

Stable Versions of Transient Push-Pull Carbenes: Extending Lifetimes from Nanoseconds to Weeks

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A (phosphanyl)(trifluoromethyl)carbene is shown to be stable for weeks in solution at temperatures up to -30°C . Its chemical behavior exactly matches that of its transient congeners, even to the extent that subtle effects, such as the recently discovered weak π interaction with aromatics, are observed. The influence of substituents on the structure of push-pull carbenes is demonstrated by a single-crystal x-ray diffraction study of a (phosphanyl)[2,6-bis(trifluoromethyl)phenyl]carbene. The lifetime of these molecules makes them accessible to a wider range of standard techniques, allowing their chemical and physical behaviors to be studied in more detail than was previously possible.

Carbenes are compounds with a neutral dicoordinate carbon atom featuring either two singly occupied nonbonding orbitals (a triplet state) or both a lone pair and an accessible vacant orbital (a singlet state). Since the pioneering work of Buchner and Curtius (1) and Staudinger and Kupfer (2), carbenes have played a prominent role as transient intermediates (3–6). Introduced by Doering and Hoffmann into organic chemistry in the 1950's (7) and by Fischer and Maasböl into organometallic chemistry in the 1960's (8), these fascinating species are involved in many reactions of synthetic interest.

The recent preparation of persistent triplet diarylcarbenes (9, 10) and the isolation of stable singlet diheteroatom-substituted carbenes (11–13) represent spectacular synthetic achievements. However, the reactivity of the latter is strongly influenced by the interaction of the two heteroatom substituents with the carbene center and therefore is somewhat different from that of their transient cousins.

Here, we report the synthesis of a singlet carbene that is stable for weeks in solution up to -30°C and whose chemistry exactly parallels that of its transient congeners. This work demonstrates that a singlet carbene can be stabilized without modifying the reactivity expected of this class of compound. Moreover, we present the solid state structure of a monoheteroatom-substituted carbene.

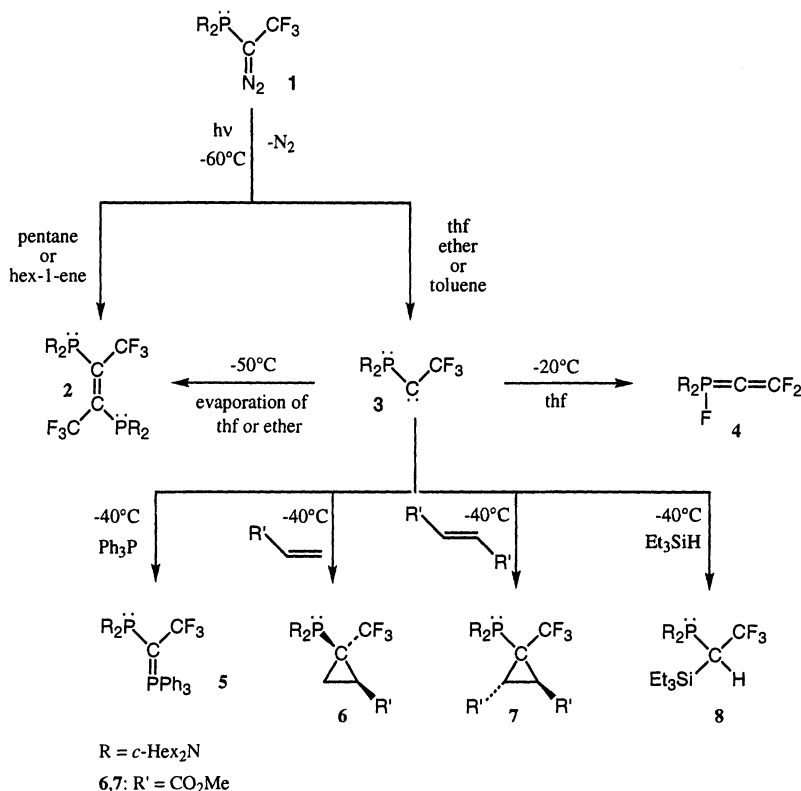
As early as 1980, Pauling (14) predicted that substituents of opposing electronic properties (the so-called push-pull effect) should stabilize singlet carbenes by preserving the

electroneutrality of the carbene center. The validity of this approach was investigated by Moss *et al.* (15) and Dailey *et al.* (16, 17), who independently studied methoxytrifluoromethylcarbene ($\text{MeO}-\text{C}-\text{CF}_3$). This derivative was, however, highly unstable and electronically indiscriminate in its reaction with alkenes. This behavior was attributed to the pull inductive effect ($-I$) of the CF_3 group, which predominates over the push resonance effect ($+M$) of the MeO group. Rec-

ognizing that the methoxy group also has a pull inductive effect ($-I$), we chose to introduce a phosphanyl group in its place. This substituent features both resonance ($+M$) and inductive push ($+I$) effects and, in addition, provides considerably greater steric bulk (Fig. 1).

