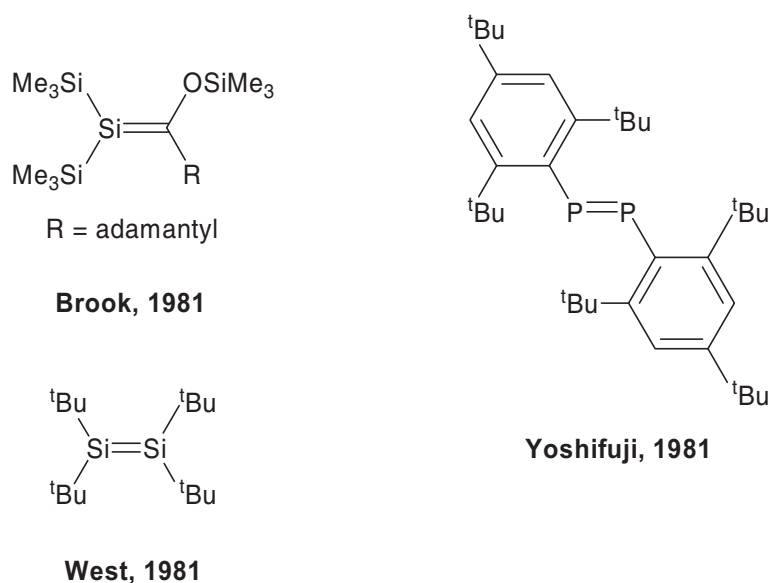


## 1. Introduction

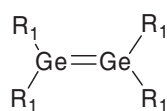
### 1.1 Heavy group 14 element analogues of alkenes

Multiple bonding in compounds containing carbon and the lighter element atoms can readily be explained by simple models such as valence bond theory and hybridisation<sup>[1]</sup> and is a common ingredient in most introductory undergraduate textbooks. Early attempts at preparing compounds containing Si=Si bonds by Kipping<sup>[2]</sup> were dashed when he realised he had actually isolated oligomeric Si cyclic compounds as opposed to unsaturated Si compounds.<sup>[3,4]</sup> He later concluded that multiple bonds to silicon were simply not possible.<sup>[5]</sup> A similar picture emerged for As and P,<sup>[6]</sup> and these persistent failures to isolate multiply bonded compounds containing heavier main group element atoms lead to the formulation of the so-called “double bond rule” by Pitzer<sup>[7]</sup> and Mulliken.<sup>[8]</sup> This rule stated that elements with a principal quantum number greater than 2 cannot form multiple bonds, a conclusion which was accepted as fact as late as 1980.<sup>[9]</sup> By 1975 a few exceptions to this rule were known involving (p–p) $\pi$  bonding between C and the elements P, As, Sb, Bi, Si and Ge,<sup>[10]</sup> but it was only conclusively overturned in 1981<sup>[11]</sup> by the report of the first stable silene by Brook and co-workers<sup>[12,13]</sup> and that of the first stable disilene by West and co-workers.<sup>[14]</sup> This, together with a report the same year by Yoshifuji of the first stable diphosphene,<sup>[15]</sup> initiated substantial academic interest in this field. By the end of the 1980s, germenenes<sup>[16,17,18]</sup> and stannenes<sup>[19]</sup> had also made an appearance in the literature.

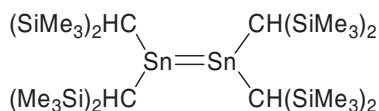


**Figure 1.1:** The first report of a silene, disilene and diphosphene in 1981: the “double bond rule” was disproved.

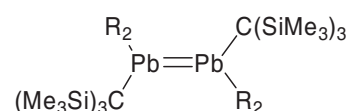
Symmetrical heavy alkene analogues, those being homodinuclear<sup>[20]</sup> were also reported for Ge by Masamune and Hanzawa,<sup>[21,22]</sup> by Lappert and co-workers for Sn,<sup>[23]</sup> and by Grützmacher and Klinkhammer for Pb, completing the series of symmetrical alkene analogues (Figure 1.2).<sup>[24]</sup>



