3704 *J. Phys. Chem. A* **2003,** *107,* 3704−3707

A Laser Flash Photolysis Study of Diphenylphosphoryl Azide. Kinetics of Singlet and Triplet Nitrene Processes

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Received: December 17, 2002; In Final Form: February 28, 2003

Laser flash photolysis (266 nm) of diphenylphosphoryl azide **1** produces singlet diphenylphosphorylnitrene **2s** (not observed), which can either react with solvent or relax to form the lower energy triplet nitrene **2t**. Triplet **2t** absorbs at 345 nm in chloroform, cyclohexane, 1,2-dichloroethane, dichloromethane, ethyl acetate, 1,1,2-trichlorotrifluoroethane, and tetrahydrofuran, but the intensity and shape of the absorption band is solvent-dependent. The triplet lifetime is several tens of microseconds in the aforementioned solvents. The magnitude of $1/\tau$ is linearly dependent on the concentration of diphenylphosphoryl azide **1** ($k^3_{\mathbf{1}} = 1.2 \times 10^6$ M^{-1} s^{-1}) in methylene chloride. The extrapolated lifetime of **2t** in the absence of precursor is 500 μs in methylene chloride at ambient temperature. Thus, the long triplet lifetime in the aforementioned solvents is controlled by nitrene reaction with precursor. The one exception is methanol as solvent for which the triplet lifetime is only 6 μs. The reciprocal of the lifetime of **2t** is linearly dependent on the concentration of tris-trimethylsilylsilane ($(Me_3Si)_3SiH$), and the absolute rate constants to hydrogen transfer ($k^3_{\mathrm{Si-H}}$) are 3.4×10^5 M^{-1} s^{-1} in 1,2-dichloroethane and 3.1×10^5 M^{-1} s^{-1} in 1,1,2-trifluorotrichloroethane. A polar effect on k^3_{SiH} increases the rate constant to reaction with the silane in methanol and shortens the lifetime of **2t** in this solvent. $(MeSi)_3SiH$ reduces the yield of triplet **2t** (ϕ) by the trapping of singlet nitrene **2s**. Stern−Volmer analyses reveal that the singlet lifetime **2s** is 1, 1, and 4 ns in 1,2-dichloroethane, methanol, and 1,1,2-trifluorotrichloroethane, respectively, assuming that k^1_{SiH} is 5×10^9 M^{-1} s^{-1}. The rapid rate of nitrene intersystem crossing is attributed to a N−O bonding interaction in the singlet nitrene, which results in a closed-shell electronic structure of the singlet.

I. Introduction

Photolysis of phosphoryl azides **1** (R = ethyl or phenyl, Scheme 1) produces phosphorylnitrenes in their singlet states. The singlet nitrenes efficiently insert into the unactivated C−H bonds of alkanes (Scheme 1, k^1) in concerted processes to form adducts. Breslow and co-workers[1] and Maslak[2] noted the lack of selectivity of these singlet nitrene reactions and concluded that they proceed at near a diffusion-controlled rate. The products observed upon photolysis of azide precursor in 2,3-dimethylbutane change upon dilution of the alkane with perfluorohexane.[2] This led Maslak to conclude that deceleration of the rate of CH insertion allows relaxation of singlet nitrene **2s** to the lower energy triplet nitrene **2t**, which exhibits a reactivity pattern that is distinctly different from the singlet.[2]

Maslak concluded that photolysis of azide precursor does not exclusively produce singlet nitrene. Some triplet nitrene is formed in hydrocarbon solvent after intersystem crossing in the azide excited state followed by nitrogen extrusion.[2]

These studies demonstrated that singlet phosphorylnitrenes undergo CH insertion reactions and intersystem cross with rate constants that are several orders of magnitude larger than the corresponding processes in singlet arylnitrenes.[3] To investigate these differences, laser flash photolysis (LFP) studies were performed with a phosphoryl azide.

