Stable Non-Push–Pull Phosphanylcarbenes: NMR Spectroscopic Characterization of a Methylcarbene**

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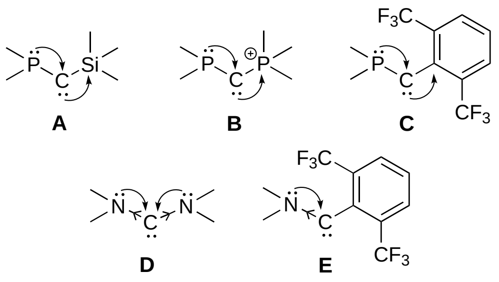
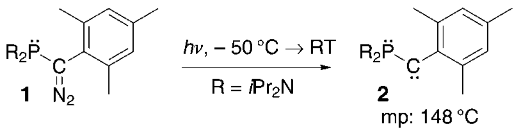
Carbenes are compounds with a neutral dicoordinate carbon atom featuring either two singly occupied nonbonding orbitals (triplet state) or both a lone pair and an accessible vacant orbital (singlet state). The recent preparation of persistent triplet diarylcarbenes[1] and isolation of singlet carbenes[2] represent spectacular achievements. The former are potential building units for organic magnets,[3] while the latter, when used as ligands for transition metal centers, afford complexes with enhanced catalytic activities.[4] All of the stable singlet carbenes known to date possess bulky protecting groups and follow, to some extent, Pauling's predictions[5] that the substituents should preserve the electroneutrality of the carbene center (Scheme 1). This situation is apparent for push–pull carbenes **A**–**C**,[6–8] in which the carbene bears both a π-donating and a π-withdrawing substituent. Carbenes **D**[9] have two π-donor substituents, and are sometimes referred to as push–push carbenes, but the amino groups also act as strong σ-electron-withdrawing substituents. Lastly, carbene **E**[10] features a spectator substituent and an amino group, which is again both a π donor and σ attractor. Here we report the synthesis of stable and persistent carbenes featuring a π- and σ-donor phosphanyl group and a spectator substituent, including a methyl group.



Scheme 1. Stable singlet carbenes **A**–**E**.

We first investigated the synthesis of a phosphanylcarbene featuring an electron-rich aryl group. The phosphanyl(mesityl)carbene (**2**) was generated by photolysis (254 nm, −50 °C) of a tetrahydrofuran solution of the corresponding diazo compound **1** (Scheme 2). The ^{31}P and ^{13}C NMR chemical shifts of **2** (^{31}P: $\delta = -23.5$ ppm; ^{13}C: $\delta = 151.1$ ppm) compare well with those observed for neutral push–pull phosphanylcarbenes **A** and **C**[2a] (^{31}P: $\delta = -40$ to -20 ppm; ^{13}C: $\delta = 120$ to 150 ppm). The only noticeable difference is the magnitude of the coupling constant between the phosphorus atom and the carbene center, which is significantly smaller for **2** ($^{1}J_{P,C} = 65$ Hz) than for **A** ($^{1}J_{P,C} = 150-200$ Hz) and **C** ($^{1}J_{P,C} = 271$ Hz). Although these data are difficult to rationalize (it is not possible to predict the influence of orbital, spin-dipolar, Fermi contact, nor higher order quantum mechanical contributions to the magnitude of the coupling constants), it is likely to indicate some peculiarity in the electronic structure of **2**.



Scheme 2. Synthesis of the phosphanyl(mesityl)carbene **2**.

Pale yellow crystals of **2** suitable for an X-ray diffraction study were obtained by cooling a saturated pentane solution to −80 °C. The molecular structure of **2** is shown in Figure 1.[11] As expected, because of the donation of the lone pair of electrons on the phosphorus atom into the vacant orbital of the carbene, the phosphorus atom is in a planar environment and the P1–C1 bond length is short (1.564(3) Å). The P1-C1-C2 angle (148.7(2)°) is significantly smaller than in **C** (162.1(3)°); the C1–C2 bond length (1.438(3) Å) is in the range typical for C(sp^2)–C(sp^2) single bonds, and is longer than that observed for the push–pull system **C** (1.390(4) Å). These results strongly suggest the absence of delocalization of the lone pair of electrons on the carbene into the aromatic ring. In other words, the carbene center interacts only with the phosphanyl group, while the mesityl substituent remains merely an electronic spectator.

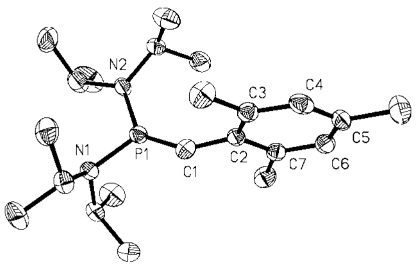


Figure 1. Thermal ellipsoid diagram (50% probability) of **2**. For clarity the hydrogen atoms are omitted. Selected bond lengths [Å] and angles [°]: P1-N1 1.678(2), P1-N2 1.661(2), P1-C1 1.564(3), C1-C2 1.438(3); N1-P1-C1 120.09(13), N2-P1-C1 134.24(13), N1-P1-N2 105.44(11), P1-C1-C2 148.7(2).