**Masamune and Hanzawa,  
1982**



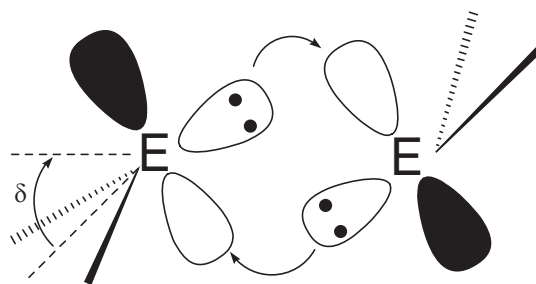
**Lappert, 1976**



**Grützmacher, 1998**

**Figure 1.2:** The first symmetrical heavy alkene analogues (congeners) for Ge, Sn and Pb. ( $R_1 = 2,6$ -diethylphenyl;  $R_2 = 2,4,6$ -trimethylphenyl).

Subsequently a large array of other heavy symmetrical alkene congeners have appeared in the literature.<sup>[25]</sup> In many experimental solid state structural studies on these compounds, a *trans*-bending geometry is observed for the substituents bound to the tetrel atom, in contrast to that of ethene. In the case of disilene compounds this ranges from  $\delta = 0^\circ$  to  $18^\circ$ ; for digermenes from  $\delta = 0^\circ$  to  $47.3^\circ$ ; for distannenes from  $\delta = 21.1^\circ$  to  $64.4^\circ$  and for lead from  $\delta = 34.2^\circ$  to  $71^\circ$  (Figure 1.3). The degree of *trans* bending within each group (Si, Ge, Sn and Pb) is governed by the electronegativity and  $\pi$ -donor ability of the ligands,<sup>[26,27,28]</sup> but this is difficult to separate from the steric influences. The trend, nevertheless, on average points to an increase in this *trans*-bending angle on descending from Si to Pb, with corresponding increased pyramidalisation of the tetrel atom. This phenomenon is due to the increasing energy difference between s and p electrons on descending group 14 resulting in the decreased participation of the s electrons in bonding, decreased hybridisation with p orbitals, and increased lone pair character on the tetrel atoms.<sup>[29]</sup> The bonding picture in these heavy alkene analogues can be explained by two sets of donor acceptor interactions  $n_\sigma \rightarrow p_\pi$ , between two carbene-like monomers taking into account the fact that the higher homologues of carbenes possess a singlet, rather than triplet ground state (Figure 1.3).<sup>[30,31,32]</sup>



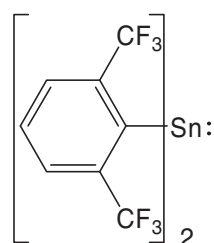
**Figure 1.3:** Bonding model explaining the *trans* bent geometry (defined by  $\delta$ ) of substituents of heavy alkene analogues (E = Si – Pb).

This bonding interaction becomes weaker in the case of Ge, Sn and Pb and often results in dissociation of the dimers in solution, to give monomeric singlet carbene analogues,<sup>[33]</sup> referred to as ylens further on in the discussion. This is typically not the case for Si, where this is not usually observed, probably due to the fact that Si adopts a more classical  $\sigma$  and  $\pi$  bonding picture, as with ethene, on the basis of solid state  $^{29}\text{Si}$  NMR data, according to one investigation.<sup>[34]</sup>

