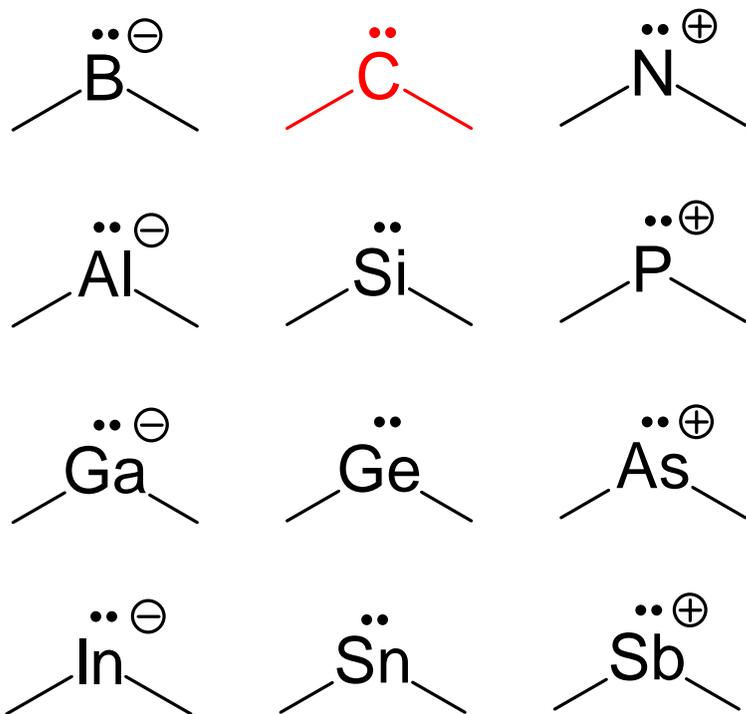


# Chem 59-651 **Carbenoids and Related Species**

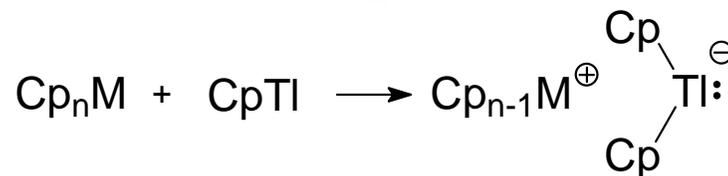
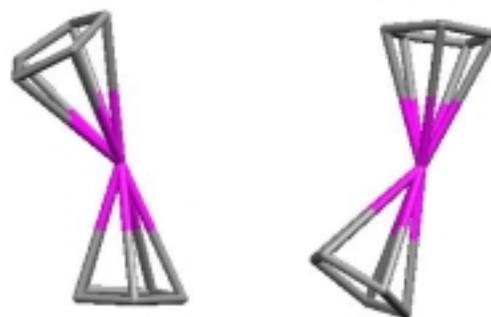
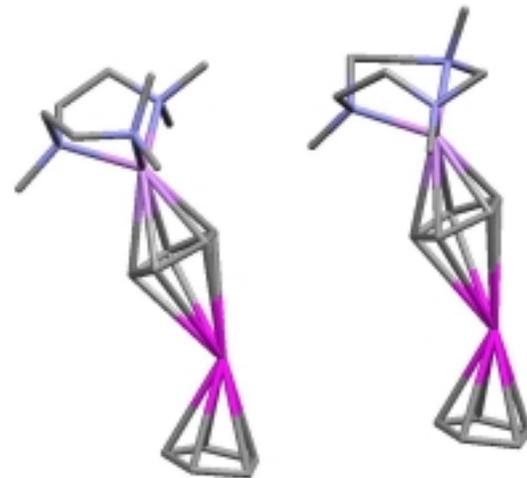
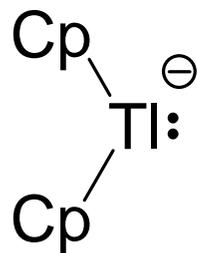
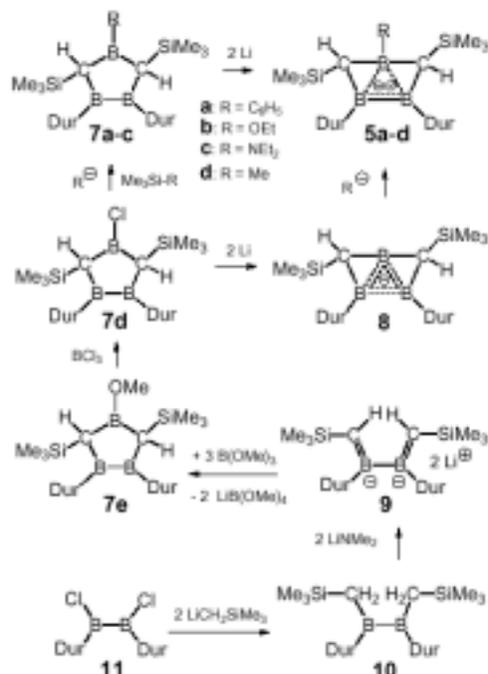
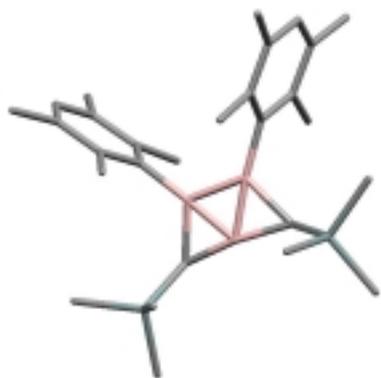
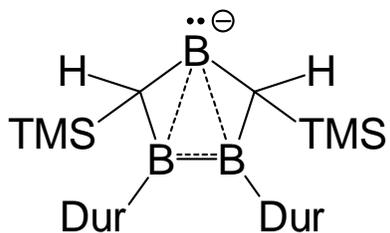
In contrast to carbenes, the heavier group 14 analogues and numerous group 15 analogues have been known for considerably longer. Probably the most important difference between the second row carbenoids and their heavier analogues is that the singlet ground states are always favoured for the compounds containing the heavier elements. This is attributable to the increased energy difference between the ns and np orbitals, which makes hybridization less favourable.



