Table II. Deuterium Incorporation[a]

solvent	D	D′	A	5-d_1,[b] %
CH_3CN	1a	2b-d_1[c]	3a	20
CH_3CN	1a	2b-d_1[d]	3a	30
CH_3CN	1a	2b-d_1[d]	3b	30
CD_3CN	1a	2b	3a	30
CD_3CN	1a	2b-d_1[d]	3a	65
CH_3CN–CH_3OD (9:1)	1a	2b	3a	94

[a] Deaerated solutions, [1a] = 0.16 M, [2b] = [2b-d_1] = 0.6 M, [3a] = 0.04 M. [b] Irradiated to 80–90% conversion at 313 nm. Crude products 5 and 5-d_1 were analyzed for deuterium content by 100-MHz NMR spectroscopy. [c] Deuterium content of 2b-d_1 is 67%. [d] Deuterium content of 2b-d_1 is 93%.

1,1-diphenyl-2-methoxyethane was produced.[2b] No photoreaction occurred in nonpolar solvents such as benzene or cyclohexane even in the presence of **3a**.

The maximum quantum yield for the formation of **5** ([**2b**] = 0.1 M) was 0.13 ± 0.01 at 313 nm. Plot of the reciprocal quantum yield for the formation of **5** vs. concentration of **2b** (Stern–Volmer plot) displayed the curved line (Figure 1), suggesting that at the higher concentrations, **2b** acts as a quencher of this photoaddition. The formation of **5** was also quenched by the addition of **2e**,**g**, and 1,4-dimethoxybenzene which have lower oxidation potentials than **1a**.[13]

On the basis of these results, we propose the mechanism involving heterodimer cation radical (DD$'^{+}\cdot$) (Scheme II). The first step is the photoinduced electron transfer from an electron-donating aromatic olefin (**1a**) to an excited electron acceptor (**3a**) to form the cation radical (**1a**$^{+}\cdot$) and the anion radical (**3a**$^{-}\cdot$). Negative ΔG value (−6.3 kcal/mol) estimated from Weller's equation[14] and a near diffusion controlled rate (1.6×10^{10} s^{-1} M^{-1}) for the fluorescence quenching of **3a** by **1a** in acetonitrile ensure the efficient photoinduced electron transfer. If the cation radical **2b**$^{+}\cdot$ is formed, it would be quenched without formation of a crossed adduct; the nucleophilic reactivity of **1a** is too low to react with **2b**$^{+}\cdot$; hence **2b**$^{+}\cdot$ is quenched by a back electron transfer from **3a**$^{-}\cdot$.[15]

The second step is the formation of heterodimer cation radical (DD$'^{+}\cdot$). The third step is the back electron transfer from **3a**$^{-}\cdot$ to DD$'^{+}\cdot$, giving crossed adducts DD′ and **3a**. A support for the intermediacy of DD$'^{+}\cdot$ was obtained from the results of the photoreaction of **1a** and 2-methylfuran-5-*d* (**2b**-d_1) in the presence of **3a**. The results suggest that the cation radical X and the biradical intermediate Y are involved in this reaction. The NMR analyses of the products indicated that the α position of diphenylethyl group in **5** is selectively deuterated (Table II and Scheme II). The deuteration is achieved via a 1,3-hydrogen shift from the 5 position of the furan ring to the α position of the diphenylethyl group in Y. The efficient deuteration of **5** occurred in the photoreaction of **1a** and **2b** in acetonitrile containing 10% methanol-*O-d*, probably through the intermediate Z.

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(13) The oxidation potential of 1,4-dimethoxybenzene vs. Ag/Ag$^+$ in acetonitrile using a Pt electrode is 0.95 V. The photoreaction of the **1a** (0.05 M)–**2b** (0.1 M)–**3a** (0.05 M) system was completely quenched by the addition of 1,4-dimethoxybenzene (0.1 M).