II. Experimental Section

Diphenylphosphoryl azide (Aldrich) was used without further purification. Acetonitrile, methanol, ethyl acetate, and cyclohexane are Fisher HPLC grade solvents. Freon-113, 1,2-dichloroethane, *n*-pentane, triethylsilane, and tris-trimethylsilylsilane were purchased from Aldrich and used without further purification. Chloroform was purchased from Mallinckrodt. Tetrahydrofuran (THF, Mallinckrodt AR) was distilled over sodium metal under nitrogen, and dichloromethane (Mallinckrodt AR) was distilled over calcium hydride. The deuterated solvents chloroform-*d*, methanol-d_4, cyclohexane-d_{12}, and acetonitrile-d_3 were purchased from Cambridge Isotope Laboratories. Acetonitrile-d_3 was distilled over phosphorus pentoxide.

Laser Flash Photolysis Apparatus. The current design of the flash photolysis instrument is based upon the previously described instrument[4] with the following changes. The older version of the instrument was based on a hard-wired computer interface. The upgrade of this basic design is software-centered using the LabView graphic programming language, which allows for greater ease in the optimization, integration, and use of the instrument. The current version employs a single ARC SP-308 monochromator/spectrograph with 1-015-300 grating. This model features dual ports, one with a slit and a photomultiplier for kinetic measurements and the other with a flat field and a Roper ICCD-Max 512T digital ICCD camera for spectroscopic measurements with up to 2 ns temporal resolution. The single monochromator/spectrograph negates the need for separate optimization of kinetic or spectral measurement system

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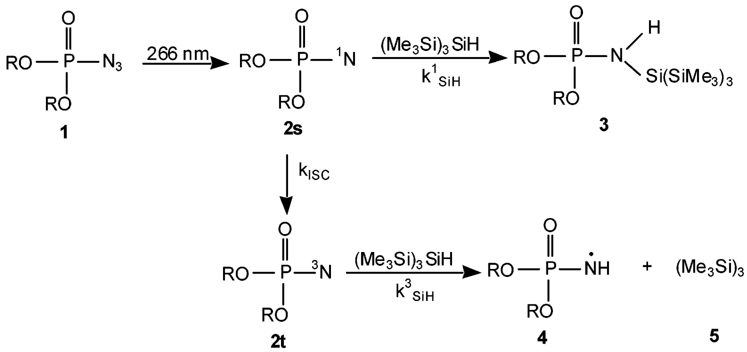
10.1021/jp022611e CCC: $25.00

SCHEME 1



alignment, thus facilitating the usage of both types of measurements. The ICCD controller is directly interfaced to the computer using the Roper WinView software and ST-133A controller. Kinetic data acquisition uses a Tektronix TDS 680C 5Gs/s 1 GHz oscilloscope directly interfaced via a National PCI-GPIB to the Columbus Microsystems 400 MHz Pentium II computer running a custom LabView control and acquisition program. Laser, arc lamp, and shutter and other timing and control signals are routed through a National PCI-6602 DAQ interface. The excitation of the samples was provided by a Spectra Physics LAB-150-10 (~5 ns) water-cooled laser, which was configured to supply 266 nm radiation. The measurement beam is supplied by a PTI 150 W xenon arc lamp with an LPS 210 power supply, LPS 221 stand alone igniter, A-500 compact arc lamp housing and MCP-2010 pulser, which allows for controlled pulsing of the arc lamp with pulses 0.5−2.0 ms in duration and up to 160 A in amplitude.

Laser Flash Photolysis Protocols. The concentration of diphenylphosphoryl azide (**1**) solutions were adjusted so that the absorbance was 1.8−2.0 at 266 nm. Samples were irradiated in suprasil quartz cells with 1 cm path lengths. Solutions of **1** were deoxygenated prior to LFP with a stream of deoxygenated nitrogen bubbling through the sample.

The effects of the tris-trimethylsilylsilane (TRIS) on the ϕ_o/ϕ ratio, as well as on the lifetime of the transient absorbing at 340 nm from (**1**) in different solvents, were determined by using 11.2×10^{-3} M stock solutions of **1** and by accurate dilution of the stock. The sample solutions were changed after each laser shot to avoid effects due to accumulation of photoproducts.

III. Results and Discussion

Maloney and co-workers have previously studied the photochemistry of diphenylphosphoryl azide ($R = C_6H_5$, Scheme 1).[5] Laser flash photolysis (LFP, 266 nm) of **1** was found to produce transient absorption at 345 nm. Maloney and co-workers reported that the transient absorption was relatively intense in methanol in which the lifetime was 3.6 μs. A small (1.1) kinetic isotope effect on the lifetime was observed in methanol-d_4. Rather weak and longer-lived ($\tau \gg 10$ μs) transient absorption was observed in cyclohexane by the Maloney group.[5] The lifetime in cyclohexane was too long to be precisely measured in this study.