We do not have the time to discuss many of these compounds in too much detail, but there are many reviews and books about the group 14 and 15 compounds that describe the synthesis and chemistry of these species. In addition to the reviews that I have already given you, you may wish to see some of the literature that I have listed in the coming pages.

# Chem 59-651 Group 13 Carbenoids and Related Species

Only a few carbene analogues have been synthesized for the elements of group 13, many of which were made in the last few years.

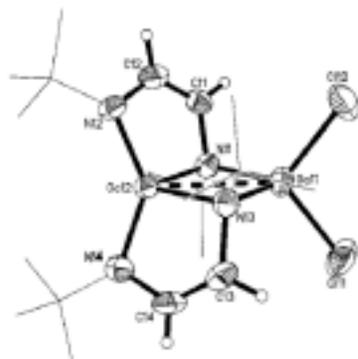
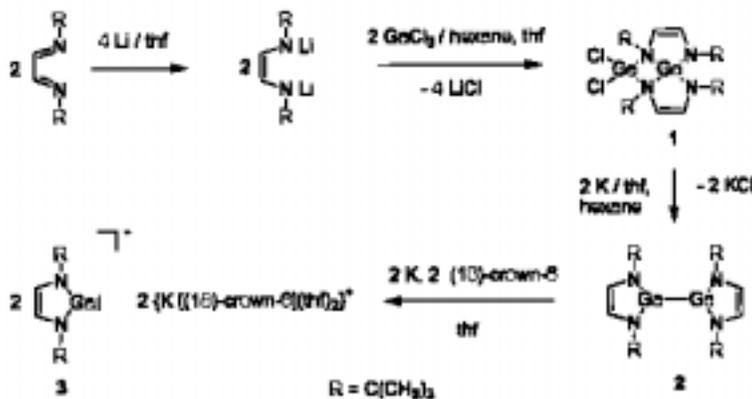
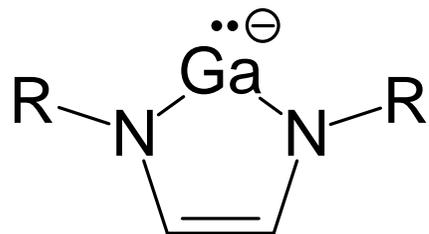


Metallocene anions (Wright, *Angew. Chem., Int. Ed.*, 1993, 32, 1774)

Bis-homoaromatic or “doubly aromatic” heterocycles (Berndt, *Angew. Chem., Int. Ed.*, 1997, 36, 1469 and *Angew. Chem., Int. Ed.*, 2000, 39, 1272)

