(*17*)—which can straddle the whole polymerase enzyme—opens up the DNA further downstream and so disengages the rest of the DNA such that it does not begin to drag on the actual region of DNA being transcribed.

Whatever the case, we shall probably soon find out how GTFs cooperate in the initiation of transcription. The two Kornberg papers (*1*, *2*) mention work in progress on 3D cocrystals of RNA polymerase together with various GTFs. The determination of these structures should fill the gaps in our picture of promoter-dependent transcription. This is structural biology on a grand scale. So great is its power when combined with biochemistry and genetics that we should eventually even be able to see Mediator regulating the enzyme complex. We look forward to further chapters in the saga of this voyage of discovery.

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PERSPECTIVES: CHEMISTRY

Fleeting Molecules Extend Their Stay

Curt Wentrup

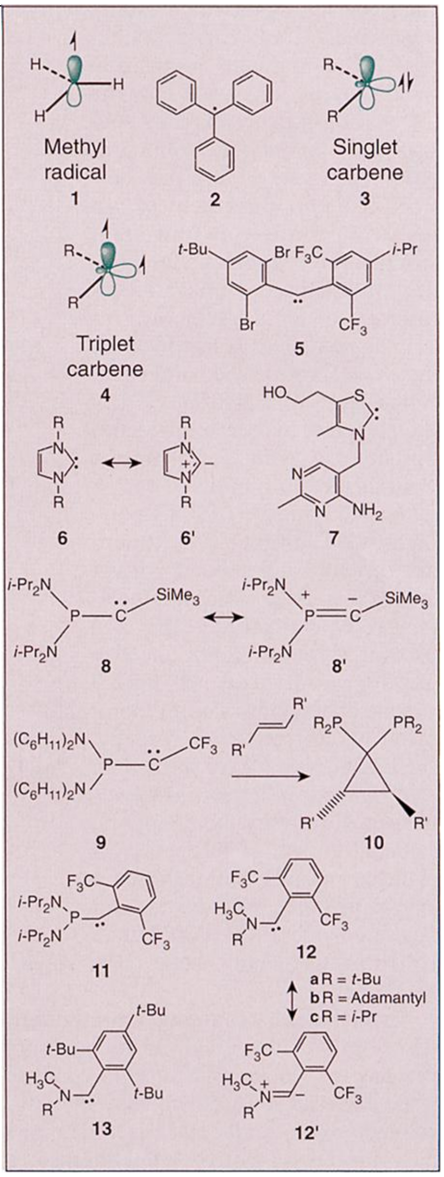
In its stable saturated compounds, such as methane (CH_4), carbon is bound to four other atoms. Molecules with carbon valencies other than 4—such as free radicals, carbocations, carbanions, and carbenes—are usually reactive intermediates with short lifetimes. These fleeting species can sometimes be stabilized. Stable free radicals were first prepared in 1900, but carbenes long remained elusive. On page 1901 of this issue, Solé *et al.* (*1*) report an important synthetic advance that enables the preparation of unusually stable yet highly reactive carbenes. Related species may find future application as efficient catalysts.

In free radicals, the carbon atom is bound to three atoms, with one nonbonded electron remaining on the carbon. A simple example is the methyl radical, CH_3 (**1**) (see the figure). Many free radicals are transient reactive intermediates, but numerous radicals have been made that are stable at room temperature, starting with the pioneering preparation of triphenylmethyl (**2**) by Gomberg in 1900 (*2*). This molecule is stabilized through delocalization of the free electron into the aromatic rings and remains stable because the bulky groups prevent access to the radical center ("steric hindrance").

It took much longer to prepare stable carbenes. The carbon atom in a carbene is surrounded by only six electrons, rather than the usual eight that confer electronic stability. With just two bound atoms, two nonbonded electrons remain on the carbon atom. These electrons may be in the same orbital (singlet state, **3**) or in different orbitals (triplet state, **4**). Attempts to make the simplest carbene, methylene (CH_2), were made before the tetravalency of carbon became generally known (*3*). Just over 100 years ago, Nef still believed that stable simple carbenes could be prepared (*4*, *5*). The existence of carbenes as reactive intermediates was established in the 1950s and 1960s (*6*, *7*). Since then, carbenes have become well-established synthetic intermediates. Their high reactivity makes them versatile targets for preparative, mechanistic, and theoretical work.

In recent years, much progress has been made in the stabilization of triplet di(aryl)carbenes, particularly through the work of Tomioka (*8*). The stability record is currently held by triplet carbene **5**, which has a half-life of 16 minutes in solution at room temperature and is stable indefinitely at –40°C (*9*, *10*). The stabilization of this and related carbenes largely results from steric hindrance of the carbene center by large groups or atoms.

In 1991, the first stable singlet di(amino)carbene (**6**) was prepared by Arduengo *et al.* (*11*). Di(amino)carbenes are stabilized in the singlet state by electron donation from the two nitrogen lone pairs into the vacant carbon p orbital on the carbon. This stabilization is also termed "push-push" stabilization. Many cyclic and acyclic di(amino)carbenes have been prepared, but they do not have typical carbene reactivity because of the electronic stabilization (best described by the resonance structure **6′**) (*12*, *13*). A related species (**7**) is involved in the action of the coenzyme thiamin (*14*, *15*).



How to make stable radicals and carbenes. Free radicals (**1**) were stabilized many years ago (**2**). Carbenes (**3** and **4**) have proved more difficult to stabilize. Recent synthetic advances have led to the successful preparation of stable carbenes (**5** to **13**), some of which retain their reactivity. See text for detailed descriptions of the depicted molecules.