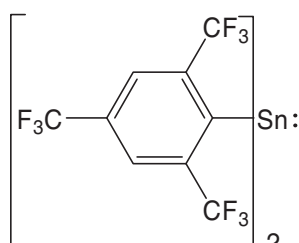
Monomeric ylens for Ge, Sn and Pb in the solid state are well known, but their existence in the solid state is largely dependent on the nature of the substituents. For example,  $(\text{Me}_3\text{Si})_3\text{CGeCH}(\text{SiMe}_3)_2$  reported by Jutzi and co-workers is reported to be a monomer in the solid state,<sup>[35]</sup> in contrast to the closely related  $\text{Ge}\{\text{CH}(\text{SiMe}_3)_2\}_2$ , reported by Lappert and co-workers to be dimeric in the solid state.<sup>[36]</sup> Similarly, the stannylene  $[\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2]_2$  is dimeric in the solid state, but the closely related cyclic version reported by Kira and co-workers is monomeric.<sup>[37]</sup> Monomeric silylenes are far less accessible, and more reactive than their Ge, Sn or Pb counterparts. For example, the silylene  $\text{Si}\{\text{N}(\text{SiMe}_3)_2\}_2$  reported by West and co-workers was found to be thermally labile undergoing rapid decomposition above 0 °C in solution.<sup>[38]</sup> This is in contrast to the Ge, Sn and Pb analogues found by Lappert and co-workers, 30 years earlier, which are thermally stable.<sup>[39]</sup>

Monomeric homoleptic stannylenes bearing purely  $\sigma$ -bonded aromatic substituents were reported by Zuckerman and co-workers<sup>[40]</sup> and Edlmann and co-workers.<sup>[41]</sup> These were stabilised sterically but more importantly, through fluorine tin contacts from peripheral  $\text{CF}_3$  groups, which prevented dimerisation, or oligomerisation of the monomers. The analogous monomeric plumblylene,<sup>[42]</sup> and germylene have also been reported.<sup>[43]</sup> Homoleptic monomeric ylens (Ge, Sn and Pb) stabilised exclusively on steric grounds have been

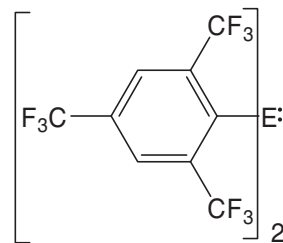
reported by Power and co-workers. These make use of kinetically stabilising, sterically very demanding *m*-terphenyl substituents:<sup>[44]</sup> C<sub>6</sub>H<sub>3</sub>-2,6-R<sub>2</sub> (R: Mes = 2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>,<sup>[45]</sup> Dipp = 2,6-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>2</sub><sup>[46]</sup>).



**Zuckerman, 1981**

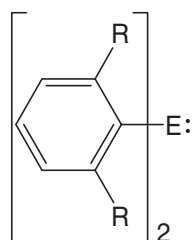


**Edelmann, 1991**



E = Ge, **Kampf, 1997**

E = Pb, **Edelmann, 1991**



E = Ge, Sn, Pb; R = Mes

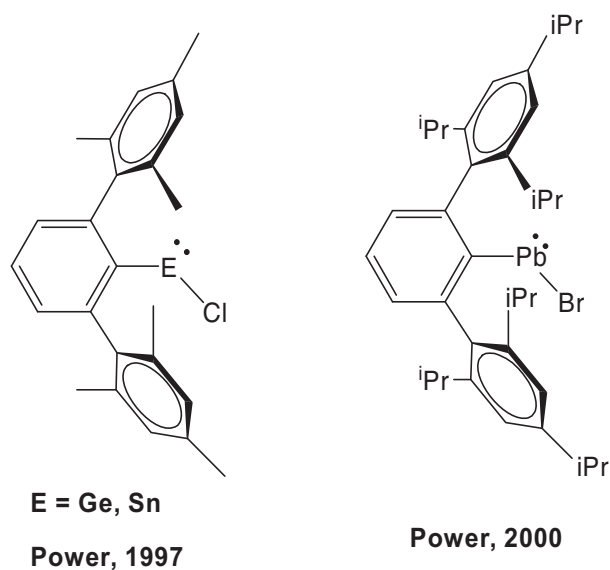
**Power 1997**

E = Ge, Sn, Pb; R = Dipp

**Power 2006**

**Figure 1.4:** Monomeric ylens using steric protection and CF<sub>3</sub> groups, enabling stabilisation through intramolecular F-Sn contacts.