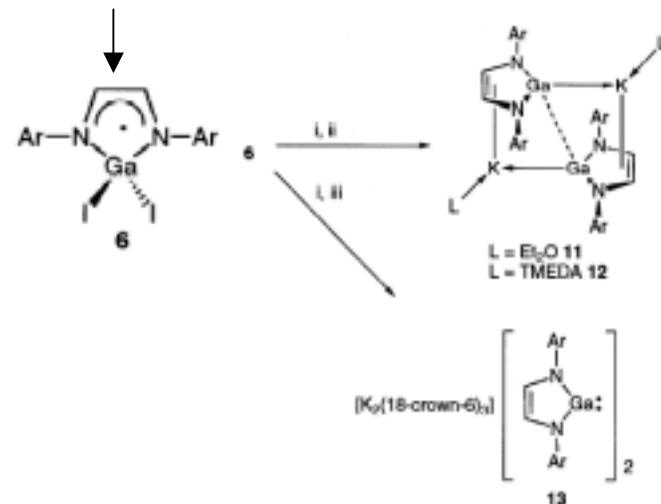
# Chem 59-651 Group 13 Carbenoids and Related Species

Probably the most important examples are those that are similar to the NHC-type carbenes we have examined.

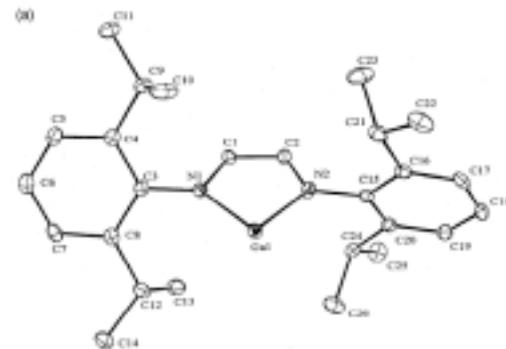
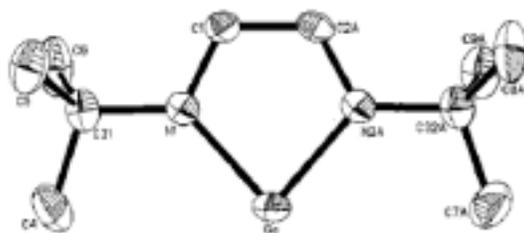


(Schmidtbaur, JACS, 1999,121, 9759)

DAB + "Gal"



Scheme 2 Reagents and conditions: i, K, THF; ii, Et<sub>2</sub>O or TMEDA/Et<sub>2</sub>O; iii, 18-crown-6.

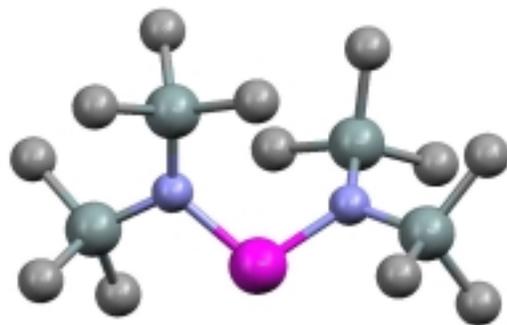
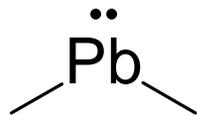
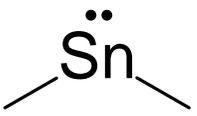
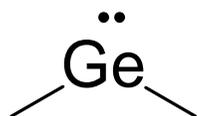
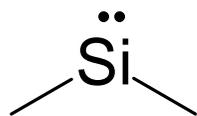


(Jones, J.C.S., Dalton, 2002, 3844)

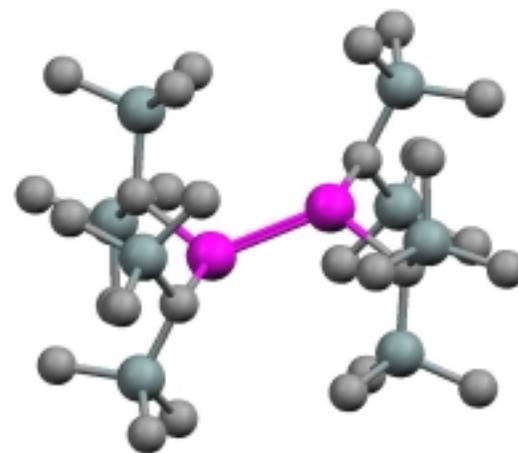


# Chem 59-651 Group 14 Carbenoids and Related Species

The heavier group 14 carbenoids have been known for much longer than the carbenes themselves. A reasonably recent review was done by Tokito and Okazaki (*Coord. Chem. Rev.*, 2000, 210, 251), which also provides references to several other books and reviews (E.g.: Weidenbruch, *Eur. J. Inorg. Chem.*, 1999, 373). The synthesis and chemistry of such carbenoids is too extensive to examine in detail in this course so we will only examine some enlightening examples.