(14) $\Delta G\ (\mathrm{kcal/mol}) = 23.06[E(\mathrm{D/D^+})_\mathrm{V} - E(\mathrm{A^-/A})_\mathrm{V} - e^2{}_0/(\epsilon a)] - E_{0-0}$. Rehm, D.; Weller, A. *Israel J. Chem.* **1970**, *8*, 259.

(15) There is a high possibility that **2b**$^{+}\cdot$ is formed through electron transfer from **2b** to the excited state of **3a** in the photoreaction of the **1a**–**2b**–**3a** system, since a negative ΔG value (−11.3 kcal/mol) and a near diffusion controlled rate (7.4×10^9 s^{-1} M^{-1}) were obtained for the fluorescence quenching of **3a** by **2b**. The similarity in the oxidation potentials of **1a** and **2b** also suggests that there exists the charge exchange equilibrium, **1a**$^{+}\cdot$ + **2b** $\rightleftharpoons$ **1a** + **2b**$^{+}\cdot$. However, the unreactivity of **2b**$^{+}\cdot$ prohibits the possibility of the reaction of **2b**$^{+}\cdot$ with **1a** to give the crossed addition product. The most probable fate of **2b**$^{+}\cdot$ is the quenching by a back electron transfer from **3a**$^{-}\cdot$ to **2b**$^{+}\cdot$.

Pentamethylcyclopentadienyl-Substituted Phosphorus and Arsenic Cations: Evidence for Multihapto Bonding between Group 5A Elements and Carbocyclic Ligands

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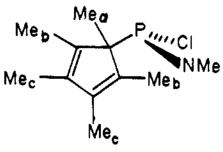
Cyclopentadienyl- and pentamethylcyclopentadienyl-substituted cations of the group 5A elements, $(R_5C_5)_2E^+$, E = P, As, Sb, Bi; R = H, Me, are isoelectronic with the corresponding neutral compounds of the group 4A elements, viz., $(R_5C_5)_2M$, M = Si, Ge, Sn, Pb. Since $(R_5C_5)_2Sn$,[1] $(R_5C_5)_2Pb$,[2] and $(Me_5C_5)_2Ge$[3] feature pentahapto bonding of the cyclopentadienyl ligands, it seemed possible that the group 5A cations might also exhibit multihapto bonding.

Treatment of $(Me_5C_5)ECl_2$, E = P, As,[4] with Me_3SiNMe_2 affords $(Me_5C_5)(Me_2N)PCl$ (**1**) and $(Me_5C_5)(Me_2N)AsCl$ (**2**). Compound **1** was characterized by elemental analysis, mass spectroscopy (parent peak, *m/e* 245), and NMR spectroscopy. ^1H NMR (60 MHz) Me_2N (d, δ 2.58 J_{PNCH} = 11.3 Hz), Me_5C_5 (br s, δ 1.9); $^{13}C\{^1H\}$ NMR (20.0 MHz) (Me_4Si) Me_2N (d, δ 41.51, J_{PNC} = 17.5 Hz), $C_5\mathit{Me}_5$ (s, δ 11.8), C_5Me_5 (br, δ 138.6); $^{31}P\{^1H\}$ NMR (36.43 MHz) (s, δ 144.8).[5] The Me_5C_5 ring of **1** is bonded in the monohapto manner, since on cooling to −40 °C, the 200-MHz ^1H NMR spectrum of the pentamethylcyclopentadienyl methyl protons exhibits three resonances: Me_a (d, 3 H, δ 1.37, J_{PCCH_a} = 6.65 Hz), Me_b (d, 6 H, δ 1.77, J_{PCCCH_b} = 6.3 Hz), Me_c (s, 6 H, δ 1.83). Compound **2** is not stable at ambient temperature, thus precluding elemental analysis. It was characterized by NMR and mass spectroscopy: ^1H NMR (200 MHz) Me_2N (s, 6 H, δ 2.75), Me_5C_5 (s, 15 H, δ 1.84); $^{13}C\{^1H\}$ NMR (20.0 MHz) (Me_4Si) Me_2N (s, δ 42.45), Me_5C_5 (s, δ 11.59), $Me_5\mathit{C}_5$ (s, δ 125.16).



