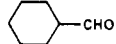
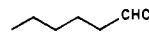
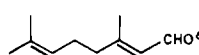


Table II. RCHO → RCH=CHCN<sup>a</sup>

entry	aldehyde	reagent	yield, <sup>b</sup> %	olefin ratio <sup>c</sup> (Z/E)
A		<i>t</i> -BuMe <sub>2</sub> SiCH <sub>2</sub> CN <sup>d</sup> Ph <sub>3</sub> SiCH <sub>2</sub> CN <sup>d</sup>	76 80	6:1 9:1
B		<i>t</i> -BuMe <sub>2</sub> SiCH <sub>2</sub> CN Ph <sub>3</sub> SiCH <sub>2</sub> CN	62 63	3:1 5:1
C		<i>t</i> -BuMe <sub>2</sub> SiCH <sub>2</sub> CN Ph <sub>3</sub> SiCH <sub>2</sub> CN	79 85	2:1 2:1

<sup>a</sup> All reactions were performed as described in the text. <sup>b</sup> Values reported are isolated. <sup>c</sup> Olefin ratio was determined by GLC (Carbowax 20 M). Vicinal olefinic coupling constants of Z-unsaturated nitriles: entry A, 11 Hz; B, 11 Hz; C, 11 Hz. <sup>d</sup> See ref 21. <sup>e</sup> Ca. 93% pure (*E*)-citraol was used.

2.0 mmol of *tert*-butyllithium in pentane (1.8 M) under an argon atmosphere. [After 1 h at -78 °C, a freshly prepared ethereal solution (6 mL) of magnesium bromide (2.2 mmol)<sup>15</sup> was added and the stirring continued for an additional 15 min.<sup>16</sup>] The carbonyl compound (1.6 mmol) was then added. After 5 min, the solution was gradually warmed to 50 °C and stirred there for 2-3 h to complete the elimination.<sup>17</sup> The product was extracted with ether repeatedly, washed with dilute hydrochloric acid and water, dried, and concentrated in vacuo. The residual liquid was subjected to column chromatography on silica gel (hexane) to give the enyne.<sup>18</sup>

Due to the observed high stereoselectivities in our enyne synthesis, we have sought to extend the investigation to other systems, with the object of finding the generality of Scheme I. An interesting and synthetically important result was obtained with the carbanion derived from  $\alpha$ -silylated acetonitrile,<sup>19</sup> which in principle is capable of reacting with carbonyl compounds in a similar mechanism as reagent 1.<sup>20</sup> Thus, (triphenylsilyl)acetonitrile<sup>21</sup> was treated first with lithium diisopropylamide (1.0 equiv, -20 °C, THF, 30 min) and then with magnesium iodide<sup>22</sup> (1.1 equiv, 0.3 M solution in ether, -20 °C, THF, 5 min). To the resulting milky white suspension at -78 °C was added cyclohexanecarboxaldehyde (1.0 equiv), and the mixture was stirred at -78 °C for 5 min, 20 °C for 15 min, and 50 °C for 1 h. After the usual workup followed by column chromatography the  $\alpha,\beta$ -unsaturated nitrile **5** was obtained in 80% yield (Z/E = 9:1). The examples cited in Table II illustrate the synthesis of unsaturated nitriles using the indicated reagents and reactants.

(15) Prepared from ethylene dibromide and magnesium in ether.

(16) This procedure was omitted in the case of lithium reagent. Thus, after 1 h at -78 °C, the carbonyl compound was introduced.

(17) We have observed that magnesium salts of  $\beta$ -hydroxysilanes undergo elimination more readily when the silyl group is trimethylsilyl than when it is *tert*-butyldimethylsilyl.

