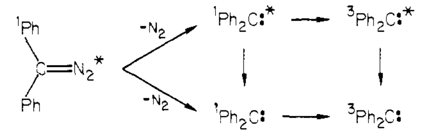
Scheme I



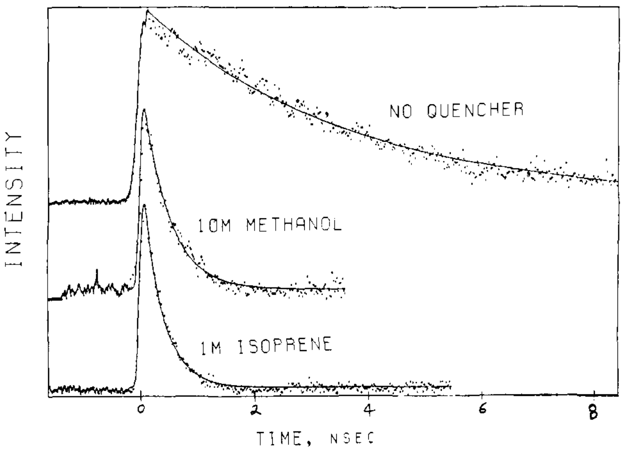


Figure 1. Decay curves of excited triplet diphenylcarbene with no quencher, 10 M methanol, and 1 M isoprene in degassed acetonitrile at room temperature. The points are experimental, and the solid curves are theoretical.

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 ($3.5 \times 10^5\ M^{-1}\ s^{-1}$)[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.

Acknowledgment. We thank the National Science Foundation, the Air Force Office of Scientific Research, and the Joint Services Electronics Program No. 29-79-0079 for their support of this work.

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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[1] Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261–262. Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268–2274.

[2] The synthesis of $[(i\text{-}Pr_2N)_2P]^+[AlCl_4]^-$ follows the method pioneered by Parry and co-workers. See, e.g.: Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994–1001. For the X-ray crystal structure of $[(i\text{-}Pr_2N)_2P]^+[AlCl_4]^-$, see: Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784–7786.

[3] For the synthesis of stannocene, see: (a) Dave, L. D.; Evans, D. F.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3684–3688. (b) Fischer, E. O.; Grubert, H. *Z. Naturforsch.* **1956**, *11b*, 423–424. For the X-ray crystal structure of stannocene, see: Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *J. Chem. Soc., Chem. Commun.* **1981**, 925–927.

[4] Satisfactory elemental analyses were obtained for compounds **1** and **2**.

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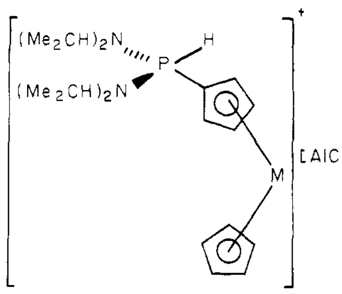