$\text{Sn}(\text{N}(\text{TMS})_2)_2$   
(Lappert, *Chem. Comm.*, 1983, 639)

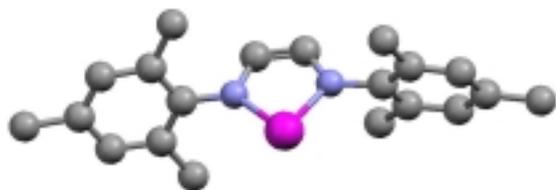
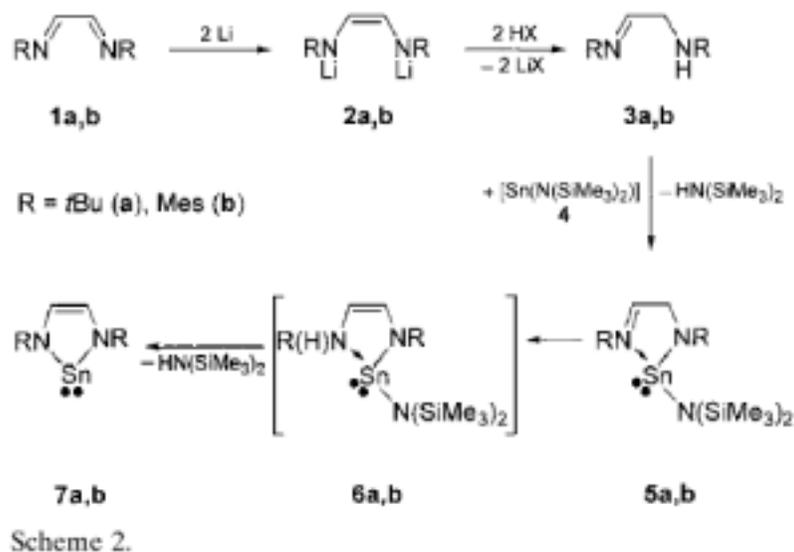


Dimer of  $\text{Sn}(\text{CH}(\text{TMS})_2)_2$   
(Lappert, *JCS, Dalton.*, 1986, 1551 and 2387)

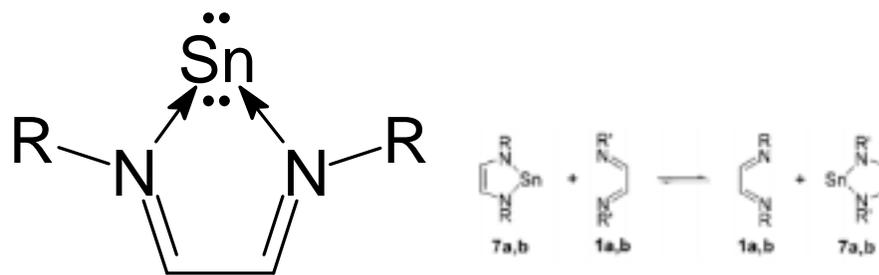
The amido analogue is monomeric in all phases while the alkyl version dimerizes in the solid state.

# Chem 59-651 Group 14 Carbenoids and Related Species

The heavier group 14 NHC analogues have been made for Si, Ge, and Sn, although they are not nearly as common as the carbenes. The Sn compound was surprisingly difficult to make and was only recently reported by Gudat (*Angew. Chem., Int. Ed.*, 2002, 41, 1888). Furthermore, the reactivity of the stannylene is considerably different from those of the NHC, the silylene and the germylene analogues.