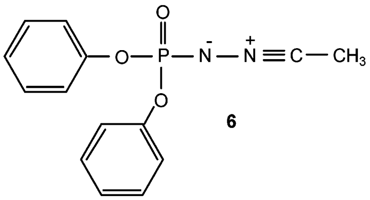
The carrier of the transient absorption was attributed to triplet nitrene **2t** because photolysis of azide precursor **1** in a rigid glass at 77 K produced both a persistent absorption at 345 nm and the persistent electron paramagnetic resonance (EPR) spectrum ($|D/(hc)| = 1.548$ cm^{-1} and $|E/(hc)| = 0.007\,39$ cm^{-1}) of a triplet nitrene. The relative strength of the transient absorption in methanol was attributed to enhanced nitrene intersystem crossing in alcohol,[5] an effect previously observed with polyfluorinated arylnitrenes.[6]

TABLE 1: Triplet Nitrene 2t ($R = C_6H_5$) Lifetimes at Ambient Temperature in Various Solvents

solvent	τ^a (μs)
$CHCl_3$	43 ± 6
cyclohexane	78 ± 4
1,2-dichloroethane	94 ± 6
dichloromethane	108 ± 4
ethyl acetate	37 ± 1
1,1,2-trifluorotrichloroethane	71 ± 4
methanol	6.0 ± 0.1
tetrahydrofuran	53 ± 2

[a] Measured at 345 nm; [**1**] = 5.6×10^{-3} M; excitation wavelength = 266 nm.

Relatively intense transient absorption in acetonitrile was attributed to ylide **6** by Maloney and co-workers.[5] Our LFP studies of azide **1** (R = phenyl) are in agreement with the report of Maloney and co-workers[5] where they overlap, although we did not observe the same variation in the intensity of the transient spectra with solvent observed by that group. Transient spectra and lifetimes as a function of solvent are given in Figure 1 and Table 1, respectively. Transient absorption at 345 nm is observed in every solvent, but the intensity and the sharpness of the absorption maximum varies with solvent. Well-defined maxima are observed in methanol, acetonitrile, and 1,2-dichloroethane but broad, tailing end absorption is detected in 1,1,2-trifluorotrichloroethane. It is clear that either different intermediates are detected in different solvents or the same species is formed but its spectrum varies with solvent. In all cases, the transient absorption is formed within 5 ns of the laser pulse, the time resolution of the spectrometer.



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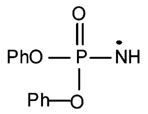
The long lifetimes of the transients in every solvent, except methanol, are consistent with either triplet nitrene **2t** or a free radical species, such as **4**, as the carrier of the transient



$PhO-\overset{\overset{\large O}{\|}}{\underset{\underset{\large Ph-O}{|}}{P}}-\dot{N}H$ **4**

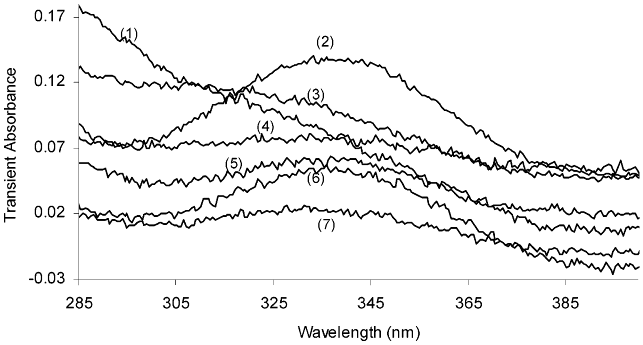


Figure 1. The transient absorption spectra produced upon LFP (266 nm) of 5.6 × 10^{-3} M diphenylphosphoryl azide (**1**) in (1) Freon-113, (2) acetonitrile, (3) ethyl acetate, (4) cyclohexane, (5) 1,2-dichloroethane, (6) methanol, and (7) THF at ambient temperature. The spectra were recorded over a 20 ns window immediately following the laser pulse.