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A different type of stable carbene, **8**, was prepared by Bertrand and co-workers (*16*). Here, the stabilization comes largely from donation of a pair of electrons from the phosphorus atom. Consequently, **8′** is a better description of this kind of compound (*17*). **8** retains typical singlet carbene reactivity, including stereospecific addition to olefins to form cyclopropanes.

Last year, Bertrand and co-workers reported the "push-pull" stabilized carbene **9** (*18*). The molecule is stabilized by electron donation from phosphorus (as in **8**). In addition, stabilization is derived from electron withdrawal by the electronegative $\mathrm{CF_3}$ group. The molecule is stable in solution for several days at –30°C and shows singlet carbene reactivity, such as stereospecific addition to olefins to afford cyclopropanes **10** and insertion into the Si-H bond of $\mathrm{Et_3SiH}$. The related carbene **11** is stable for weeks at room temperature. Its structure is similar to that of **8**, with a short P-C bond (1.544 Å) and a PCC angle of 162°. The carbene lone pair is delocalized into the electronegatively substituted aromatic ring, thus providing push-pull stabilization. Consequently, the C-C bond between the carbene center and the aromatic ring is also short (1.390 Å) (*18*).

The latest report from Bertrand and co-workers (*1*) describes the synthesis of stable (amino)(aryl)carbenes **12**. The species **12a** has a melting point of 16°C and an NCC angle of 121°, as expected for an ordinary singlet carbene; the C-C bond between the carbene center and the aromatic ring is essentially a single bond (1.453 Å). The N-C bond is 1.283 Å, shorter than in di(amino)carbenes. Thus, carbene **12a** exists essentially in the resonance structure **12′**. It retains the geometry of a typical singlet carbene, and its reactivity indicates typical carbene behavior. Unlike compound **11**, electron delocalization into the aromatic ring promoted by the electronegative $\mathrm{CF_3}$ groups is apparently not crucial for stability: The (amino)(aryl)carbene **13** was stable in solution at –50°C for days and underwent C-H insertion into a *tert*-butyl group, typical of (aryl)carbenes.

This latest work by Bertrand and co-workers (*1*) shows that a single amine substituent, in combination with steric hindrance, can be sufficient to stabilize a singlet carbene that retains typical singlet carbene reactivity. It opens the way for a new wave of preparative chemistry of stable carbenes. Apart from the fundamental insight into the nature of divalent carbon compounds that can be expected to emanate from such work, stable carbenes are of much potential interest in catalysis. For example, di(amino)carbenes of type **6** have been shown to form exceptionally strong bonds with virtually all the transition elements and many lanthanides, and may thus surpass the ubiquitous phosphine ligands in organometallic catalytic chemistry.

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PERSPECTIVES: APPLIED PHYSICS

Toward Diamond Lasers

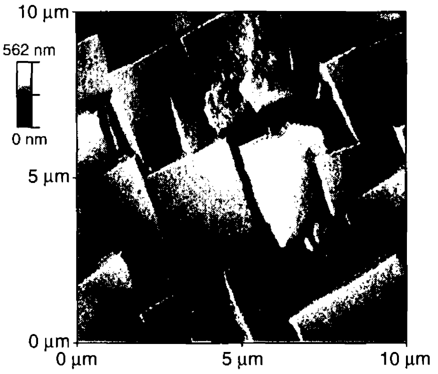
Phillip John

Most devices that emit light at ultraviolet and visible wavelengths, from visual displays to optical data storage, use II-VI and III-V binary materials, where the Roman numerals denote elements in the main groups II to V in the Periodic Table. The larger the band gaps of these insulating materials, the shorter the wavelength of the emitted light is. Shorter wavelengths are desirable because they potentially allow greater data storage, but suitable materials at these wavelengths are harder to find. Blue lasers were thus a much greater challenge than red or green ones until Akasaki (Meijo University) and Nakamura (Nichia Chemical Industries) developed a room-temperature blue laser based on GaN, which emits at wavelengths below 450 nm (*1*). Nichia now fabricates commercial quantities of blue lasers, and many groups worldwide are developing GaN light emitters and photodetectors with promising commercial prospects (*1*).

For light emission at even shorter wavelengths, diamond is a potentially promising material because of its large band gap (about 5.5 eV). Optimism for diamond electronics has, however, been tempered by the difficulty of synthesizing single-crystal diamond by chemical vapor deposition (CVD), necessary to achieve sufficiently high charge carrier mobility for electronic applications. New reports indicate that these problems may soon be overcome. On page 1899 of this issue, Koizumi *et al.* (*2*) report a diamond-on-diamond (homoepitaxial) pn junction made by CVD that emits at 235 nm. This report is an important milestone and complements similar reports by Tokyo Gas Company and Kobe Steel.

The electronic properties of CVD diamond films have been improved steadily over the last decade. The growth technologies have been refined, and concomitant progress has been made in doping methodologies, which are used to tune the electrical conductivity. For example, doping with phosphorus results in an extra electron available for conduction (n-type dopant), whereas doping with boron results in conduction due to "holes" (p-type dopant).

Intrinsic (undoped) and boron-doped p-type materials are readily available through in situ doping during CVD growth or postgrowth ion implantation. Hole mobilities of around 50 to 100 cm^2 V^{-1} s^{-1} in randomly oriented polycrystalline films increase to about 280 cm^2 V^{-1} s^{-1} in highly oriented diamond films grown on silicon surfaces. The hole mobility of 300 cm^2 V^{-1} s^{-1} quoted by Koizumi *et al.* for their homoepitaxial junction is of the same order



Epitaxial diamond. This atomic force microscope image shows the typical faceting of epitaxial diamond films grown on silicon by CVD. As Koizumi *et al.* show, appropriately doped diamond-on diamond films can form pn junctions emitting in the ultraviolet.

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