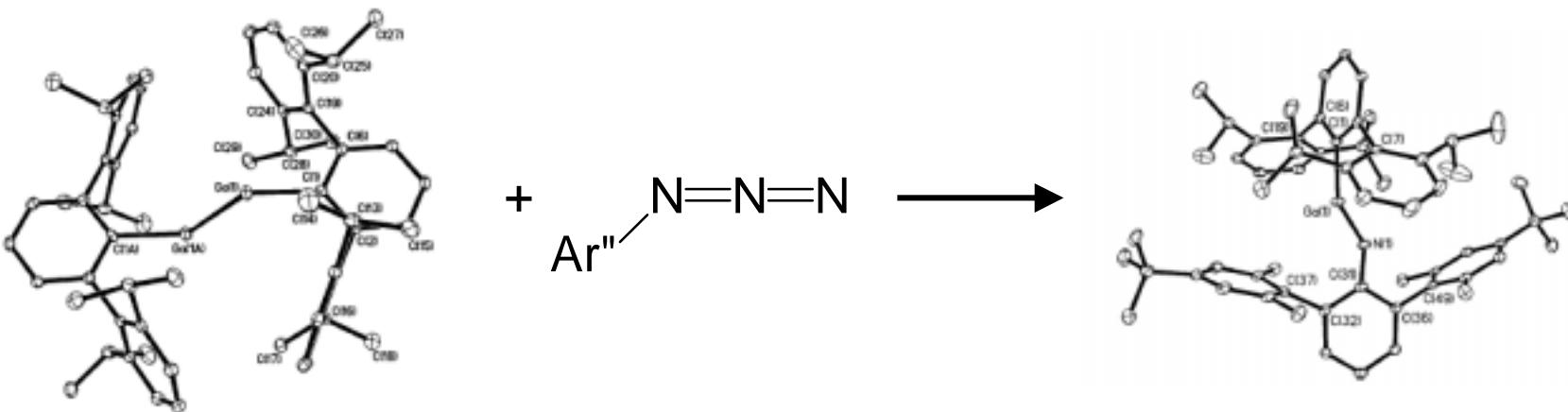
(See also: Tokitoh and Okazaki, Coord. Chem. Rev., 2000, 210, 251)



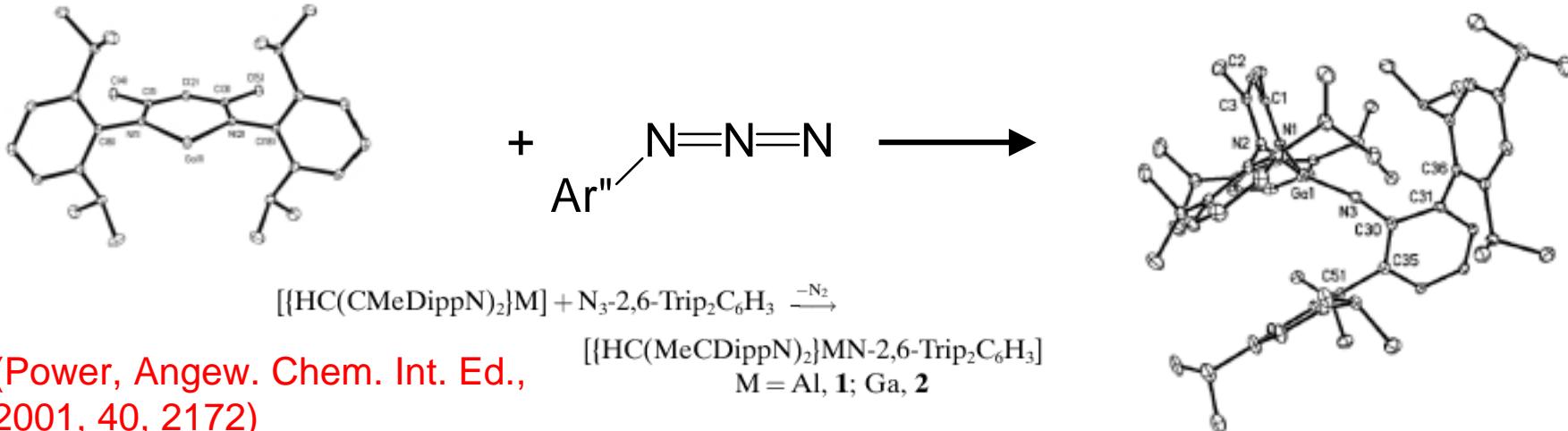
Chem 59-651

# Main Group Multiple Bonds: Synthesis

Some very recent examples of this oxidation approach include classes of compounds that had not been previously accessible.