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Treatment of **1** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 solution at −78 °C, followed by warming to room temperature, affords a red-brown solution. The presence of the $AlCl_4^-$ anion as the sole aluminum-containing species was evidenced by the presence of a sharp singlet ($w_h \sim 9$ Hz, δ 103)[6] in the ^{27}Al NMR, thus indicating the formation of the phosphenium ion $[(Me_5C_5)(Me_2N)P]^+$ (**3**). ^1H NMR (60.0 MHz) Me_2N (d, 6 H, δ 3.18, J_{PNCH} = 9.1 Hz), C_5Me_5 (d, 15 H, δ 2.14, J_{PCCH} = 2.6

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(1) (a) For the X-ray crystal structure of $(C_5H_5)_2Sn$, see: Atwood, J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A., to be published. For an electron diffraction study of $(C_5H_5)_2Sn$ in the vapor phase, see: (b) Almenningen, A.; Haaland, A.; Motzfeldt, T. *J. Organomet. Chem.* **1967**, *7*, 97–104. For the X-ray crystal structure of $(Me_5C_5)_2Sn$, see: (c) Jutzi, P.; Kohl, F.; Hoffman, P.; Krüger, C.; Tsay, Y.-H. *Chem. Ber.* **1980**, *113*, 757–769.

(2) The solid-state structure of $(C_5H_5)_2Pb$ comprises a polymeric zigzag chain with alternating bridging and terminal η^5-cyclopentadienyl groups: Panattoni, C.; Bombieri, G.; Croatto, U. *Acta Crystallogr.* **1966**, *21*, 823–826. In the vapor state, however, $(C_5H_5)_2Pb$ is monomeric.[1b] We have synthesized $(Me_5C_5)_2Pb$ recently and found that this compound is monomeric in the solid state.[1a]

(3) The structure of $(C_5H_5)_2Ge$ is unknown, but vibrational spectroscopic evidence suggests that it is isostructural with the Sn and Pb analogues. Scibelli, J. V.; Curtis, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 924–925. However, the structure of the permethylated compound, $(Me_5C_5)_2Ge$, has been determined recently by electron diffraction and found to involve pentahapto bonding by both Me_5C_5 rings. Fernholt, L.; Haaland, A.; Jutzi, P.; Seip, R. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 585–588.

(4) Jutzi, P.; Saleske, H.; Nadler, D. *J. Organomet. Chem.* **1976**, *118*, C8–10.

(5) Positive ^{31}P chemical shifts are downfield from external 85% H_3PO_4.

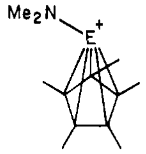
(6) Akitt, J. W. *Annu. Rep. NMR Spectrosc.* **1972**, *5A*, 465–556.

0002-7863/81/1503-5572$01.25/0

Hz); $^{13}C\{^1H\}$ NMR (20.0 MHz) (Me_4Si) Me_2N (d, δ 43.04, J_{PNC} = 12.9 Hz), C_5Me_5 (s, δ 10.76), C_5Me_5 (d, δ 130.4, J_{PC} = 11.8 Hz). Several pieces of spectroscopic evidence lead to the conclusion the Me_5C_5 ring of **3** is not bonded in the monohapto manner: (i) The ^1H and ^{13}C NMR spectra of **3** indicate that the ring and Me carbons of the Me_5C_5 moiety are equivalent; moreover, the equivalence of the methyl groups persists to −100 and −80 °C in ^1H and ^{13}C NMR experiments, respectively. (ii) The ^{31}P chemical shift of **3** (111.0 ppm)[5] is 33.8 ppm *upfield* (i.e., shielded) compared to that of the phosphorus(III) chloride precursor, **1**. In all cases reported thus far, phosphenium ion formation via halide ion abstraction from precursor phosphorus(III) halides has been accompanied by a downfield ^{31}P NMR chemical shift of >100 ppm.[7] We attribute the upfield shift to multihapto bonding between P^+ and the Me_5C_5 ligand and concomitant delocalization of the positive charge in the resulting cluster. Support for this suggestion is provided by the fact that ~100 ppm upfield ^{11}B NMR chemical shifts have been observed[8] when pentahapto boron cations, $[\eta^5\text{-}Me_5C_5)BX]^+$, are formed via X^- abstraction from the corresponding monohapto boron dihalides, $(\eta^1\text{-}Me_5C_5)BX_2$.