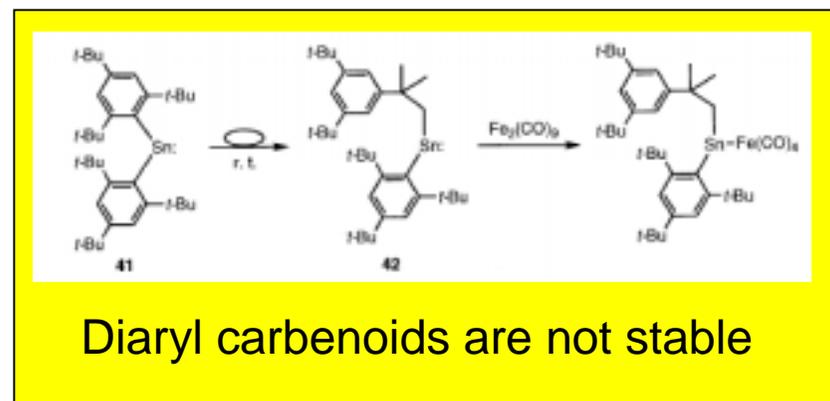
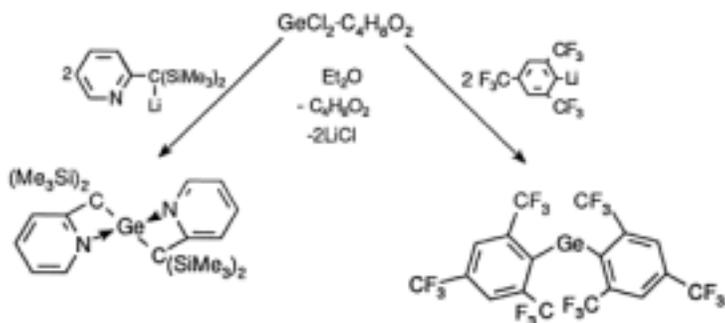
The Si analogues have been studied significantly by Denk and West (See, for example: *JACS*, 1994, 116, 10813; *JACS*, 1998, 120, 12714; and, West, *Acc. Chem. Res.*, 2000, 33, 704)



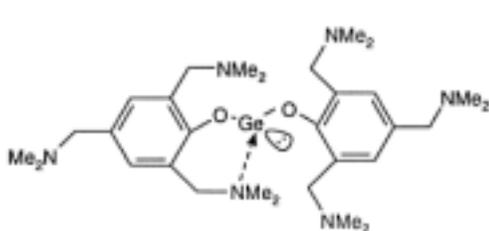
A DAB-stabilized Sn atom ?

# Chem 59-651 Group 14 Carbenoids and Related Species

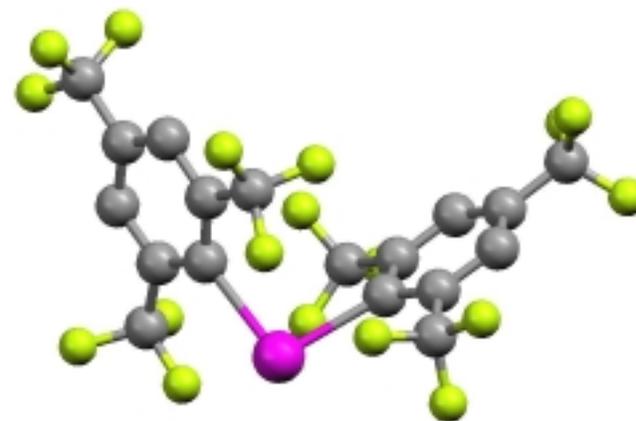
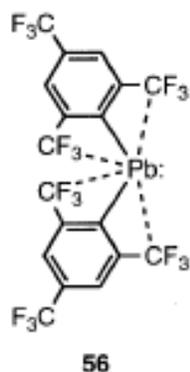
Some members of the group 14 carbenoids show us a different way to stabilize electron-deficient or coordinatively-unsaturated centers. In particular, this mode of *intra-molecular base stabilization* is exemplified by the use of  $R_f$  (Fmes) groups and Van Koten type ligands to stabilize diaryl germylenes, stannylenes and plumbylenes.



(From Barreau, *Coord. Chem. Rev.*, 1998, 178-180, 593)

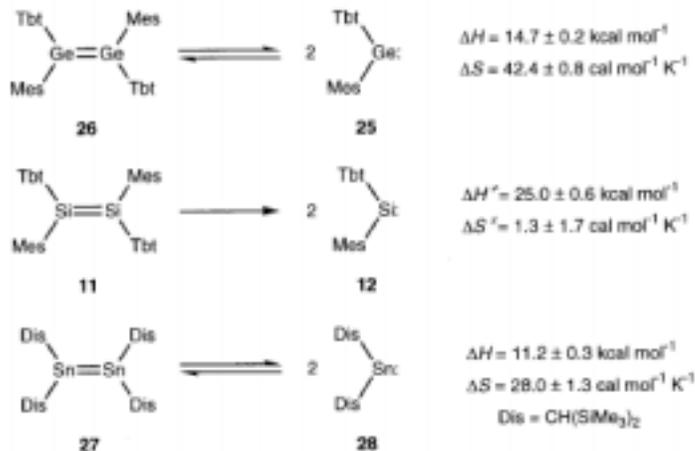
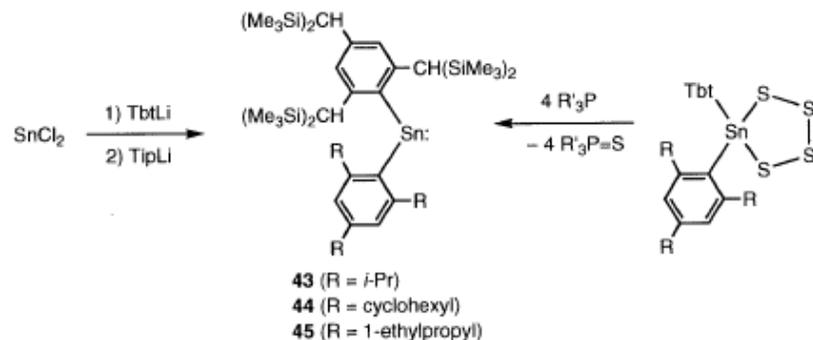