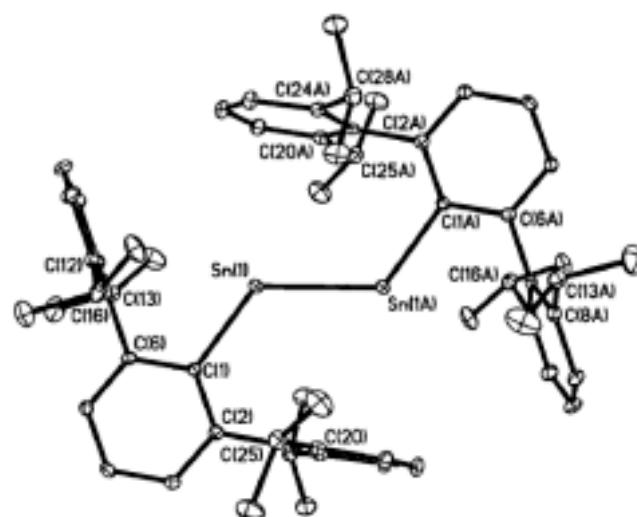
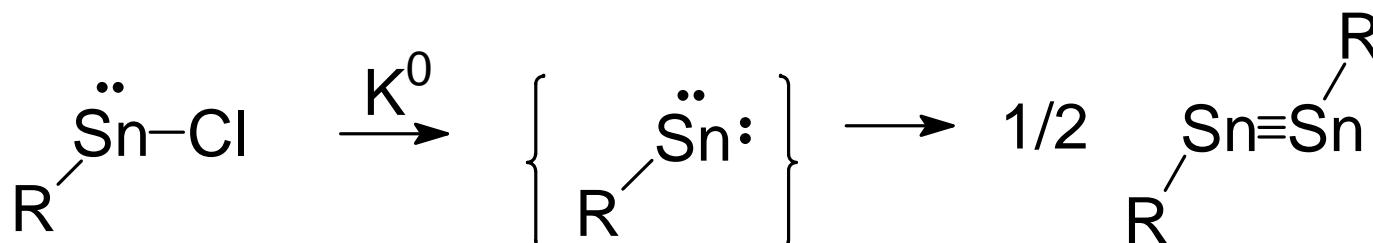


(Power, JACS, 2003, 125, 1694)





Making triple bonds for groups 13 and 14 is usually accomplished using the direct reduction of a suitable halogenated precursor.



**Figure 1.** Selected bond lengths ( $\text{\AA}$ ) and angles (deg) for **1**. H atoms are not shown.  $\text{Sn}(1)-\text{Sn}(1\text{A}) = 2.6675(4)$ ,  $\text{Sn}(1)-\text{C}(1) = 2.191(3)$ ,  $\text{C}(1)-\text{C}(2) = 1.403(4)$ ,  $\text{C}(1)-\text{C}(6) = 1.405(4)$ ,  $\text{Sn}(1\text{A})-\text{Sn}(1)-\text{C}(1) = 125.24(7)$ ,  $\text{Sn}(1)-\text{C}(1)-\text{C}(2) = 124.9(2)$ ,  $\text{Sn}(1)-\text{C}(1)-\text{C}(6) = 115.8(2)$ ,  $\text{C}(1)-\text{C}(2)-\text{C}(19) = 119.8(2)$ ,  $\text{C}(1)-\text{C}(6)-\text{C}(7) = 118.6(2)$ ,  $\text{C}(2)-\text{C}(1)-\text{C}(6) = 119.3(3)$ .

**Table 1.** Selected Bond Distances and Angles for Reduced  $\text{Ar}^*\text{SnSnAr}^*$  Species and **1**

cmpd	$\text{Sn}-\text{Sn}(\text{\AA})$	$\text{Sn}-\text{Sn}-\text{C}$ (deg)	ref
$[\text{K}(\text{THF})_6][\text{Ar}^*\text{SnSnAr}^*]^a$	2.8123(9)	95.20(13)	1
$[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Ar}^*\text{SnSnAr}^*]$	2.7821(14) 2.8236(14)	93.6(4), 95.0(4) 97.3(2)	1
$[(\text{THF})_3\text{Na}[\text{Ar}^*\text{SnSnAr}^*]]$	2.8107(13)	97.9(3), 98.0(4)	3
$[\text{K}_2\text{Ar}^*\text{SnSnAr}^*]$	2.7763(9)	107.50(14)	2
$\text{Ar}'\text{SnSnAr}'$ ( <b>1</b> ) <sup>b</sup>	2.6675(4)	125.24(7)	this work

<sup>a</sup>  $\text{Ar}^* = \text{C}_6\text{H}_3\text{-2,6-Trip}_2$ , <sup>b</sup>  $\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-Dipp}_2$ .

