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Carbones: divalent C(0) compounds

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Carbon is known to form covalent bonds and give stable tetravalent species with C(IV) oxidation state. Though several other possibilities like free radicals, carbenes and carbenes are known, they are all considered to be reactive intermediates. Stabilizing these unusual states of carbon became a laboratory curiosity for several chemists during the past five decades, and efforts in this directions led to several new species like ‘stable bottlable carbenes’ – *N*-heterocyclic carbenes (**A**, Figure 1), also found to be useful, offering exciting opportunities¹. Other examples in this class which provided immense scope for novel chemistry are triplet persistent carbenes (**B**)², pentacoordinate (**C**)³ and hexacoordinate carbon (**D**)⁴ system. The latest member in this group of carbon compounds are carbones (**1–8**, Figure 2) with C(0) oxidation state. Such carbon compounds are characterized by the presence of a central carbon atom carrying two lone pairs of electrons, i.e. none of the four electrons of carbon is involved in bond formation. This is possible because the central carbon accepts electrons from Lewis bases and is involved in the formation of the coordination (captodative) bonds; thus carbon behaves like an electron-accepting metal.

Compounds with C(0) state are known⁵ since 1961. $C(\leftarrow PR_3)_2$ was obtained in a reaction of methylidenebis-(triphenylphosphonium)bromide with a suspension of potassium in boiling purified diglyme. This species was considered as a carbene or allene or ylide to satisfy known chemical bonding knowledge. Such erroneous description prevented the growth

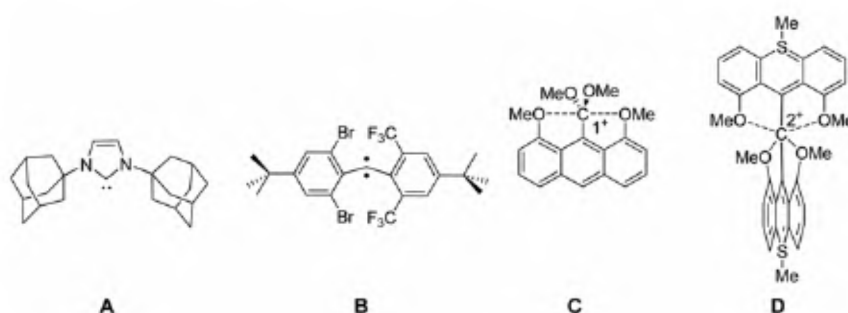


Figure 1. Novel bonding environments identified for carbon.

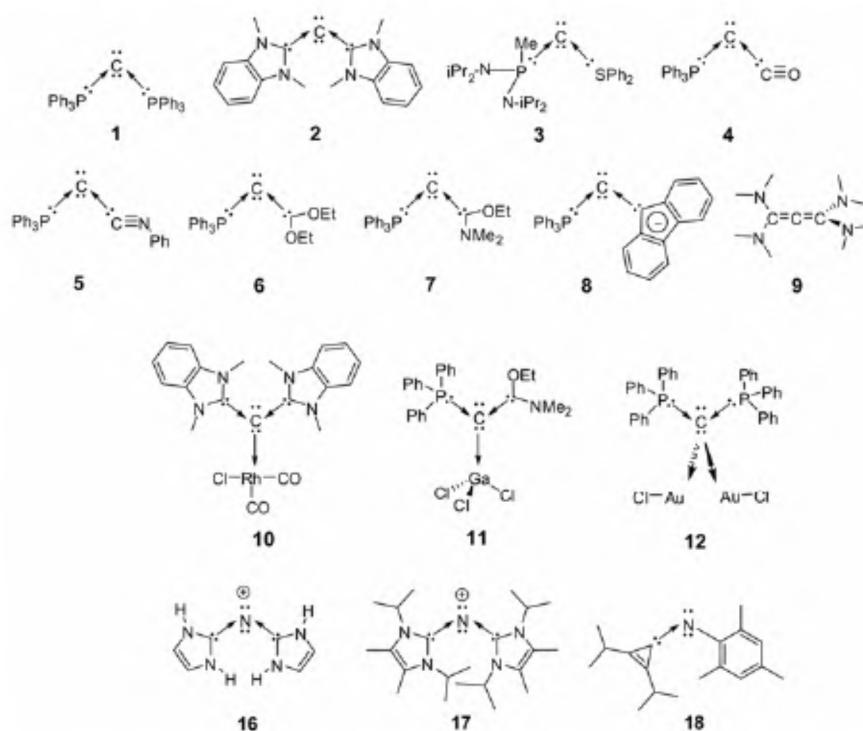


Figure 2. Examples of recently generated carbones, their metallic complexes and their nitrogen analogues.