Jutzi and Leue reported the first monomeric heteroleptic germylene, containing a  $\sigma$ -bonded aromatic substituent and a halogen: GeClMes\* (Mes\* = 2,4,6-<sup>t</sup>Bu<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>).<sup>[47]</sup> Power and co-workers followed by reporting [SnCl(2,6-Mes<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>] and [GeCl(2,6-Mes<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>] (Mes = 2,4,6-Me<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>),<sup>[45a]</sup> prepared by metathetical exchange using [Li(2,6-Mes<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>].<sup>[48]</sup> This was followed by the lead analogue, [PbBr(2,6-Trip<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>] (Trip = 2,4,6-<sup>i</sup>Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>),<sup>[49]</sup> prepared in an analogous way. The propensity of these ylens to dimerise typically via halogen bridging is strongly dependant on the nature of the halogen, and *m*-terphenyl substituent, but generally are assumed to form monomers in solution.

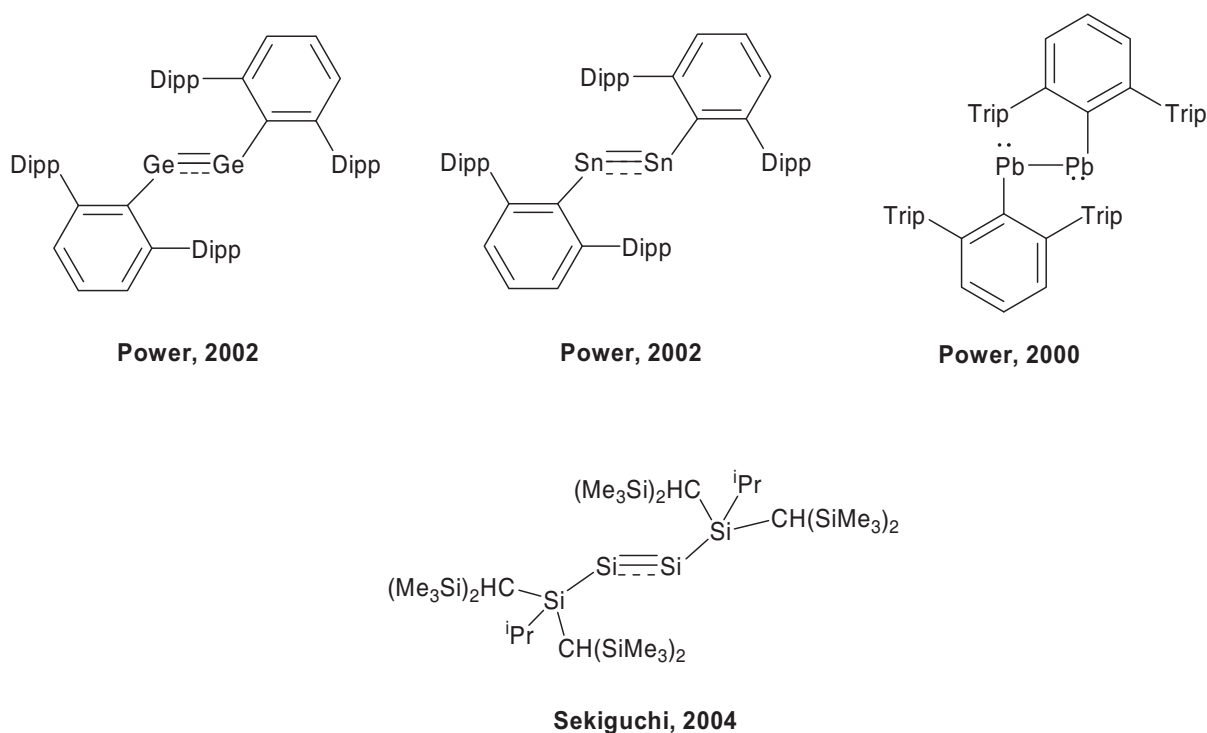


**Figure 1.5:** Heteroleptic sterically encumbered *m*-terphenyl ylens by Power (The monomeric forms are depicted here, which are their assumed form in solution).