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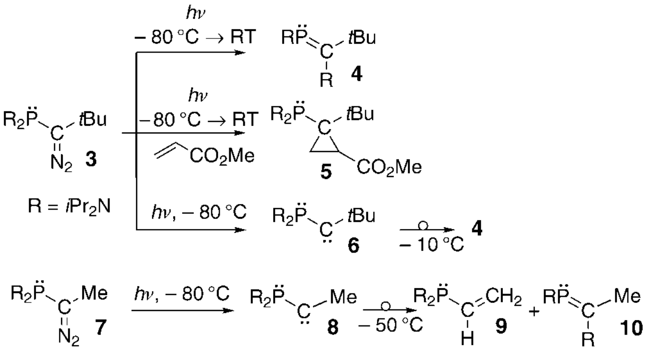
Direct observation of singlet alkylcarbenes usually requires matrix-isolation conditions.[12] Indirect observation and kinetic measurements in solution can be performed by laser-flash photolysis (LFP) using the pyridine ylide method.[13] By incorporating the π-donating and σ-attracting methoxy substituent, Moss et al. were able to characterize the methoxy(methyl)carbene MeOCMe by UV and IR spectroscopies, but only in a nitrogen matrix (at 10 K) or in solution, thanks to a nanosecond time-resolved LFP technique ($t_{1/2} < 2$ μs at 20 °C).[14] The remarkable stability of carbene **2** both in the solid state (m.p. 148 °C) and in solution (no degradation observed after several weeks at room temperature) prompted us to investigate the preparation of phosphanyl(alkyl)carbenes. Photolysis (254 nm, −80 °C) of a toluene solution of the phosphanyl(*tert*-butyl)diazomethane **3**[15] afforded the phosphaalkene **4** in near quantitative yield upon warming to room temperature. Cyclopropane **5** was obtained in high yield when the low-temperature photolysis of **3** was performed in the presence of methyl acrylate (Scheme 3).[16] These results suggested the transient formation of the phosphanyl(*tert*-butyl)carbene **6**.[17] This alkylcarbene could indeed be characterized spectroscopically by multinuclear NMR spectroscopy at low temperature (−50 °C). The ^{31}P NMR chemical shift ($\delta = -36.4$ ppm) is in the expected range, while the ^{13}C NMR chemical shift ($\delta = 186.3$ ppm) is the highest reported for a phosphanylcarbene. The small coupling constant ($^{1}J_{P,C} = 32$ Hz) is consistent with that observed for **2**.



Scheme 3. Synthesis and reactivity of the phosphanyl(alkyl)carbenes **6** and **8**.

Although the alkylcarbene **6** rearranges within a few minutes above −10 °C to afford the 1,2-migration product **4**, it is still observable by ^{31}P NMR spectroscopy below −20 °C. We thus decided to reduce the steric hindrance of the spectator alkyl group, and hence studied the photolysis of the phosphanyl(methyl)diazomethane (**7**)[18] (254 nm, −85 °C, toluene solution). A 1.6:1 mixture of derivatives **9**[19] and **10**, which results from the 1,2-migration of a hydrogen atom and an amino group, respectively, was obtained on warming the solution to room temperature. The corresponding phosphanyl(methyl)carbene (**8**) was characterized spectroscopically at −85 °C. The ^{31}P and ^{13}C NMR data for **8** (^{31}P: $\delta = -17.8$ ppm; ^{13}C: $\delta = 164.8$ ppm, $^{1}J_{P,C} = 44$ Hz) are similar to those for **6**. Despite the poor steric protection and the potential to undergo 1,2-shifts,[20, 21] the methylcarbene **8** could be observed by ^{31}P NMR spectroscopy up to −50 °C ($t_{1/2} \sim 10$ min at −50 °C), where it quickly isomerizes.

The preparation of stable or persistent non-push–pull phosphanyl(aryl)- and phosphanyl(alkyl)carbenes demonstrates that a single substituent with even relatively weak π- and σ-donor effects allows for the spectroscopic characterization of singlet carbenes under standard laboratory conditions. Since the steric bulk of the spectator substituent can be decreased even to the size of a methyl group, these results open the way to a variety of new "observable" carbenes and consequently to new synthetic developments and applications in various fields.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry argon, by using standard Schlenk techniques.