(Tokitoh, *Coord. Chem. Rev.*, 2000, 210, 251)

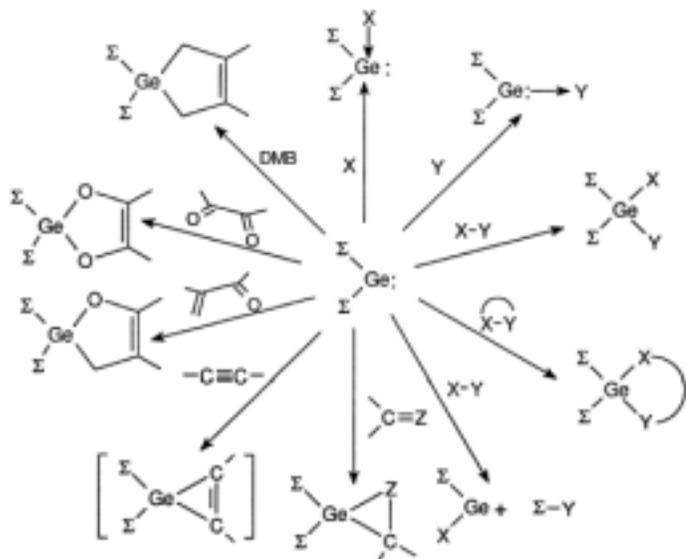


# Chem 59-651 Group 14 Carbenoids and Related Species

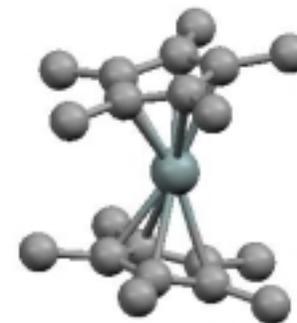
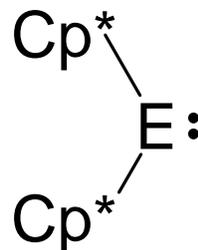
As you probably expect, steric factors are almost always important in determining whether a carbenoid will be stable or not.



Just so that you have an idea of the reactivity of these compounds.

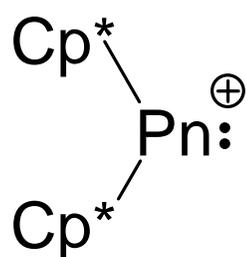
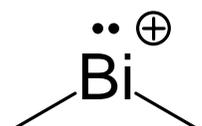
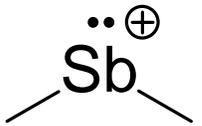
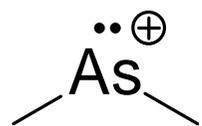
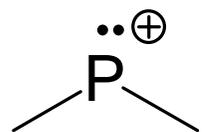
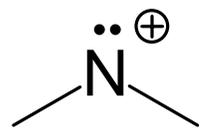


These carbenoid compounds also have an extensive chemistry as ligands for transition metal complexes and as precursors for materials.

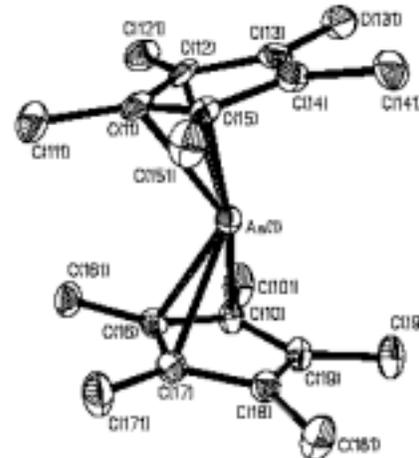
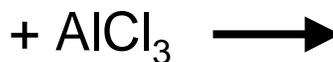
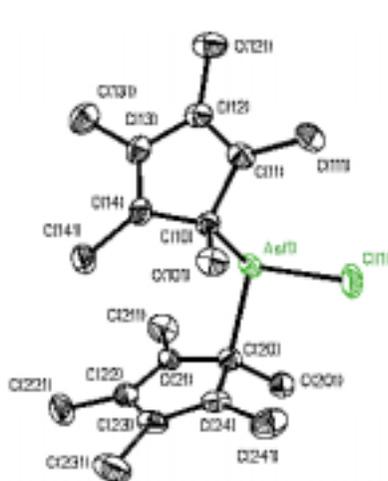