Treatment of **2** with Al_2Cl_6 in CH_2Cl_2 solution results in the arsenium salt $[(Me_5C_5)(Me_2N)As]^+[AlCl_4]^-$ (**4**).[9] ^1H NMR (200 MHz) Me_2N (s, δ 3.32) Me_5C_5 (s, δ 2.17); $^{13}C\{^1H\}$ NMR (20.0 MHz) (Me_4Si) Me_2N (s, δ 38.14), Me_5C_5 (s, δ 10.98), Me_5C_5 (s, δ 126.88); ^{27}Al NMR (s, 103.5 ppm, w_h ~ 14 Hz). The ^1H and ^{13}C chemical shift equivalence of the Me_5C_5 ring persisted to −80 °C.

The foregoing NMR observations on cations **3** and **4** are consistent with a static pentahapto structure (**5**) or with tri- and dihapto structures with low barriers to migration such as **6** and **7**, respectively. Structure **6** is analogous to phosphonium or arsonium ions, while **7** is, in essence, a phosphiran or arsiran stabilized by allyl cation attachment.[10] MNDO calculations[11] on $[(Me_5C_5)(Me_2N)P]^+$ reveal the following: (i) the global minimum is **7**, (ii) **5** and **6** do not correspond to minima,[12] and (iii) the barrier to circumannular migration of the Me_2NP moiety in **7** via an η^1 intermediate is very low (<2 kcal/mol).[13]



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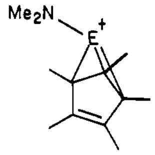

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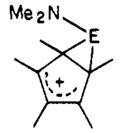

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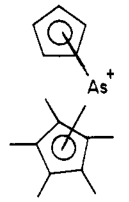
The reaction of $(Me_5C_5)PCl_2$ with C_5H_5Li results in many products; however, the reaction of $(Me_5C_5)AsCl_2$ with C_5H_5Li proceeds cleanly and results in $(Me_5C_5)(C_5H_5)AsCl$ (**8**). ^1H NMR (60 MHz) Me_5C_5 (s, 15 H, δ 1.73), C_5H_5 (s, 5 H, δ 5.74); $^{13}C\{^1H\}$ NMR (20.0 MHz) (Me_4Si) Me_5C_5 (s, δ 132.6), Me_5C_5 (s, δ 12.37), C_5H_5 (br, δ 124.03). Treatment of **8** with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 results in the arsenium salt $[(Me_5C_5)(C_5H_5)As]^+[AlCl_4]^-$ (**9**).[9] ^1H NMR (200 MHz) Me_5C_5 (s, 15 H, δ 2.17), C_5H_5 (s, 5 H, δ 6.72); $^{13}C\{^1H\}$ NMR (20.0 MHz) (Me_4Si) Me_5C_5 (s, δ 130.9), Me_5C_5 (s, δ 10.46), C_5H_5 (s, δ 119.8); ^{27}Al NMR (s, δ 103.5, w_h ~14 Hz). The chemical shift equivalence in both cyclopentadienyl rings persists to −80 °C, and MNDO calculations on the model compound $(C_5H_5)_2P^+$ indicate that the bis(pentahapto) structure represents a global minimum which is 16 kcal/mol more stable than the bis(monohapto) structure. We therefore suggest the following structure for **9**.



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Acknowledgment. We are grateful to the National Science Foundation (Grant CHE79-10155) and the Robert A. Welch Foundation for generous financial support.