1: A solution of the lithium salt of hexamethyldisilazane ($(Me_3Si)_2NLi \cdot Et_2O$; 0.27 g, 1.1 mmol) in diethyl ether (4 mL) was added to a solution of mesityldiazomethane[22] (0.18 g, 1.1 mmol) in diethyl ether (3 mL) at −78 °C. The reaction mixture was kept at this temperature for 1 h, before bis(diisopropylamino)chlorophosphane (0.29 g, 1.1 mmol) was added. After 30 min, the reaction mixture was allowed to warm to room temperature over a period of 1 h. After evaporation of the solvent under vacuum, the residue was extracted with pentane (20 mL) and filtered on neutral alumina. Orange crystals of **1** (0.2 g, 47 %) were obtained by recrystallization from acetonitrile (10 mL) at −20 °C: m.p. 120 °C; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 63.1$ ppm; IR (diethyl ether): $\tilde{\nu} = 2031$ cm^{-1} (CN_2); UV (toluene): $\lambda_{max} = 291$ nm.

2: A solution of **1** (100 mg, 0.26 mmol) in pentane (3 mL) was irradiated (254 nm) at −50 °C for 6 h. Pale yellow crystals of **2** (33 mg, 35 %) were obtained by cooling the reaction mixture to −80 °C: m.p. 148 °C; ^{31}P{^{1}H} NMR (C_4D_8O): $\delta = -23.5$ ppm; ^{13}C{^{1}H} NMR (C_4D_8O): $\delta = 151.1$ ppm (d, $^{1}J_{P,C} = 65$ Hz, $C_{carbene}$).

4: A solution of **3**[15] (0.12 g, 0.37 mmol) in tetrahydrofuran (4 mL) was irradiated (254 nm) at −80 °C for 4 h, and then warmed to room temperature. ^{31}P NMR spectroscopy indicated the quantitative formation of the corresponding phosphaalkene **4**: ^{31}P{^{1}H} NMR (C_7D_8): $\delta = 268.5$ ppm; ^{13}C{^{1}H} NMR (C_7D_8): $\delta = 204.2$ (d, $^{1}J_{P,C} = 69$ Hz, C=P), 44.5 (d, $^{2}J_{P,C} = 5$ Hz, $C(CH_3)_3$), 31.2 ppm (s, $C(CH_3)_3$); elemental analysis calcd (%) for $C_{17}H_{37}N_2P$ (300.47): C 67.96, H 12.41, N 9.32; found: C 67.64, H 12.27, N 9.68.

5: A solution of **3**[15] (0.12 g, 0.37 mmol) and methyl acrylate (0.16 g, 1.83 mmol) in tetrahydrofuran (4 mL) was irradiated (254 nm) at −80 °C for 4 h, before warming to room temperature. After evaporation of the solvent and excess methyl acrylate, **5** was obtained as a yellow oil (0.1 g, 70 %) by extraction with pentane (20 mL): ^{31}P{^{1}H} NMR (C_7D_8): $\delta = 71.8$ ppm; ^{13}C{^{1}H} NMR (C_7D_8): $\delta = 51.6$ (s, OCH_3), 30.1 (s, CH(ring)), 19.2 ppm (s, CH_2(ring)); elemental analysis calcd (%) for $C_{21}H_{43}N_2O_2P$ (386.56): C 65.25, H 11.21, N 7.25; found: C 64.88, H 11.07, N 7.51.

9 and **10**: A solution of **7**[18] (0.14 g, 0.49 mmol) in toluene (2 mL) was irradiated (254 nm) at −80 °C for 6 h, before warming to room temperature. ^{31}P NMR spectroscopy indicated the formation of vinylphosphane **9**[19] and phosphaalkene **10** as the major products (1.6:1). **10**: ^{31}P{^{1}H} NMR (C_7D_8): $\delta = 146.5$ ppm; ^{13}C{^{1}H} NMR (C_7D_8): $\delta = 203.7$ (d, $^{1}J_{P,C} = 72$ Hz, C=P), 20.0 ppm (d, $^{2}J_{P,C} = 4$ Hz, CCH_3).

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Stereoselective Pinacol-Type Rearrangement of 2,3-Epoxy Alcohols with Retention of Configuration Mediated by Bis(iodozincio)methane**

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gem-Dizinc reagents that possess two nucleophilic sites on a carbon atom have been used for a variety of molecular transformations based on a repetition of C–C-bond formation on the same carbon atom.[1] To understand and design these characteristic reactions, one should recognize that dimetallic reagents work not only as a double nucleophile but also as a double Lewis acid.[2] The structure of *gem*-dizinc reagents allows them to act as double Lewis acids with substrates that contain heteroatoms at the 1,2- or 1,3-positions. In fact, we reported an example that emphasizes the importance of its double Lewis acidity through the nucleophilic reaction with 1,2-dicarbonyl compounds.[3] Along this line, we treated 2,3-epoxy alcohols with bis(iodozincio)methane (**1**), anticipating a pinacol-type rearrangement.[4, 5] The substrates are readily available in an enantiomerically enriched form by the Sharpless epoxidation.[6]

Treatment of racemic **2a** (diastereomeric mixture, *erythro*/*threo* 84:16, 1.0 mmol) in THF (2.0 mL) with **1** (0.5 M in THF, 2.2 mmol) at 20 °C gave alkenol **3a** in 77 % yield (Scheme 1).

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