# Chem 59-651 Group 15 Carbenoids and Related Species

The group 15 carbenoids are cations and the most studied members of the group are phosphonium cations because of the ease of  $^{31}\text{P}$  NMR spectroscopy. Nitrenium cations without adequate electronic stabilization are highly reactive and are thought to be an intermediate in the degradation of diarylamines (which are carcinogenic).

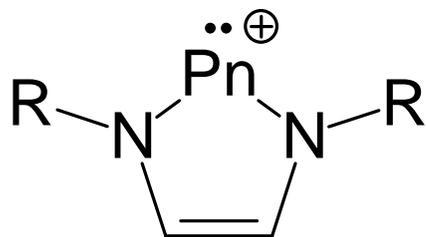


Among the first examples of carbenoid compounds that were isolated for group 15 were the metallocenium salts (Jutzi, *Angew. Chem., Int. Ed.*, 1983, 22, 250). Such cations are usually made by halide ion abstraction using a Lewis Acid.

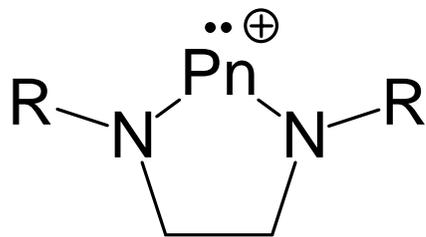


# Chem 59-651 Group 15 Carbenoids and Related Species

Cations analogous to NHCs have also been made. As with the carbenes, aromatic cations tend to be more stable than the saturated species. Because of this, the nature of the counter anions is particularly critical for the formation of stable carbenoid salts (Burford, *Inorg. Chem.*, 1994, 33, 1434). Although some books (e.g. "Multiple Bonds and Low Coordination in Phosphorus Chemistry" and "Phosphorus: The Carbon Copy") are better reference material, some reviews provide reasonable background (Cowley, *Chem. Rev.*, 1985, 85, 367). Most of the current reviews deal with the chemistry of such salts.