1, M = Sn
2, M = Pb

$[(\eta^5\text{-}C_5H_5)Pb(\eta^5\text{-}C_5H_4)(i\text{-}Pr_2N)_2PH]^+[AlCl_4]^-$ (**2**) can be produced as a white microcrystalline solid in 89.6% yield by using plumbocene[5] and a virtually identical reaction procedure.[4] The presence of the $AlCl_4^-$ anion in both compounds is demonstrated by the presence of a sharp singlet at 102.5 ppm (w_{h} = 15–18 Hz) in the ^{27}Al NMR.[6] The increase in coordination number accompanying the reaction was apparent from the >300-ppm upfield shifts in the $^{31}P\{^1H\}$ resonances:[7] **1** (s, +5.99); **2** (s, +4.72). Of special significance was the fact that the coupled ^{31}P spectra of both compounds consisted of doublets (**1**, $^1J_{PH}$ = 535.1 Hz; **2**, $^1J_{PH}$ = 540.7 Hz), which demonstrate unequivocally the presence of P–H bonds. The 20-MHz $^{13}C\{^1H\}$ NMR spectra of **1** and **2** were particularly useful for elucidating the rest of the cationic structures. Thus, peaks A and B of **1** (Figure 1) at δ 23.1 and 23.6 with J_{PNCC} = 2.2 and 2.6 Hz, respectively, correspond to the anisochronous isopropyl methyl groups. The diastereotopic nature of the isopropyl methyl groups is a consequence of the existence of five prochiral centers[8,9] in **1** and **2** and has been observed in closely related molecules.[10] The anisochrony does not arise from, e.g., restricted N–P bond rotation inter alia because the methine carbons are isochronous (peak C, δ 47.6, J_{PNC} = 4.8 Hz). Peak D, which we attribute to the α carbon of the monosubstituted cyclopentadienyl ring, is difficult to detect in a normal $^{13}C\{^1H\}$ experiment; however, in an off-resonance experiment it appears as a doublet at δ 100.9 with J_{PC} = 150.0 Hz. The intense singlet, E, at δ 111.8 corresponds to the carbons of the unsubstituted ring. Finally, doublets F and G at δ 115.7 and 120.9 with coupling constants of 17.0 and 17.6 Hz, respectively, correspond to the β and γ carbons of the monosubstituted cyclopentadienyl ring. The foregoing structure assignment was confirmed by 90-MHz ^{1}H NMR: Me (d, 12 H, δ 1.31, J_{HCHH} = 7.1 Hz), Me′ (d, 12 H, δ 1.34, $J_{HCCH'}$ = 7.2 Hz), Me_2CH (m, 4 H, δ 3.7), C_5H_5 (s, 5 H, δ 6.1), C_5H_4 (H_β) (m, 2 H, δ 6.2), C_5H_4 (H_γ) (m, 2 H, δ 6.6). The NMR data for **2** were very similar to those of **1**, thus leading to the conclusion that the compounds are isostructural; ^{1}H NMR (90 MHz) Me, Me′ (d, 24 H, δ 1.32, J_{HCCH} = 6.9 Hz),[11] Me_2CH (m, 4 H, δ 3.7), C_5H_5 (s, 5 H, δ 6.1), $C_5H_4(H_\beta)$ (m, 2 H, δ 6.2), $C_5H_4(H_\gamma)$ (m, 2 H, δ 6.5); $^{13}C\{^1H\}$ (20.0 MHz, Me$_4$Si); Me (d, δ 23.4, J_{PNCC} = 1.4 Hz), Me′ (d, δ 23.9, J_{PNCC} = 1.4 Hz), Me_2CH (d, δ 47.9, J_{PNC} = 4.2 Hz), C_5H_5 (s, δ 113,1), $C_5H_4(C_\beta)$ (d, δ 117.0, J_{PCC} = 17.8 Hz), $C_5H_4(C_\gamma)$ (d, δ 120.6, J_{PCCC} = 16.7 Hz).