Photolysis (300 nm) of [bis(dicyclohexylamino)phosphanyl](trifluoromethyl)diazomethane **1** at -60°C in pentane does not afford carbene **3** but its dimer **2**, which precipitates from the solution as orange crystals (75% yield) (Scheme 1). The alkene **2** was fully characterized (18), including by a single-crystal x-ray diffraction study (19).

We then investigated the photolysis of **1** in donor solvents, using the well-known Platz method for observing "invisible" carbenes through ylide formation (20, 21). Irradiation of **1** in tetrahydrofuran (thf) or diethylether (300 nm, -60°C) cleanly generated the desired carbene **3**, which is stable for days in solution at -30°C and was characterized spectroscopically (18). Evaporation of the solvent, even at -50°C , resulted in dimerization generating exclusively the alkene **2**. In contrast, upon warming the thf solution of **3** to -20°C , a clean rearrangement occurs affording the cumulene **4**, with no trace of the carbene dimer **2** being observed (Scheme 1). Cumulene **4** most probably results from two successive 1,2-F migrations (22). These observations are in perfect agreement with pre-



Scheme 1. h , Planck constant; ν , photon frequency; Et, ethyl.

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vious work on transient carbenes. It has been shown that the extent of 1,2 migration processes increases, relative to intermolecular reaction (like the dimerization leading to **2**), as the solvent is changed from an alkane to a donor solvent (23).

To confirm the interaction of thf and ether with **3** and therefore the Lewis acid character of the carbene, we treated the thf solution of **3** at -40°C with triphenylphosphine, a strong Lewis base. As expected, phosphorus ylide **5** was obtained and isolated in near quantitative yield (24) (Scheme 1).

Even subtle effects observed with transient carbenes can be reproduced with **3**. Ruck and Jones (23), Moss and co-workers (25, 26), and Khan and Goodman (27) recently showed that transient singlet carbenes (such as chlorocarbenes) interact weakly with aromatics but not with simple olefins. For example, this interaction led to an extension of the benzylchlorocarbene lifetime from 23 ns (isooctane) to 285 ns (benzene) (26). Similarly, we found that photolysis of **1** in hex-1-ene at -60°C led to the carbene dimer **2**, whereas in toluene we obtained the carbene **3**, which is stable up to -30°C (Scheme 1).

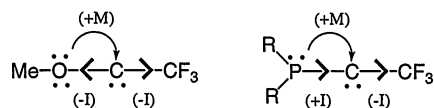


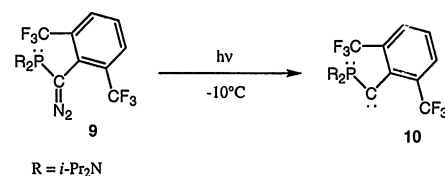
Fig. 1. Mesomeric and inductive effects of substituents on methoxytrifluoromethylcarbene and phosphanyltrifluoromethylcarbene. Me, methyl.

The addition of a carbene to an alkene to form a cyclopropane (cyclopropanation) is one of the most fundamental reactions of transient carbenes and a fundamental component of synthetic chemistry. (Phosphanyl)(trifluoromethyl)carbene **3** does not react with electron-rich alkenes but cleanly undergoes cyclopropanation reactions (toluene, -78°C) with methyl acrylate and dimethyl fumarate, demonstrating its nucleophilic character. The corresponding cyclopropanes **6** and **7** were isolated in 80 and 60% yield, respectively, as only one diastereomer [according to nuclear magnetic resonance (NMR) data] (28) (Scheme 1). Finally, carbene **3** is reactive enough to insert at -40°C into the silicon-hydrogen bond of triethylsilane to afford phosphine **8** in 58% yield (29) (Scheme 1).

Recent calculations (30) carried out on the simplified model compound **3'** ($\text{R} = \text{NH}_2$) predict the molecule to be substantially bent (P-C-C bond angle: 126.4°), the phosphorus planar, and the P-C bond length short (1.584 Å), as expected for this type of singlet carbene. The singlet-triplet energy gap was predicted to be small (49 kJ/mol) but in favor of the singlet state, and the energy barrier for the dimerization negligible, in perfect agreement with the experimental results.

We also investigated the possibility of replacing the σ attracting CF_3 group ($-I$) by the bulky 2,6-bis(trifluoromethyl)phenyl group, which is both a σ and a π attractor ($-I$, $-M$). For all solvents used, photolysis of the diazo precursor **9** at -10°C afforded the corresponding carbene **10**, which is stable for weeks at room temperature both in solu-

tion and in the solid state (melting point: 68° to 70°C) (Scheme 2).