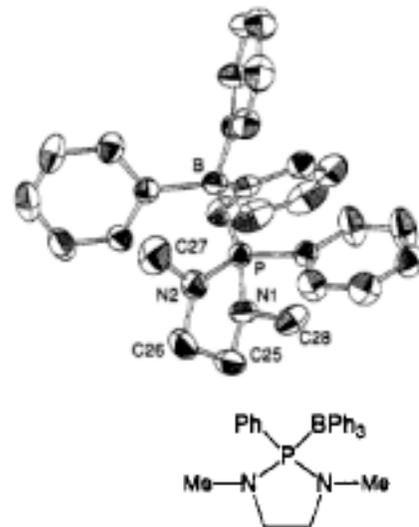


1



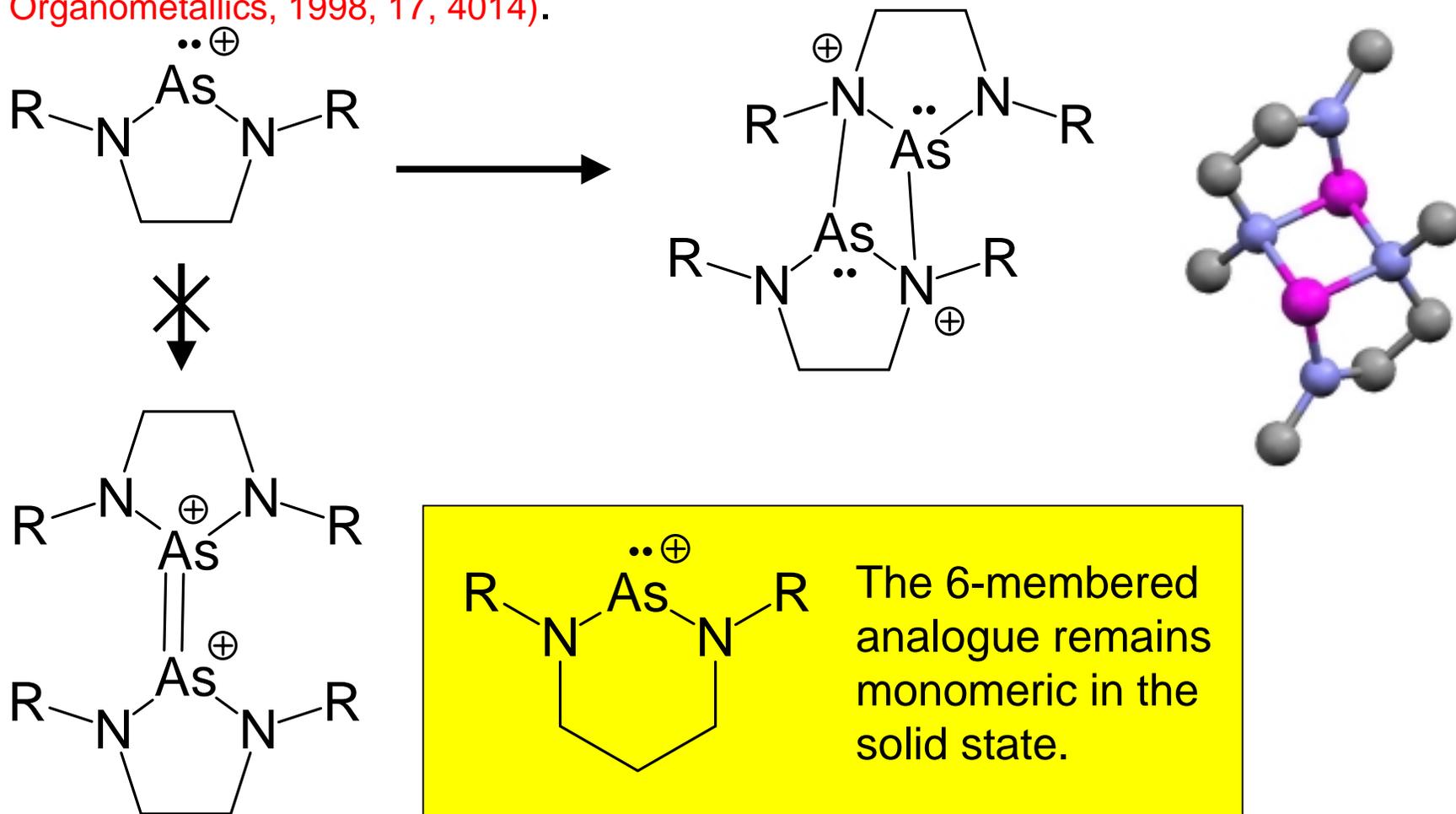
2

If the anion is  $[\text{AlCl}_4]$ , the salt of **2** is stable in  $\text{CH}_2\text{Cl}_2$ , if it is  $[\text{BPh}_4]$ , the cation attacks the anion.



# Chem 59-651 Group 15 Carbenoids and Related Species

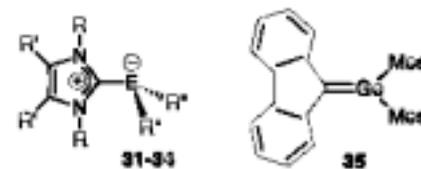
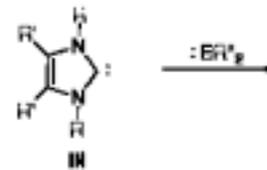
One aspect of the chemistry of the pnictogenium salts that is particularly different from those of some of the group 14 carbenoids is that of dimerization. Phosphenium cations do not seem to dimerize and the cyclic arsenic analogues do not dimerize in the solid state in the same way as carbenes (Burford, *JACS*, 1992, 114, 8147; *Can. J. Chem.*, 1996, 74, 2209; *Organometallics*, 1998, 17, 4014).





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.



	R'	R	E	R'	yield
31	(CH) <sub>3</sub>	CH <sub>2</sub> (F-Du)	Si	(NN)	63%
32	H	Me	Ge	I	65%
33a	Me	iPr	Sn	Tipp	37%
33b	Me	iPr	Sn	Cl	30%
34	Me	iPr	Pb	Tipp	43%

(NN) = 1,2-(N(CH<sub>2</sub>F-Du))<sub>2</sub>C<sub>2</sub>H<sub>4</sub>  
Tipp = 2,4,6-(iPr)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>