## 1.2 Heavy group 14 element analogues of alkynes

Up until 1999, the isolation of heavy alkyne congeners was still an open question, owing in part to the fact that each tetrel would only bear one substituent, resulting in increased steric requirements to stabilise the emerging compound. The previous facile entry to sterically very demanding ylens by Power, however, enabled the isolation of a diplumbylene: 2,6-Trip<sub>2</sub>-H<sub>3</sub>C<sub>6</sub>Pb—PbC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub> (Trip = 2,4,6-<sup>i</sup>Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>), in 2000, obtained serendipitously during an attempt at preparing PbH(2,6-Trip<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) from PbBr(2,6-Trip<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) by action of HAl<sup>i</sup>Bu<sub>2</sub>.<sup>[50]</sup> The molecular structure of this compound, revealed a heavily *trans*-bent configuration, in contrast to that of a linear arrangement of atoms as seen with ethyne<sup>[51]</sup> (Pb—Pb—C 94.26(4)°), pointing to localised lone pairs on each lead centre. In addition, the Pb—Pb bond length of 3.1881(1) Å was significantly longer than that of typical diplumbanes such as Ph<sub>3</sub>Pb—PbPh<sub>3</sub> at 2.844(4) Å.<sup>[52]</sup> These two facts illustrated a complete lack of hybridisation in the lead atoms, and almost exclusive use of p orbitals in σ-bonding.<sup>[53]</sup> This was followed 2002 by the report of the first digermine: 2,6-Dipp<sub>2</sub>-H<sub>3</sub>C<sub>6</sub>Ge—GeC<sub>6</sub>H<sub>3</sub>-2,6-Dipp<sub>2</sub> (Dipp = 2,6-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>).<sup>[54]</sup> In this case, the Ge—Ge bond length of 2.2850(6) Å was found to be considerably shorter than normal Ge—Ge single bonds (2.44 Å)<sup>[55]</sup> and indicative of multiple bonding character.<sup>[56]</sup> A *trans* bent configuration was also observed for this compound (Ge—Ge—C 128.67(8)°), albeit not to the same extent as that of the Pb compound. The distannyne was reported in the same year<sup>[57]</sup> and featured a Sn—Sn bond length of

2.6675(4) Å, shorter compared to Sn—Sn single bonds,<sup>[58]</sup> and again indicative, of multiple bond character. The Sn-Sn-C angle in this case was found to be 125.24(7)°, which was also later found to depend on the nature of the terphenyl substituent.<sup>[59]</sup> The series of heavy alkyne congeners was completed in 2004 for Si, in a report by Sekiguchi and co-workers, presenting the first disilyne.<sup>[60]</sup> The Si—Si bond length was observed to be 2.0622(9) Å, considerably shorter (13.5 %) than that of typical Si—Si single bonds, and 3.8 % shorter than that of typical Si=Si double bonds.<sup>[61]</sup> The authors, and subsequent investigations assert the bond order to be three,<sup>[62]</sup> but others have suggested, on the basis of calculations, the bond order to be two, rather than three.<sup>[63,64]</sup> This case in point draws attention to the contentious issue surrounding the assignment of bond order in these higher homologues. A further example of this includes the first example of a gallyne by Robinson, claimed to be a Ga≡Ga triple bond.<sup>[65]</sup> This was subsequently disputed by Cotton as rather being a “double bond with a significant role for noncovalent interactions” on the basis of density functional theory.<sup>[66]</sup>