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[7] (a) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534-2540. (b) Maryanoff, B. E.; Hutchins, R. O. *J. Org. Chem.* **1972**, *37*, 3475-3480. (c) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994-1001. (d) Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789-797. (e) Baxter, S. G.; Cowley, A. H.; Collins, R. L.; Sena, S. F. *J. Am. Chem. Soc.* **1981**, *102*, 714-715.

[8] Jutzi, P.; Seufert, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 330-1. Jutzi, P.; Seufert, A.; Buchner, W. *Chem. Ber.* **1979**, *112*, 2488-93.

[9] By analogy with phosphenium ions, two-coordinate arsenic cations, R_2As^+, are referred to as arsenium ions. In the adduct $AsF_3 \cdot SbF_5$ there is a contribution made from the formulation $[AsF_2]^+[SbF_6]^-$ in the solid state (Edwards, A. J.; Sills, R. J. C. *J. Chem. Soc. A* **1971**, 942-945). However, compounds **4** and **9** constitute the first clear-cut examples of arsenium ions.

[10] Amido-substituted phosphirans have been described recently and found to exhibit relatively shielded ^{31}P NMR chemical shifts. Niecke, E.; Schoeller, W. W.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 131-132. For the synthesis of other substituted phosphirans, see: Chan, S.; Goldwhite, H.; Keyzer, H.; Rowsell, D. G.; Tang, R. *Tetrahedron* **1969**, *25*, 1097-1103.

[11] For MNDO parameters for third period elements, see: Dewar, M. J. S.; McKee, M.; Rzepa, H. *J. Am. Chem. Soc.* **1978**, *100*, 3607.

[12] The pentahapto structure (**5**) is computed to be 28.6 kcal/mol higher in energy than the dihapto structure (**7**).

[13] The low barrier for ring migration is estimated from a detailed calculation on the model compound $[(C_5H_5)(Me_2N)P]^+$. Justification for this extrapolation is found in the close agreement of the calculated energy differences for **5** and **7** and the analogous unpermethylated structures.

Isomerization of Silene to Ketene in the Photolysis of Pentamethyldisilanyldiazoacetate

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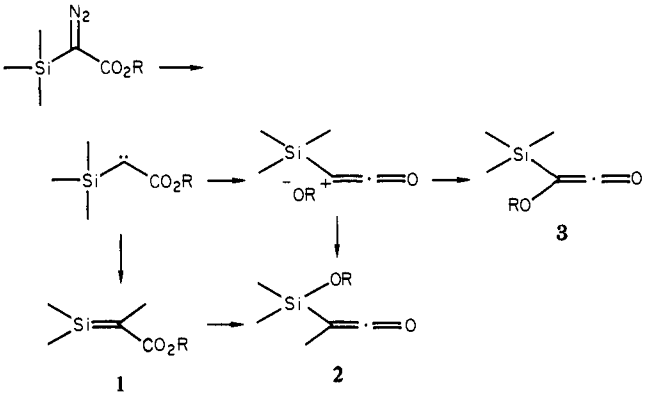
We have recently presented evidence for the formation of a silene intermediate in the decomposition of ethyl (trimethylsilyl)diazoacetate.[1] The major question remaining is the source of alkoxysilylketene **2** in the gas-phase decomposition of the silyldiazoacetate.[2,3] The Wolff rearrangement may have a radical or even ionic component. As an alkoxy group migrates to an adjacent position on its way to ketene **3**, it finds itself in the neighborhood of a silicon atom and adds with or without simultaneous migration of a methyl group to give the ketene **2**.



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[1] Ando, W.; Hagiwara, T.; Migita, T. *J. Am. Chem. Soc.* **1973**, *95*, 7518.

[2] Ando, W.; Sekiguchi, A.; Migita, T.; Kammula, S.; Green, M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3818.

[3] Ando, W.; Sekiguchi, A.; Hagiwara, T.; Migita, T.; Chowdhry, V.; Westheimer, F. H.; Kammula, S.; Green, M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6393.