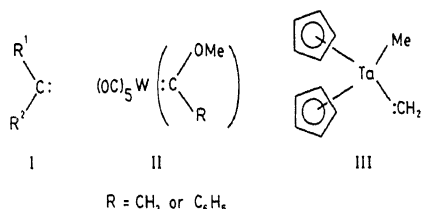


'Carbenes' in a bottle—From reactive intermediates to isolable species

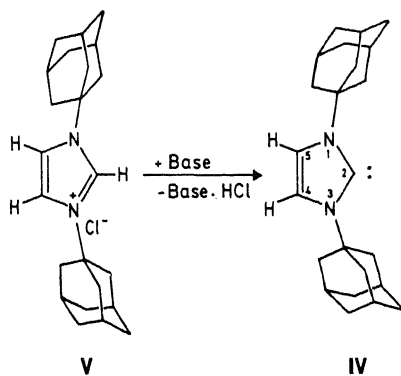
S. S. Krishnamurthy

Carbenes are divalent carbon species (I) long known to organic chemists as transient reactive intermediates. They can be stabilized by complexation with transition metals. The first stable transition-metal-carbene complexes were reported in 1964 by Fischer and co-workers¹ and were of the type II. More than a decade later, the isolation of a transition-metal complex (III) containing the parent methylene carbene (:CH₂)



was accomplished by Schrock² in Du Pont Laboratories, Wilmington, USA. From the same laboratories, Arduengo and coworkers³ now report the isolation of a stable crystalline carbene (IV)—a remarkable discovery, almost a dream come true.

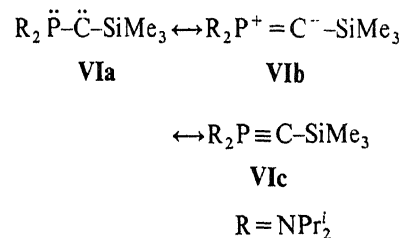
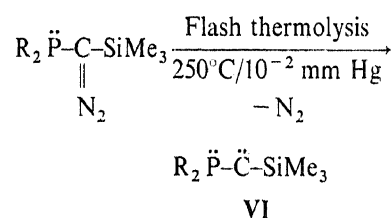
The Arduengo carbene IV was prepared by the deprotonation of 1,3-di-1-adamantylimidazolium chloride V in tetrahydrofuran with catalytic amounts of dimsyl anion (⁻CH₂S(O)CH₃) in the presence of sodium hydride or with potassium *tert*-butoxide:



Carbene IV is a solid with a melting point of 240–241°C. It crystallizes from toluene as colourless rectangular prisms. It is stable in the absence of oxygen and moisture. It has been fully characterized by elemental analyses, IR and NMR

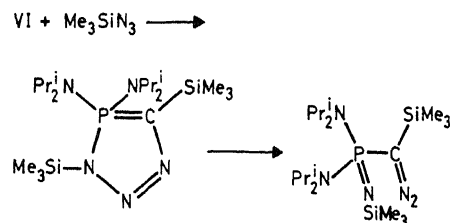
spectra, and by single-crystal X-ray diffraction. The bulky adamantyl substituents impart sufficient kinetic stability to the carbene to permit its isolation. Reinforcing this is an electronic stabilization that stems from π donation from the electron-rich π system (N–C=C–N) into the carbene out-of-plane *p*-orbital. This type of interaction as a stabilizing factor for nucleophilic carbenes was suggested by Wanzlick⁴ as long ago as 1962. In fact we can regard carbene IV as a Hückel 6- π system with 'aromatic' character, which is also in accord with its 'singlet' ground state⁵.

The Arduengo carbene (IV) is *not*, however, the first 'bottleable' carbene as has been claimed by the Du Pont researchers³. That credit must go to Bertrand and coworkers⁶ of the National Centre for Scientific Research (CNRS) in Toulouse, France. Bertrand's group prepared the first 'bottleable' carbene (VI) by flash thermolysis of a phosphino diazo precursor, as shown below:

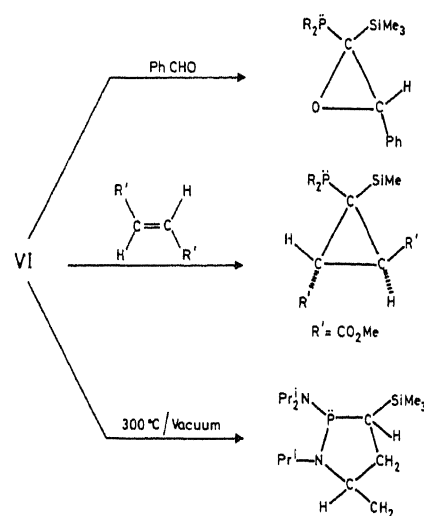


Compound VI has been isolated as a red, oily material (b.p. 75–80°C/10⁻² mm Hg) stable for several weeks at room temperature in benzene solution. Spectroscopically VI behaves as a phosphacetylene (VIa, VIc), while in terms of chemical reactivity it exhibits both carbenic (VIa) and a polarized phosphacetylenic (VIb, VIc) character. The multiple-bond character of VI is borne out by its reaction with Me₃SiN₃, which

is reminiscent of the reaction of azides with alkynes:



The carbenic character of VI is evident from its reactions with electron-poor olefins and benzaldehyde, which yield a cyclopropane and an oxirane respectively. Compound VI also undergoes an *intramolecular* C–H insertion reaction when heated under vacuum to give a five-membered ring compound (see below).



It is perhaps this *chameleonic* character of VI that led Arduengo *et al.*³ to make no reference to the earlier work of Bertrand and coworkers. This has raised the interesting controversy⁷ of how this omission went unnoticed by the referees and the editor of the *Journal of the American Chemical Society*. It may be noted that the phosphinocarbene VI has a hetero atom (P) with a lone pair adjacent to the carbenic centre, whereas in the Arduengo carbene IV the carbenic centre is flanked by two nitrogen atoms each of which bears a lone pair of electrons. Hence there is more resemblance between the two