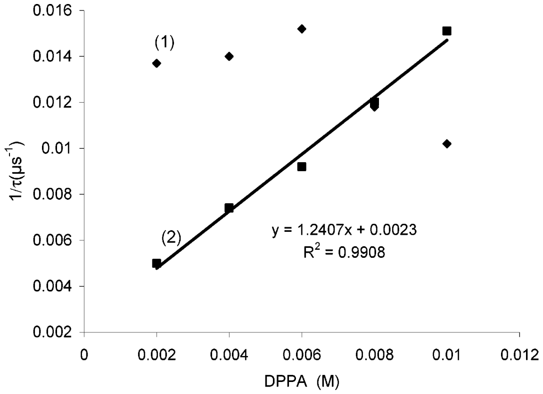


Figure 2. The effect of diphenylphosphoryl azide (**1**) on $1/\tau$ of the transient formed at 345 nm upon LFP (266 nm) in (◆) acetonitrile and (■) dichloromethane at ambient temperature.

absorption. The transient absorption observed in non-hydrogen-containing solvents, such as perfluorohexane and 1,1,2-trifluorotrichloroethane, cannot be due to **4**, of course, and is confidently attributed to triplet nitrene **2t**. The lifetime of **2t** in dichloromethane is linearly dependent on the concentration of precursor **1**. The absolute rate constant of reaction of nitrene **2t** with azide **1** is 1.2 × 10^6 M^{-1} s^{-1}. The lifetime of **2t** in dichloromethane at ambient temperature, extrapolated to infinite dilution of azide, is 500 µs.

Addition of low concentrations of hydrogen-containing solvents, such as cyclohexane, to 1,1,2-trifluorotrichloroethane does not lead to changes in the transient spectrum nor does it shorten the transient lifetime in Freon-113. These changes would be expected if triplet nitrene **2t** was being converted to radical **4** in a rapid hydrogen-transfer reaction. This implies that triplet **2t** abstracts hydrogen atoms slowly from cyclohexane and other donors and that radical **4** is not the carrier of the transient spectra observed in dichloromethane, 1,2-dichloroethane, and chloroform.

A particularly intense signal is observed upon flash photolysis of azide **1** in acetonitrile, which was previously attributed to ylide **6**.[5] Figure 2 demonstrates that the lifetime of the transient observed in acetonitrile is not dependent upon the concentration of azide precursor. Thus, the carriers of the transient spectra in Freon-113 and in acetonitrile are different species. This supports Maloney's assignment of the carrier of transient absorption in this solvent as ylide **6**, rather than as triplet nitrene **2t**,[5] although both species absorb in the same region.

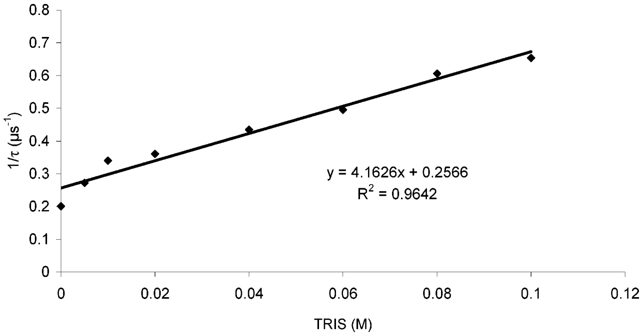


Figure 3. The effect of tris-trimethylsilylsilane (TRIS) concentration on the lifetime of the produced transient derived from LFP of **1** in methanol (340 nm) at ambient temperature.

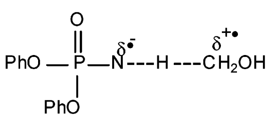
TABLE 2: Absolute Rate Constant of Reaction of Triplet 2t with $(MeSi)_3SiH$ and Stern−Volmer Quenching Constants of Singlet 2s as a Function of Solvent at Ambient Temperature

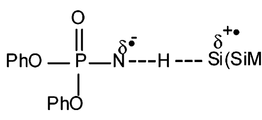
solvent[a]	k^3_{SiH} (M^{-1} s^{-1})	k^1_{SiH} (M^{-1} s^{-1})	τ (ns)[b]
1,2-dichloroethane	3.4 × 10^5	8.1	1
methanol	3.2 × 10^6	7.6	1
1,1,2-trifluorotrichloroethane	3.1 × 10^5	22.8	4

[a] [**1**] = 5.6 × 10^{-3} M. [b] Assuming k^1_{SiH} = 5 × 10^9 M^{-1} s^{-1}.