(Power, JACS, 2002, 124, 5930)



Group 15 triple bonded species have been synthesized by a variety of elimination reactions (for P compounds see: “Multiple Bonds and Low Coordination in Phosphorus Chemistry” and “Phosphorus: The Carbon Copy”). A couple of the more interesting reactions that have been used include  $\text{TMS}_2\text{O}$  elimination and flash vacuum pyrolysis.

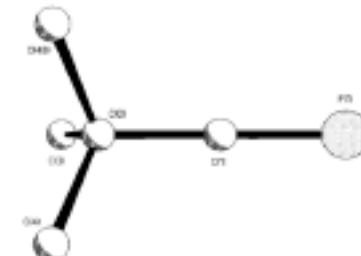
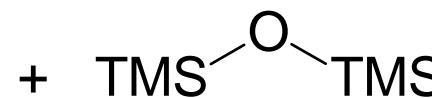
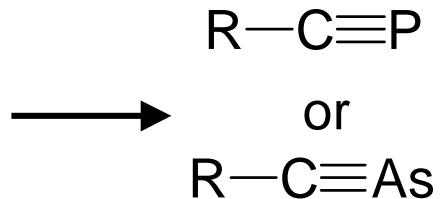
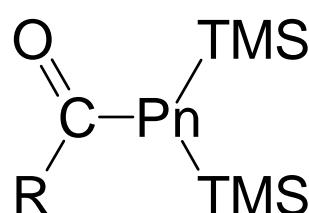
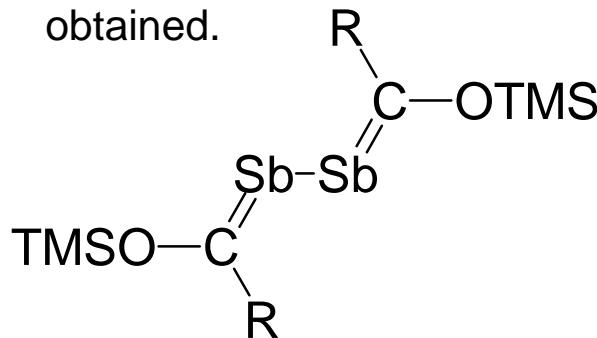


Figure 24. Structure of  $t\text{-Bu}-\text{C}\equiv\text{P}^{271}$  featuring an essentially linear carbon geometry and  $\text{P}\equiv\text{C}$  triple bond distance of 1.548(1) Å.

This does not work for Sb, instead the diene analogue is obtained.

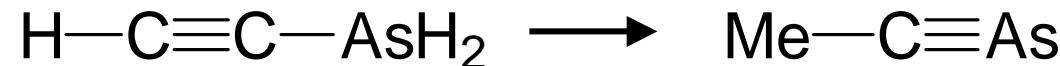


(Jones, JCS Dalton Trans, 1999, 1541)

For As, only the Mes\* derivative is stable.

---

An interesting rearrangement reaction has also been used to generate arsaalkynes:



This reaction works because of the relative H-element bond strengths (Guillemin, Organometallics, 1995, 14, 4732).



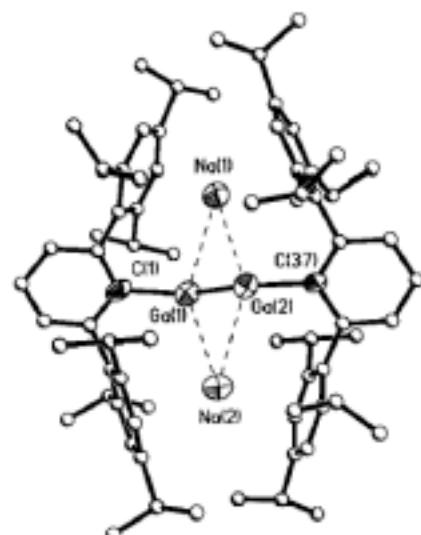
The nature of multiple bonding is sometimes very controversial.

Perhaps the most contentious debate in recent years is the “digallyne” synthesized by Robinson ([Robinson, JACS, 1997, 119, 5471; see also, Robinson, Chem. Comm., 2000, 2175](#)).

