equal to 80% and 20%, respectively (see Table I). The occurrence of two vastly different frequencies, ω_1 and ω_2, is consistent with the existence of two different coordination geometries for Cd ions in metallothionein. Since pure T_d or O_h symmetries produce a spectrum lacking NQI, our results must indicate distortion from either symmetry. Of these two options, recent spectroscopic studies[12,13] greatly favor a T_d-derived symmetry.[10,14] Interestingly, the same two frequencies with the same relative amplitudes were also seen in an experiment where 10^{-12} mol of ^{111}Cd were added to a vast excess of the metal-free protein (10^{-4} M) (Figure 1b, Table I). Since under these conditions cluster structures do not form, one can conclude that these two different types of binding sites are not affected by changes in the outer coordination sphere of the complex and, hence, by the occupation of the neighboring metal-binding sites. That the participation of the same mercaptide group to one or several Cd ions does not have to affect the first coordination sphere geometry is in keeping with the constant Cd–S binding distance of about 2.5–2.55 Å irrespective of whether S is coordinated to one or two Cd ions.[15-17] The 120-MHz frequency ω_1 corresponds in order of magnitude to the 65-MHz frequency displayed by ^{111}Cd substituted for zinc in the crystallographically defined structural metal site of liver alcohol dehydrogenase. In this site, four cysteinyl thiolate ligands are arranged in a coordination geometry very close to that of a regular tetrahedron.[18] Its presence in metallothionein thus indicates that 80% of the binding sites have a similar, only weakly distorted T_d symmetry. By contrast, the 580-MHz frequency must arise from site(s) with entirely different geometric properties. A square-planar CdS_4^{2-} complex would exhibit a frequency of about 880 MHz.[18] Additional filling up to an octahedron, e.g., with either water or carboxyl ligands, would result in frequencies of about 400 and 640 MHz, respectively. Thus, the 580-MHz frequency could originate either from an extremely distorted tetrahedral geometry approaching square-planar coordination or, less likely (vide supra), from a distorted octahedral geometry with four planar mercaptide ligands and, for example, two carboxyl ligands in the remaining axial positions. Similarly, no feature characteristic of penta- or hexacoordination has been observed thus far in the spectroscopic studies of Co(II)–metallothionein.[5,10,14]

All spectra indicate about a 20% frequency broadening[9] associated with the 120-MHz frequency. Such an effort can arise either from a distribution in position of several charged protein groups within 5 Å of the cadmium atom or from the existence of minor differences in the local metal geometries. The latter would indicate an amplitude enhancement ("beat") for seven or less NQI's at larger *t*. Its lack suggests that the former is the case of the observed broadening. It is tempting to view the proximity of the lysine residues of metallothionein to the metal-complexing Cys-X-Cys sequences as a cause for such charge fluctuation.[20] The positive charges of the lysine residues have been postulated to serve as a role in compensating the negative charges associated with each thiolate site.[3,21]

In contrast to the 120-MHz signal, the 580-MHz signal is sharp. Its relatively small amplitude P_2 (see Table I) may indicate that it arises from about one cadmium binding site.

A replacement of 1 equiv of Zn in (Zn,Cd)-metallothionein by ^{111}Cd also results in the appearance of two NQI. Since under such circumstances ^{111}Cd replaces a zinc ion,[12] one can conclude, albeit indirectly, that zinc-like cadmium ions can occupy both types of binding sites in the protein. However, these NQI are shifted significantly toward higher frequency values, i.e., ω_1 = 149 MHz and ω_2 = 714 MHz (see Table I). This is best explained by additional geometrical distortion imposed upon the overall protein structure due to the differences in the sulfur–metal distances in the crystallographically defined cadmium and zinc model complexes. It is interesting that differences between solely Cd-containing forms of metallothionein and mixed (Cd- and Zn-containing) forms are also noted in their respective CD spectra. The Cd-induced ellipticity bands are much larger in the mixed form, suggesting a distorting influence on the coordination of Cd–thiolate complexes in the mixed-metal environment within the metal–thiolate cluster.[11,19,22]

In summary, the PAC data have shown that the majority of the metal-binding sites exhibit weakly distorted tetrahedral geometry, but that these are also site(s) with an entirely different metal geometry.

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Reactions of Excited Triplet Diphenylcarbene Studied with Picosecond Lasers

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The reactivities of the lowest singlet and triplet states of carbenes with alcohols and olefins in fluid solution have been extensively investigated.[1-11,17] For the specific case of diphenylcarbene (DPC) it has been shown that it reacts preferentially from its lowest singlet state with methanol, apparently by direct insertion into the OH bond of the alcohol.[1,2,4] The triplet ground state of DPC, on the other hand, has been shown to react with far greater ease toward

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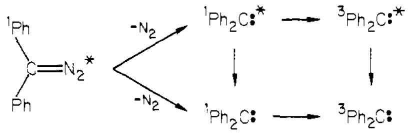
Scheme I



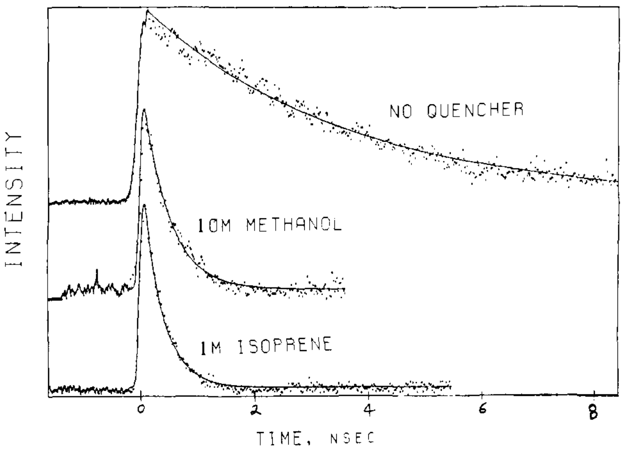


Figure 1. Decay curves of excited triplet diphenylcarbene with no quencher, 10 M methanol, and 1 M isoprene in degassed acetonitrile at room temperature. The points are experimental, and the solid curves are theoretical.

isoprene than the corresponding singlet carbene state.[11,13] These results exemplify the sharp difference that exists between the chemical properties associated with the lowest singlet and triplet electronic states of DPC. Although the absorption and emission spectra of DPC are known,[14-16] the behavior of the optically excited triplet state toward carbene quenchers remains unknown. We report here the observation of the reactions of the triplet *excited* state of DPC with methanol and isoprene.