Scheme 2.

The molecular structure of **10** (**31**) (Fig. 2) shows that the phosphorus atom is in a planar environment and the P1-C1 bond length (1.544 ± 0.003 Å) is short, as expected because of the donation of the phosphorus lone pair into the carbene vacant orbital. The aromatic ring is perpendicular to the C1P1N1N2 plan, allowing the delocalization of the carbene lone pair into the ring (32). Because of this $-M$ effect of the aromatic, the P1-C1-C2 bond angle ($162.1^{\circ} \pm 0.3^{\circ}$) is much larger than in **3**.

This work bridges the gap between the classical, highly reactive transient carbenes and their stable counterparts. It is now clear that push-pull stabilization is very effective for preparing carbenes featuring high thermodynamic stability, without destroying their typical carbene reactivity. A previously unexplored dimension in the study of stable versions of transient carbenes is thus opened.

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18. Selected spectroscopic data for derivatives **2**, **3**, **4**, and **10** are available at Science Online (33).
19. The single-crystal x-ray diffraction studies for **2** and **6** will be published elsewhere.

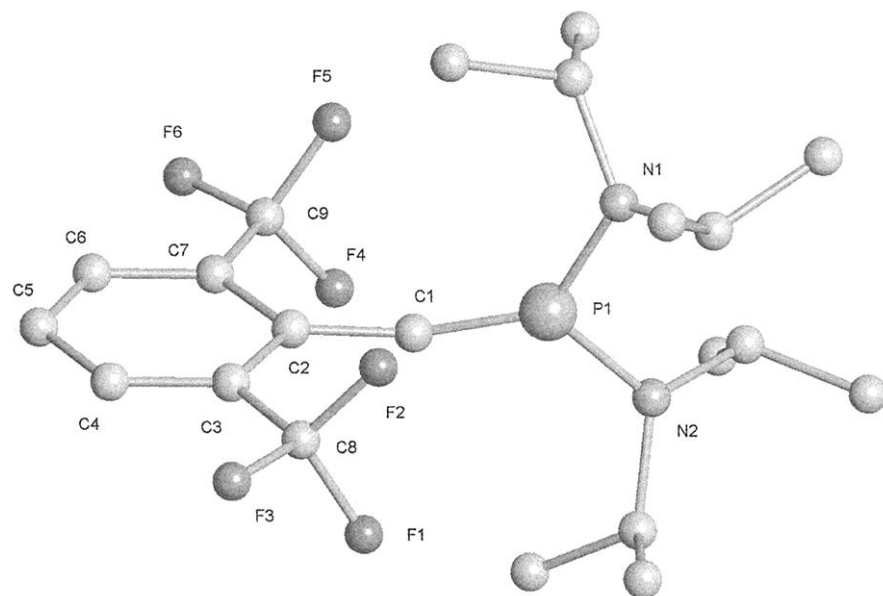


Fig. 2. Molecular view of **10** in the solid state. Selected bond lengths: P1-C1 , 1.544 ± 0.003 Å; P1-N1 , 1.643 ± 0.003 Å; P1-N2 , 1.636 ± 0.003 Å; C1-C2 , 1.390 ± 0.004 Å; C2-C3 , 1.431 ± 0.004 Å; C3-C4 , 1.372 ± 0.005 Å; C4-C5 , 1.371 ± 0.006 Å; C5-C6 , 1.379 ± 0.006 Å; and C6-C7 , 1.391 ± 0.005 Å. Selected angles: C1-P1-N1 , $130.32^{\circ} \pm 0.17^{\circ}$; C1-P1-N2 , $124.01^{\circ} \pm 0.16^{\circ}$; N1-P1-N2 , $105.60^{\circ} \pm 0.14^{\circ}$; and P1-C1-C2 , $162.1^{\circ} \pm 0.3^{\circ}$.

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28. For **6**, the trifluoromethyl group is anti to the original alkene substituent, as observed in the cycloaddition reaction of the MeO-C-CF₃ carbene with a similar alkene (75). In the latter case, steric interactions were postulated to be the cause of the observed high diastereoselectivity. Because the bis(dicyclohexylamino)phosphanyl group is rather more bulky than the CF₃ group, the stereoselectivity observed for **6** cannot be due to steric factors. In fact, for both carbenes (MeO-C-CF₃ and **3**), the results can be rationalized in terms of secondary orbital interaction control. See S. Goumri-Magnet, T. Kato, H. Gornitzka, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.*, in press.
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31. Crystal data for **10** are available at Science Online (33).
32. Further evidence for the delocalization of the carbene lone pair includes the following (i) the short C1-C2 bond length (1.390 ± 0.004 Å), which indicates a double-bond character; (ii) the C2-C3 and C2-C7 bond distances, which are longer than the other bonds of the ring; and (iii) the ¹³C NMR signals corresponding to C3, C5, and C7, which appear at high field, whereas those for C4 and C6 are more deshielded (18).
33. For supplementary data, see www.sciencemag.org/feature/data/1048933.shl.
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Radar Observations of Asteroid 216 Kleopatra