Tris-trimethylsilylsilane (SiH) is a particularly effective hydrogen atom donor. The presence of the silane reduces the yield of transient absorption at 345 nm in 1,1,2-trifluorotrichloroethane, methanol, and 1,2-dichlorothane and shortens the lifetime of triplet nitrene **2t** in these solvents. Plots of $1/\tau$ of the triplet nitrene versus silane concentration are linear (Figure 3). The absolute rate constant of triplet nitrene reaction with tris-trimethylsilane is 3.1 × 10^5 M^{-1} s^{-1} in 1,1,2-trifluorotrichloroethane. Essentially, the same rate constant is measured in 1,2-dichloroethane, a solvent with a pronounced transient absorption maximum. Because it is unlikely that triplet nitrene **2t** and radical **4** will have the same absolute rate constant with silane, it seems more likely that the transient absorption spectrum of **2t** varies with solvent than that the carrier of the spectrum in 1,2-dichloroethane is radical **4**. The low reactivity of **2t** toward tris-trimethylsilylsilane in Freon-113 (where the transient cannot be radical **4**) further supports our previous conclusion that the transient spectra observed in 1,2-dichloroethane and other hydrogen-containing solvents are not due to radical **4**, produced by reaction of triplet nitrene **2t** with solvent.

The short lifetime of **2t** in methanol and the relatively large rate constant of reaction of nitrene with silane in this solvent (Table 2) are attributed to polar effects on the transition states of the two hydrogen atom transfer reactions.


$\mathrm{PhO-\overset{\overset{O}{\|}}{\underset{\underset{PhO}{|}}{P}}-\overset{\delta^{\bullet-}}{N}---H---\overset{\delta^{+\bullet}}{C}H_2OH}$


$\mathrm{PhO-\overset{\overset{O}{\|}}{\underset{\underset{PhO}{|}}{P}}-\overset{\delta^{\bullet-}}{N}---H---\overset{\delta^{+\bullet}}{Si}(SiMe_3)_3}$

Tris-trimethylsilylsilane lowers the yield of transient absorption of **2t** by interception of singlet nitrene **2s**. Stern−Volmer plots of the data (Figure 4) are linear and give the k^1_{SiH} values listed in Table 2. Assuming that k^1_{SiH} is 5 × 10^9 M^{-1} s^{-1}, one deduces singlet nitrene lifetimes of 1 ns in 1,2-dichloroethane, acetonitrile, and methanol and 4 ns in 1,1,2-trifluorotrichloroethane.

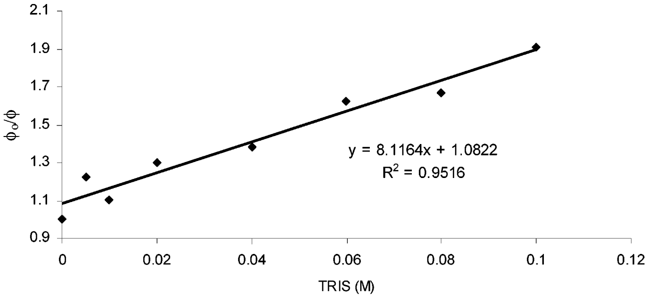


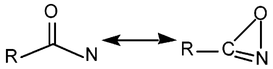
Figure 4. Stern−Volmer treatment of the quenching of transient absorption at 340 nm by tris-trimethylsilysilane in 1,2-dichloroethane.

IV. Discussion

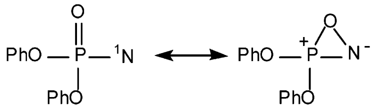
The hydrogen atom abstraction reaction of triplet imidogen (^{3}NH) with methane is endothermic because of the rehybridization of the nitrene nitrogen during this process.[7,8] As a consequence, triplet nitrenes abstract hydrogen atoms rather slowly from typical solvents, and therefore, the k^3_{SiH} data of Table 1 is not very surprising. One does not expect triplet nitrene **2t** to rapidly abstract hydrogen from methylene chloride, 1,2-dichloroethane, and cyclohexane; thus, the long triplet lifetimes observed in these solvents is unremarkable. Little is known of solvent effects on triplet nitrene spectra, but there is some relevant data on the triplet arylnitrenes.[3] These triplets tend to have sharp bands in the 300−350 nm region that show little solvent variation. The broad absorption of **2t** implies that the electronic structure of the nitrene is perturbed by the neighboring phosphorus−oxygen double bond. Calculations are in progress to clarify this issue.