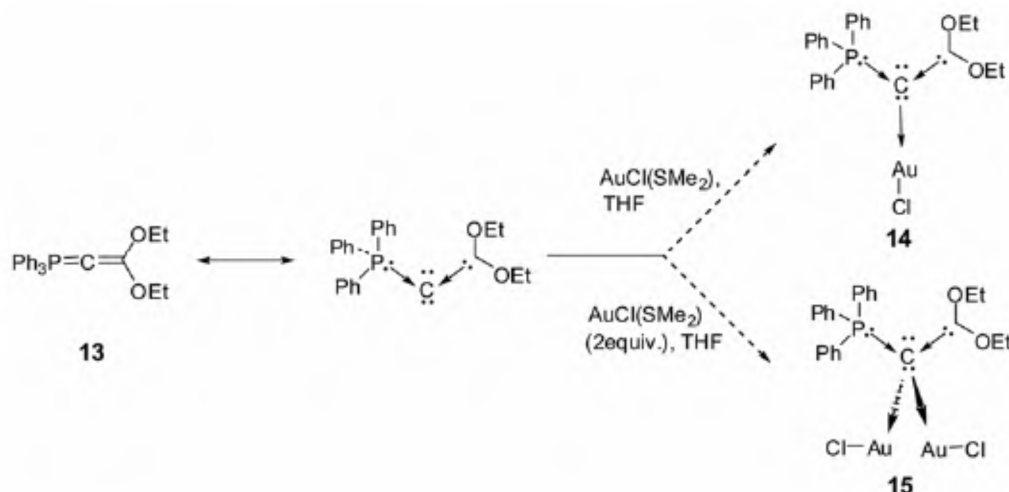


Figure 3. Mono-coordination and di-coordination properties of **13**.

of novel chemical bonding in C(0) carbon chemistry for 45 years since its first synthesis. In 2006, quantum chemical analysis showed that $\text{C}(\text{PR}_3)_2$ should be considered as $\text{C}(\leftarrow\text{PR}_3)_2$ and the central carbon atom carries two lone pairs⁶. Following this, several new species of carbodicarbenes have been designed⁷ and synthesized⁸, many new species belonging to this class generated and characterized⁹, a new name assigned (carbones) and exponential growth has been noted¹⁰.

Carbones can be formed by carbon accepting electrons from (i) PR_3 , (ii) *N*-heterocyclic carbenes, (iii) carbon monoxide, (iv) isonitriles, (v) carbenes and (vi) SR_2 . Even linear species like (**9**) were shown to be characterized by shallow bending potential and tend to behave like carbones under dynamical conditions¹⁰. Carbones are highly nucleophilic super bases; they form complexes with transition metals ML_n (Figure 2); $(\text{L}\rightarrow)_2\text{C} \rightarrow \text{Rh}(\text{CO})_2\text{Cl}$ (**10**) (ref. 8), $(\text{L}\rightarrow)_2\text{C} \rightarrow \text{AuCl}$ (ref. 10). They also form $\text{LA} \rightarrow \text{LB}$ complexes, for example, $(\text{L}\rightarrow)_2\text{C} \rightarrow \text{GaCl}_3$ (**11**) (ref. 10). The two lone pairs on the central carbon are confirmed when carbene is shown to coordinate to two metals $(\text{L}\rightarrow)_2\text{C}(\rightarrow\text{AuCl})_2$ (**12**); ref. 11. Indeed ylides like (**13**)

can be shown to possess carbene-like character, which when treated with $\text{AuCl}(\text{SMe}_2)$ in THF yielded (**14**) and (**15**) (Figure 3).

Following this exciting new chemistry of carbones, equivalent $\text{L}\rightarrow\text{N}\leftarrow\text{L}^\oplus$ systems were first computationally designed (**16**) (ref. 12) and synthesized (**17**) (Figure 2)¹³ in which the central nitrogen atom was shown to be characterized by two lone pairs of electrons. This further led to the identification of species with $\text{L} \rightarrow \text{N}-\text{R}$ (**18**) environment with two lone pairs of electrons on the central N atom¹⁴. Thus exciting new chemical bonding environment is being identified, challenging original work by Kekule, Lewis and Pauling.

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