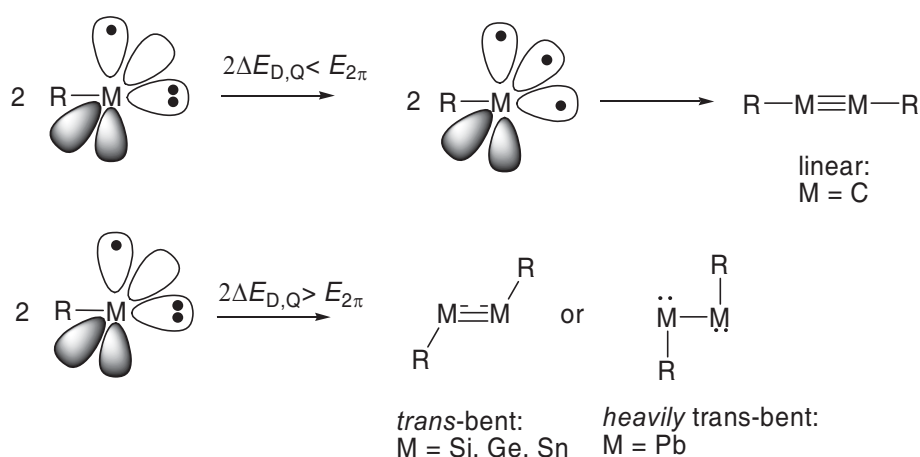


**Figure 1.6:** The first isolated examples of group 14 alkyne analogues.

The *trans* bending observed in the higher homologues can be attributed to the increased energy requirements to access the quartet state, rather than the doublet state in the M–R moiety. If twice this energy exceeds the energy gained from the two emerging  $\pi$  bonds, a bent geometry is observed, if not, as is the case with ethyne, a linear geometry results. This approximation does not take into consideration the steric or  $\sigma$ -bonding effects, but does qualitatively explain the differences.<sup>[29]</sup>

	H—C≡C—H	H—Si≡Si—H	H—Ge≡Ge—H
$2\Delta E_{D,Q}$ (kcal·mol <sup>-1</sup> )	28.9	76.0	82.4
$E_{2\pi}$ (kcal·mol <sup>-1</sup> )	120–130	46–62	44–50
	$2\Delta E_{D,Q} < E_{2\pi}$	$2\Delta E_{D,Q} > E_{2\pi}$	$2\Delta E_{D,Q} > E_{2\pi}$
Geometry	linear	<i>trans</i> -bent	<i>trans</i> -bent

**Table 1.1:** Summary of  $\pi$ -bond energies, and  $\Delta E_{D,Q}$  energies accounting for *trans*-bending in the higher alkyne analogues (from ref 29)

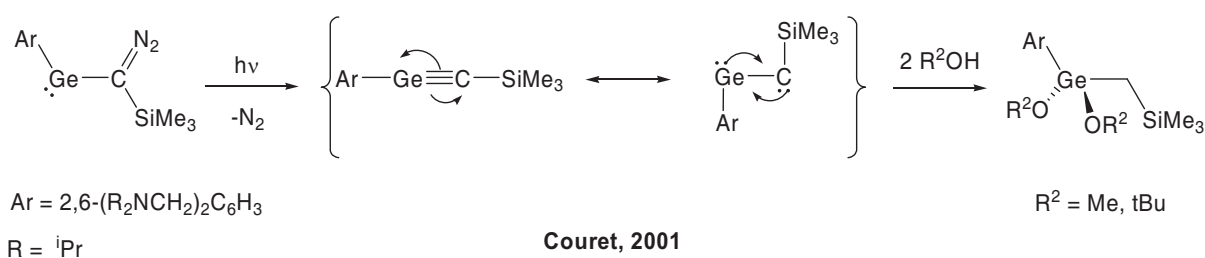


**Figure 1.7:** *trans*-bending effect in heavier alkyne homologues (adapted from ref 29)

The results obtained so far for the heavy group 14 alkynes point to an ever decreasing bond order on descending from Si to Pb, exemplified by bond lengths and the decreasing E-E-C angle. A continuum of bond orders can tentatively be imagined for these compounds: ethyne being on the one end, with a bond order of 3, and lead on the other with a bond order of 1. Si, Ge and Sn fall in-between these two extremes, with that of Si > 2, Ge  $\geq$  2, Sn  $\approx$  2.