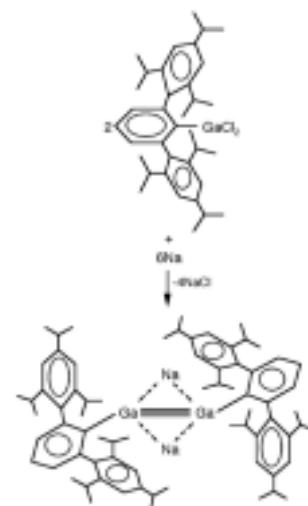
Their attempts with a slightly smaller terphenyl ligand did not work but made a metallo-aromatic compound.



([Robinson, JACS, 1995, 117, 7578](#))



**Figure 1.** Molecular structure of  $\text{Na}_2[\text{Mes}^*_2\text{C}_6\text{H}_3\text{-Ga}\equiv\text{Ga-C}_6\text{H}_3\text{Mes}^*_2]$  (thermal ellipsoids are shown at 35% probability levels). Selected bond distances (Å) and angles (deg): Ga(1)–Ga(2), 2.319(3); Ga(1)–C(1): 2.06(2); Ga(2)–C(37), 2.028(14); Ga(1)–Na(1), 3.085(7); Ga(1)–Na(2), 3.056(6); Ga(2)–Na(1), 3.078(6); Ga(2)–Na(2), 3.106(7); C(1)–Ga(1)–Ga(2): 128.5(4); C(37)–Ga(2)–Ga(1), 133.5(4); C(1)–Ga(1)–Na(1), 102.1(5); C(1)–Ga(1)–Na(2), 107.0(6); C(37)–Ga(2)–Na(1), 101.7(5); C(37)–Ga(2)–Na(2), 106.5(6); Ga(1)–Ga(2)–Na(1), 68.1(2); Ga(1)–Ga(2)–Na(2), 66.76(13).



The compound had the shortest Ga-Ga distance and was said to be the first example of a triple bond between the heavier group 13 elements.

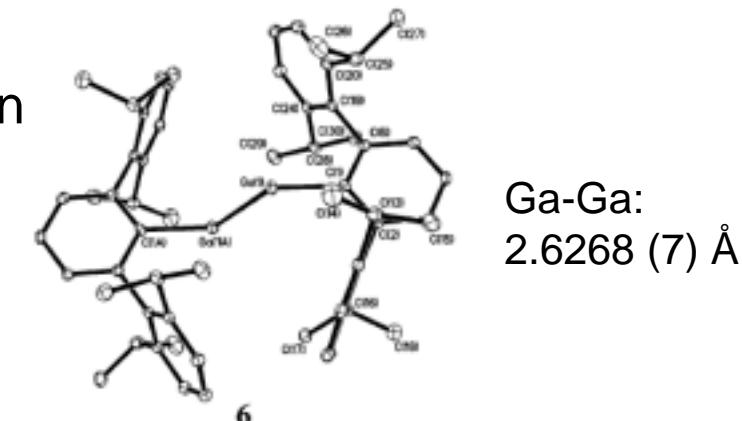
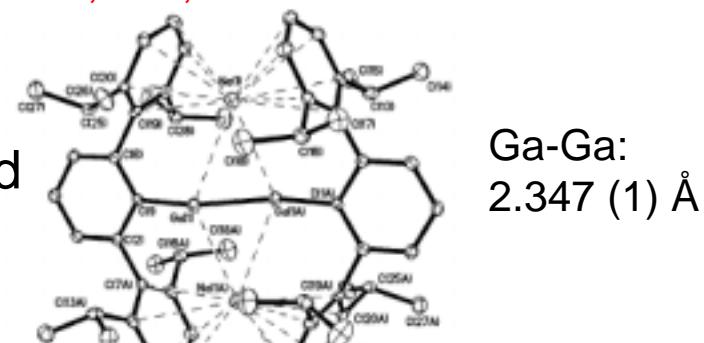


# Chem 59-651 Main Group Multiple Bonds: Synthesis

The controversial nature of the bonding between the Ga atoms in such compounds has generated a large series of experimental and theoretical papers arguing both for and against the description of Robinson's compound as a triple bond. Important papers include: Cotton, JACS, 1998, 120, 1799; Klinkhammer, Angew. Chem. Int. Ed., 1997, 36, 2320; Schaefer III, Power, JCS Dalton Trans, 2000, 407; Power, JACS, 2003, 125, 2667.

The primary arguments regard what factors determine whether or not a compound should be said to have a triple bond.

One of the complicating features is the presence of the two Na cations that are sandwiched by the *ortho*-aryl groups of the terphenyl ligands. These interactions shorten the Ga-Ga distance and thus make it appear more like a triple bond.



(Power, JACS, 2003, 125, 2667)