Excitation of a degassed acetonitrile solution containing diphenyldiazomethane (10^{-3} M) with a single pulse from a frequency-quadrupled (264 nm) Nd:phosphate glass laser leads to N_2 extrusion from the excited precursor, thereby producing the carbene. We have observed[12] two routes for generating the ground triplet state carbene. The first one proceeds via the excited triplet state carbene, while the other, the major route,[4] proceeds through the lowest singlet carbene. The proposed mechanism is shown in Scheme I.

A picosecond streak camera-optical multichannel analyzer system was used to monitor the fluorescence from ^{3}DPC* produced by either the excited-state pathway or by excitation of ground ^{3}DPC with a second delayed laser pulse. The observed decay kinetics reported here are independent of the method chosen for producing ^{3}DPC*. The fluorescence lifetime of ^{3}DPC* in acetonitrile with no quenchers present was found to be 3.8 ns. The rise time of the ^{3}DPC* following the 264-nm excitation pulse was less than 15 ps. Figure 1 shows the exponential decay of the carbene fluorescence as a function of added methanol and isoprene. With these results a plot of the decay constant against reactant concentration is used to obtain the bimolecular reaction rate constant. From the slope of the lines fitted to the data in the low concentration limit, values of $(2.1 \pm 0.3) \times 10^9$ M^{-1} s^{-1} for isoprene and $(3.1 \pm 0.4) \times 10^8$ M^{-1} s^{-1} for methanol[18] are obtained.

These results are to be compared to the known data for the reaction of the lowest singlet and ground triplet states of diphenylcarbene with methanol and isoprene. There is presently no direct evidence for the reaction of methanol with diphenylcarbene in its ground triplet state.[1,4,17] The previously observed[4,11] rapid diffusion-controlled reaction of methanol with diphenylcarbene ($\simeq 2 \times 10^{10}$ M^{-1} s^{-1}) is thought to occur via the low-lying singlet state, i.e., ^{1}DPC. The reaction we have observed here is indeed a reaction between the triplet carbene and methanol, but it is the excited triplet carbene.

We also note a marked increase in the reactivity of isoprene in going from the ground triplet carbene to its excited triplet state. There is roughly a factor of 10^4 difference in the rate constants between the ground ^{3}DPC (3.5×10^5 M^{-1} s^{-1})[11,13] and the excited ^{3}DPC* ($(2.1 \pm 0.3) \times 10^9$ M^{-1} s^{-1}). Whether this jump in reactivity results from the greater energy of 58 kcal/mol available or the nature of the ^{3}DPC* electronic state is not yet established.

Experiments are presently underway to determine the possible excited triplet reaction pathways, e.g., hydrogen atom abstraction from CH and/or OH insertion. In addition the separation of excited ^{3}DPC* reactions from reactions in the lower states with time-delayed picosecond laser pulses is being actively pursued.

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Registry No. Diphenyldiazomethane, 883-40-9; diphenylcarbene, 3129-17-7.

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[18] At high methanol concentrations (>3 M) a concave deviation from linear behavior is seen.

Reaction of Stannocene and Plumbocene with Phosphenium Ions: Oxidative Addition of C–H Bonds to Low-Coordination-Number Main-Group Species

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Two-coordinate neutral compounds of group 4A and two-coordinate cations of group 5A are carbenoids in the sense that they both possess a lone pair of electrons and a formally vacant orbital on the heteroatom. Given that R_2M species (M = Ge, Sn) are known to dimerize in the solid state,[1] we were prompted to explore the reactions of R_2M with R_2E^+ in an effort to prepare compounds with formal double bonding between Sn or Pb with P^+. However, the reaction of stannocene or plumbocene with $[(i\text{-}Pr_2N)_2P]^+$ results in phosphonium salt formation via oxidative addition of a C–H bond to the two-coordinate phosphorus cation.

In a typical reaction, the phosphenium salt $[(i\text{-}Pr_2N)_2P]^+[AlCl_4]^-$ was made in situ[2] by treatment of $(i\text{-}Pr_2N)_2PCl$ (1.620 g, 6.08 mmol) with Al_2Cl_6 (0.812 g, 3.04 mmol) in 15 mL of CH_2Cl_2 at −78 °C. The reaction mixture was allowed to warm to room temperature, stirred for 30 min, then recooled to −20 °C prior to the addition of freshly sublimed $(\eta^5\text{-}C_5H_5)_2Sn$[3] (1.51 g, 6.08 mmol). Following this addition, the reaction mixture gradually assumed ambient temperature, resulting in a tan precipitate and a peach-colored solution. Filtration followed by storage of the filtrate at −20 °C afforded 3.72 g (5.73 mmol) of off-white microcrystalline $[(\eta^5\text{-}C_5H_5)Sn(\eta^5\text{-}C_5H_4)(i\text{-}Pr_2N)_2PH]^+[AlCl_4]^-$ (**1**) (structures of **1** and **2** are suggested on the basis of NMR evidence) in 94.2% yield.[4] The lead analogue,

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