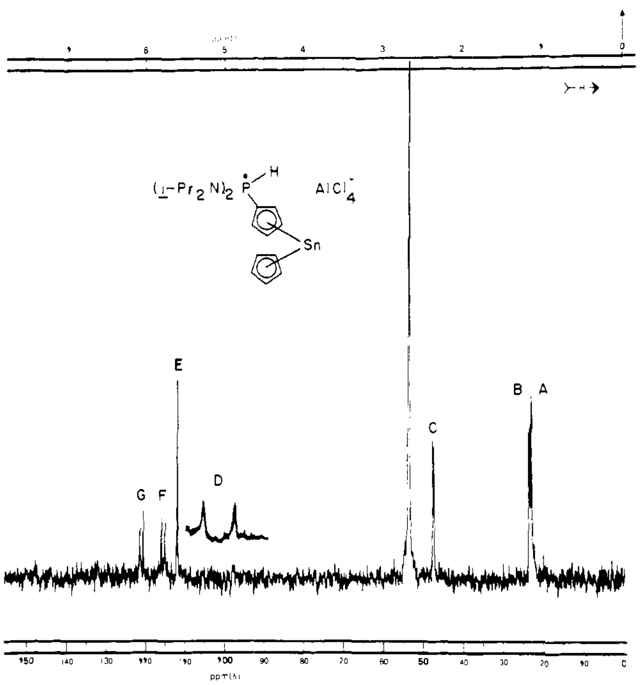

Figure 1. $^{13}C\{^1H\}$ NMR spectrum of **1** recorded at 20.0 MHz, 30 °C in CH_2Cl_2 solution. Peak D is only detectable in an off-resonance experiment.

We are presently assessing the scope of these oxidative addition reactions. Preliminary experiments indicate that nickelocene reacts with $[(i\text{-}Pr_2N)_2P]^+$ in the same manner as $(\eta^5\text{-}C_5H_5)_2Sn$ and $(\eta^5\text{-}C_5H_5)_2Pb$. The permethylated analogues, $(\eta^5\text{-}Me_5C_5)_2M$ (M = Sn, Pb), fail to react with phosphenium ions even though the oxidative addition of C–C bonds to phosphenium ions is almost as thermodynamically favorable as the C–H oxidative addition.

Finally, we note that treatment of **1** and **2** with i-Pr$_2$NLi in THF/CH$_2$Cl$_2$ solution results in removal of the phosphonium proton and formation of the corresponding $(R_2N)_2P$-substituted stannocene (**3**) and plumbocene (**4**). These reactions represent the first direct syntheses of monosubstituted stannocenes and plumbocenes. The only previously reported approach to such compounds involves the use of preformed monosubstituted cyclopentadienyl rings.[12]

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Registry No. 1, 81655-95-0; **2**, 81655-97-2; **3**, 81655-94-9; **4**, 81655-96-1; $[(i\text{-}Pr_2N)_2P]^+[AlCl_4]^-$, 68880-45-5; $(\eta^5\text{-}CsH_5)_2Sn$, 1294-75-3; $(\eta^5\text{-}C_5H_5)_2Pb$, 1294-74-2.

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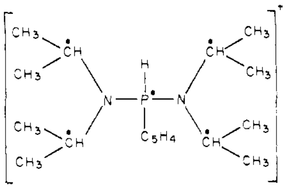
[5] For the synthesis of plumbocene, see ref 3a, and Fischer (Fischer, E. O.; Grubert, H. *Z. Anorg. Chem.* **1956**, *286*, 237–242). For the X-ray crystal structure of plumbocene, see: Panattoni, C.; Bombieri, G.; Croatto, U. *Acta Crystallogr.* **1966**, *21*, 823–826.

[6] Akitt, J. W. *Annu. Rep. NMR Spectrosc.* **1972**, *5*, 465–556.

[7] Positive ^{31}P chemical shifts are in ppm downfield from external 85% H_3PO_4.

[8] For an excellent review of the NMR aspects of prochiral assemblies, see: Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307–322.

[9] This number of prochiral centers (•) assumes rapid nitrogen inversion on the NMR time scale:



[10] For the $^{13}C\{^1H\}$ NMR spectra of $(i\text{-}Pr_2N)_2P(Cl)Fe(CO)_4$ and $(i\text{-}Pr_2N)_2PCl$, see: Cowley, A. H.; Kemp, R. A.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 4289–4293. Cushner, M. C. Ph.D. Dissertation, The University of Texas at Austin, Austin, TX, 1979.

[11] The Me and Me′ ^{1}H resonances of **2** exhibit accidental chemical shift degeneracy; however, the diastereotopy of the *i*-Pr groups is demonstrated by the anisochrony of the $^{13}C\{^1H\}$ resonances of Me and Me′ (vide supra).

[12] Dory, T. S.; Zuckerman, J. J.; Rausch, M. D. 182nd ACS National Meeting of the American Chemical Society, New York, NY, August 23–28, 1981; American Chemical Society: Washington, D.C., 1981; INOR 268.