The lifetime of **2s** should be longest in 1,1,2- trifluorotrichloroethane in which C−H insertion reactions are not possible. The lifetime of **2s** in this solvent is most likely controlled by intersystem crossing (ISC) to the lower energy triplet state; thus, $k_{\mathrm{isc}} = 2.5 \times 10^8$ s^{-1}. This ISC rate is hundreds of times larger than that of phenylnitrene[3,8,9] and approaches the rapid rates observed with carbenes.[10] Carbene ISC is rapid because singlet carbenes have closed-shell zwitterionic singlet states. Arylnitrenes, in contrast, have biradical-like open-shell singlet configurations.[7−9]

Gritsan and Pritchina[11] have recently reported density functional theoretical calculations on an acylnitrene (R = C_6H_5) that indicate that this nitrene has a closed-shell configuration because of a bonding interaction between the nitrene nitrogen and carbonyl oxygen.



We propose that there is a corresponding interaction in singlet **2s**.



2s

This resonance interaction will lead to a carbene-like zwitterionic closed-shell singlet and rapid ISC rates.

Our data do not support the idea of hydrogen-bonding catalysis of ISC of **2s** in methanol. It seems more likely that solvent variation influences the shape of the transient absorption of **2t**.

V. Conclusions

Laser flash photolysis (LFP, 266 nm) of diphenylphosphoryl azide **1** produces triplet diphenylphosphoryl nitrene **2t**. The spectra of **2t** are solvent-dependent. The lifetime of **2t** in 1,1,2-trifluorotrichloroethane is limited by nitrene reaction with precursor ($k^3 = 1.2 \times 10^6$ M^{-1} s^{-1}, ambient temperature). The lifetime of **2t** extrapolated to infinite dilution of precursor is 500 μs in methylene chloride at ambient temperature. The absolute rate constant of reaction of **2t** with tris-trimethylsilylsilane is 3.1×10^5 M^{-1} s^{-1} in Freon-113. The same reaction proceeds with a larger rate constant of 3.2×10^6 M^{-1} s^{-1} in methanol due to a polar effect. Stern−Volmer analysis indicates that the lifetime of singlet nitrene **2s** is 4 ns in 1,1,2-trifluorotrichloroethane and that the intersystem crossing rate constant is 2.5×10^8 s^{-1}. It is proposed that the rapid rate of ISC results from a bonding interaction between the phosphoryl oxygen and nitrene nitrogen to produce a closed-shell zwitterionic structure.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

References and Notes

(1) Breslow, R.; Feiring, A.; Herman, F. *J. Am. Chem. Soc.* **1974**, *96*, 5937.

(2) Maslak, P. *J. Am. Chem. Soc.* **1989**, *111*, 820.

(3) Gritsan, N. P.; Platz, M. S. *Adv. Phys. Org. Chem.* **2001**, *36*, 255.

(4) Gritsan, N. P.; Zhai, H. B.; Yuzawa, T.; Karweik, D.; Brooke, J.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 2833.

(5) Houser, M.; Kelley, S.; Maloney, V.; Marlow, M.; Steininger, K.; Zhou, H. *J. Phys. Chem.* **1995**, *99*, 7946.

(6) (a) Poe, R.; Grayzar, J.; Young, M. J. T.; Leveya, E.; Schnapp, K.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 3209. (b) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054.

(7) Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.

(8) Karney, W. L.; Borden, W. T. *Advances in Carbene Chemistry*; Elsevier: New York, 2001; Vol. 3, p 205.

(9) Johnson, W. T. J.; Sullivan, M. B.; Cramer, C. J. *Int. J. Quamt. Chem.* **2001**, *85*, 492.

(10) (a) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868. (b) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

(11) Gritsan, N. P.; Pritchina, E. A. *Mendeleev Commun.* **2001**, 94.