Several reactivity studies, further probing the nature of the multiple bond in the case of Ge and Sn have also been carried out, for example activation of dihydrogen<sup>[67,68]</sup> at ambient conditions, activation of ethene,<sup>[69]</sup> reactivity towards N<sub>2</sub>O,<sup>[70]</sup> and reactivity towards other unsaturated molecules.<sup>[71]</sup> The nature of the reduction products of Ge and Sn alkyne analogues have also been investigated, typically resulting in singly reduced radical species of the type M[R-E-E-R], (M = Na or K, E = Ge or Sn, R = bulky terphenyl substituent), or the doubly reduced counterparts.<sup>[72]</sup>

Asymmetric alkyne analogues are very uncommon. Couret and co-workers have reported a germaacetylene generated *via* photolysis of a diazomethylgermylene,<sup>[73]</sup> and Kira and co-workers that of a stannaacetylene, generated also *via* a similar photolytic pathway.<sup>[74]</sup> In both studies the asymmetric acetylene was not formally isolated and to date none have been structurally characterised.<sup>[75]</sup>



**Scheme 1.1:** Chemical evidence for the formation of a germyne, by Couret and co-workers.

### 1.3 Heavy group 14 element analogues of alkylidene (carbene) complexes\*

Having introduced the developments in multiple bonding of the heavy homologues of carbon from a main group chemistry perspective, we now turn our attention to the analogous transition metal chemistry.

Fischer and Maasböl announced the discovery of the first alkylidene complexes, [(CO)<sub>5</sub>W=C(Me)(OMe)] and [(CO)<sub>5</sub>W=C(Ph)(OMe)] in 1964,<sup>[76]</sup> shown later by X-ray crystallographic investigation to bear a planar carbon atom bound to the metal centre,<sup>[77]</sup> as did the Cr analogues.<sup>[78]</sup> This important discovery heralded the era of carbon to metal multiple bonding, and ten years later, Schrock reported an example of an alkylidene complex of Ta: [Ta{CH<sub>2</sub><sup>t</sup>Bu}<sub>3</sub>{=CH<sup>t</sup>Bu}].<sup>[79]</sup> The Schrock compound differed from those of Fischer in the respect that the carbene carbon atom bears a hydrogen atom<sup>[80]</sup> and was not bonded to any stabilising heteroatomic substituent. This led to the formulation of two distinct classes of carbene complexes those of Fischer type, and those of Schrock type (Table 1.2).

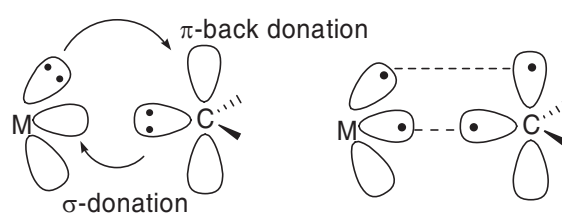
\* See as examples: (a) J. W. Herdon, *Coord. Chem. Rev.* **2009**, 86; (b) R. R. Schrock, *Chem. Rev.* **2009**, 109, 3211; (c) W. Zhang, J. S. Moore, *Adv. Synth. Cat.* **2007**, 349, 93; (d) R. R. Schrock, C. Czekelius, *Adv. Synth. Cat.* **2007**, 349, 55 and references therein; (e) A. Mortreux, O. Coutelier, *J. Mol. Cat. A* **2006**, 254, 96; (f) R. R. Schrock, *J. Chem. Soc. Chem. Commun.* **2005**, 22, 2773 and references therein; (g) A. Mayr, H. Hoffmeister, *Adv. Organomet. Chem.* **1991**, 32, 227 and references therein



Fischer Type	Schrock Type
Low oxidation state metals	High oxidation state metals
Middle to late transition metals	Early transition metals
$\pi$ -acceptor ligand	$\pi$ -donor ligand
Bond described as a $\sigma$ -donation $\pi$ -acceptor interaction with the metal	Bond described as a covalent $\sigma$ and $\pi$ interaction with metal
Carbene centre electrophilic	Carbene centre nucleophilic
Heteroatom substituents on carbene carbon atom	Alkyl or H substituents on carbene carbon atom

**Table 1.2:** Comparison of Schrock and Fischer carbene complexes.

By use of the Dewar-Chatt-Duncanson model,<sup>[81,82]</sup> the differences between Fischer and Schrock type systems can be seen (Figure 1.8).



**Figure 1.8:** Fischer (left) vs Schrock (right) carbene complexes, according to the Dewar-Chatt-Duncanson model, originally developed to explain bonding in alkene complexes.