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Radar observations of the main-belt, M-class asteroid 216 Kleopatra reveal a dumbbell-shaped object with overall dimensions of 217 kilometers by 94 kilometers by 81 kilometers ($\pm 25\%$). The asteroid's surface properties are consistent with a regolith having a metallic composition and a porosity comparable to that of lunar soil. Kleopatra's shape is probably the outcome of an exotic sequence of collisional events, and much of its interior may have an unconsolidated rubble-pile structure.

The main asteroid belt contains 42 objects whose optical spectra reveal the presence, but not the dominance, of NiFe metal. These M-class objects may include the parent bodies of some iron meteorites, which are thought to be derived from asteroids that melted, differentiated, and solidified within the first billion years of the solar system (1) and subsequently suffered collisional exposure of their metallic interiors. M-class asteroids have yet to be targeted for study by spacecraft, and detailed information about their physical properties is lacking. However, two decades of telescopic observations of the large M-class asteroid 216 Kleopatra have marked it as highly unusual. Optical light curves with large amplitudes (2–4) and stellar occultation timings (5, 6) suggest an elongated shape, and Doppler-only radar observations (7) and adaptive optics images (8) suggest some sort of shape bifurcation.

We used the S-band (2380 MHz, 12.6 cm) radar system of the recently upgraded Arecibo Observatory to obtain images on four dates in November 1999 (Table 1). Our observational and data-reduction techniques have been described by Harmon et al. (9). We transmitted a circularly polarized, nonrepeating, binary phase-coded waveform with a time resolution, or baud, equal to 0.1 ms (range resolution of 15 km) and sampled the echoes at intervals of 0.05 ms, in the same and opposite circular polarizations (SC and OC, respectively) simultaneously. Kleopatra's SC/OC radar cross-section ratio is 0.00 ± 0.05 (7), and our analyses used only the OC data.

Each run produced a 41 by 41 pixel delay-Doppler image (Fig. 1). Delay bins are 0.05 ms (7.5 km) deep, but because the echoes were double sampled, there is correlation between adjacent delay bins; our analysis took this correlation into account. For a rotating rigid object with Kleopatra's optically determined spin period (5.385 hours) (10), the distance equivalent of our frequency resolution, 19.5 Hz (chosen to optimize the trade-off between pixel size and signal-to-noise ratio), is $3.8 \text{ km}/\cos \delta$, where δ is the subradar

latitude. All data were taken with Kleopatra within 1.8° of the apparent right ascension, 61.4° , and declination, 11.8° . Our estimated pole direction (ecliptic longitude, 72° ; latitude, 27°), 8° from the pole direction (71° , 19°) estimated from optical light curves (10), corresponds to $\delta = -53^\circ$ and a frequency-pixel resolution of 6.3 km.

The asteroid's delay-Doppler signature is bimodal. In the most end-on images, which show the maximum echo-delay depth and minimum bandwidth, the leading edges of the two lobes are ~ 60 km apart. However, our view was several tens of degrees from pole on, and the actual distance between those edges is ~ 100 km. The peak echo power in any of our raw, unsmoothed images (Fig. 1) is 9 standard deviations. With such modest echo strength, the absence of echo at delays between the two lobes does not necessarily mean that the space between the two lobes is empty, but rather that there is relatively little normally oriented surface area facing the radar in those pixels. The stronger images taken in broadside orientations, which show the maximum bandwidth and minimum delay depth, do show significant echoes from the part of the asteroid between the two lobes. (Echoes from surface elements that contain the plane-of-sky projection of the asteroid's spin vector have levels of 2 to 4 standard deviations at the images' raw resolution and higher if smoothed.) Thus, the interlobe surface reflects detectable echoes only in certain orientations (Figs. 1 and 2).

We used least squares inversion (11–15) to estimate Kleopatra's shape (256 parameters), radar-scattering law (2 parameters), and pole direction (2 parameters) (Figs. 2 and 3). We adopted Kleopatra's optically derived spin period (10) and assumed principal axis rotation and uniform density. There is correlation between the object's size, its angular-scattering law, and $\cos \delta$; we adjusted the pole direction to force the scale of the model to be consistent with the scale of the stellar occultation chords reported by Dunham (5, 6).

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