The logical extension of double bonding between metals and the heavy tetrel atoms was first reported 1976 when Jutzi and co-workers reported the first germylidene complex  $[(\text{CO})_5\text{Cr}\{\text{Ge}(\text{SR}_2)_2\}]$ ,<sup>[83]</sup> and Lappert and co-workers that of  $[(\text{CO})_5\text{Cr}\{\text{Ge}(\text{CH}(\text{SiMe}_3)_2)_2\}]$ .<sup>[84]</sup> Lappert also reported the first series of analogous stannylidene complexes. It was only in 1985, however that the first plumbylidene complex was structurally characterised  $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}=\text{Pb}=\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$ .<sup>[85]</sup> Tilley and co-workers then reported the isolation of the first silylidene complex some 10 years later,  $[(\text{PCy}_3)_2\text{HPt}=\text{Si}(\text{SEt})_2][\text{BPh}_4]$ .<sup>[86]</sup> Today, a plethora of ylidene complexes exist,<sup>[87]</sup> and typically involve low oxidation state metals, and hence can for the most part be considered as Fischer type carbene complexes.<sup>[33]</sup>

These compounds can be categorised into five distinct classes:

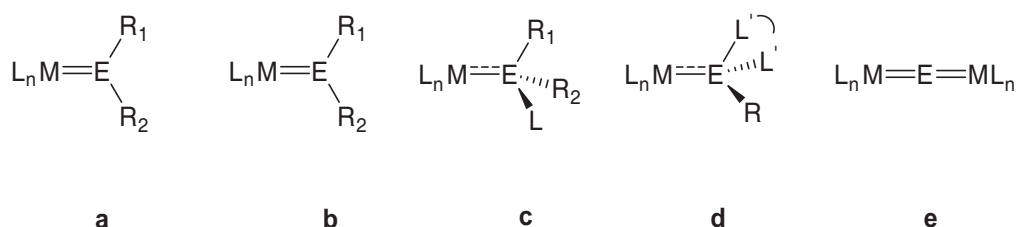
(a) Homoleptic ylidene complexes of the type  $[L_nM=ER_2]$  ( $L_n$  = ligand sphere around metal, E = Ge, Sn or Pb).

(b) Heteroleptic ylidene complexes of the type  $[L_nM=ER_1R_2]$  ( $L_n$  = ligand sphere around metal, E = Ge, Sn or Pb,  $R_1 \neq R_2$ ). An example of this is  $[(CO)_5W=Ge(Cl)(\eta^2-C_5Me_5)]^{[88]}$

(c) Neutral, typically N or O, Lewis base stabilised ylidene complexes of the type  $[L_nM=E(R_1)_x(\text{donor})_{3-x}]$ , ( $L_n$  = ligand sphere around metal,  $R_1$  = substituent(s)) which are ubiquitous,<sup>[33]</sup> (although only two examples of structurally investigated complexes of the type  $[L_nM=EX_2(\text{donor})]$  ( $L_n$  = ligand sphere around metal, X = halogen) exist, which can also be classified in this category.<sup>[89]</sup>

(d) Stabilisation of the tetrel atom with bidentate ligands e.g.  $\beta$ -diketiminato ligands, resulting in 3 coordinate tetrel atoms, which can, for example be coordinated to W, resulting in heteroleptic germylidene and stannylidene complexes.<sup>[90]</sup>

(e) “Naked” tetrel atoms bound between two metal centres. Structurally characterised examples for Ge also exist,<sup>[91,92]</sup> none for Sn, and the one for lead already mentioned.



$L_n$  = ligand sphere on metal, E = tetrel atom (Si-Pb)

**a:**  $R_1 = R_2$

**b:**  $R_1 = R_2$

**c:**  $R_1 = R_2$  or  $R_1 \neq R_2$ , L = donor ligand

**d:** R = organic substituent or halogen,  $L' - L'$  = bidentate ligand

**Figure 1.9:** Categorisation of ylidene complexes of Si-Pb