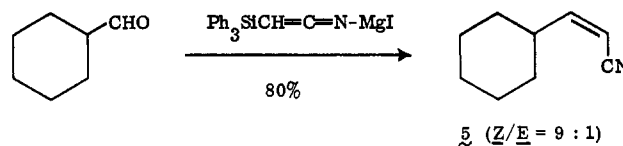
(18) The (*Z*)-enyne was characterized by an infrared absorption at ~14  $\mu$ m and a coupling constant between the vicinal olefinic hydrogens of ~11 Hz observed in the <sup>1</sup>H NMR spectrum. On the other hand, the (*E*)-enyne was characterized by an infrared absorption at ca. 10.4  $\mu$ m and a coupling constant of ~16 Hz. See ref 12 and 13.

(19) (a) Ojima, I.; Kumagai, M.; Nagai, Y. *Tetrahedron Lett.* 1974, 4005. (b) Matsuda, I.; Murata, S.; Ishii, Y. *J. Chem. Soc., Perkin Trans. 1* 1978, 26.

(20) For the stereospecific epoxy nitrile cyclization, the cyano anion in which the metal is located on the nitrogen atom was proposed as a possible structure for transition states. See: Stork, G.; Cama, L. D.; Coulson, D. R. *J. Am. Chem. Soc.* 1974, 96, 5268. Stork, G.; Cohen, J. F. *Ibid.* 1974, 96, 5270. Recently, monolithiated acetonitrile was reported to have three local singlet potential-energy surface minima, corresponding to three different structures, from minimal basis ab initio calculations, and the most stable of the three forms is the lithium atom acting as a bridge to compress the carbon-carbon bond. See: Moffat, J. B. *J. Chem. Soc., Chem. Commun.* 1980, 1108. With this proposed structure the similar five-membered-ring transition state shown in Scheme I may also be considered.

(21) Prepared from lithiated acetonitrile and chlorosilanes; see ref 19b and references cited therein. (Triphenylsilyl)acetonitrile (56% yield): mp 135.5-136 °C (acetone); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.35 (s, 2 H), 7.43 (br s, 15 H). (*tert*-Butyldimethylsilyl)acetonitrile (50%): bp 102 °C (30 mmHg); mp 71-72 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.29 (s, 6 H), 1.04 (s, 9 H), 1.68 (s, 2 H).

(22) Freshly prepared from magnesium and iodine in ether.



Although the mechanistic considerations given here can only be considered tentative, the present examples point to the importance of counterion and steric effects in the stereochemical course of the reaction. We believe that examination of other allenyl anions in this context will reveal similar stereochemical regulations.

### Photoinduced Alkylation of Five-Membered Heteroaromatic Compounds via Electron-Transfer Reaction: Heterodimer Cation Radical Intermediacy

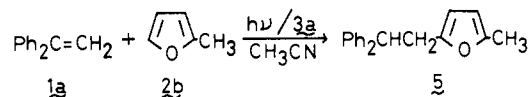
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Photoinduced intermolecular interactions between electron donor and acceptor molecules are a subject of current interest in connection with photochemical and photophysical processes involving exciplexes and radical ions.<sup>1-5</sup> Photocyclodimerization of electron-rich aromatic olefins proceeds via dimer cation radicals.<sup>2</sup> Nucleophiles such as methanol and cyanide ion can add to photochemically generated cation radicals.<sup>3</sup> However, little is known about the photocrossed addition between two different electron-rich unsaturated compounds,<sup>4,5</sup> which may occur through electron transfer. We now report a novel photocrossed addition between 1,1-diarylethylenes (D) and five-membered heteroaromatic compounds (D') such as furans and 1-methylpyrrole. A key step of this photoreaction was the reaction of photochemically generated cation radicals of diarylethylenes (D<sup>+</sup>) with neutral heteroaromatic compounds (D') to give heterodimer cation radicals (DD'<sup>+</sup>).

Irradiation of an acetonitrile solution of 1,1-diphenylethylene (**1a**) (20 mmol) and 2-methylfuran (**2b**) (200 mmol) containing a small amount of 1-cyanonaphthalene (**3a**) (2 mmol) gave 5-(2,2-diphenylethyl)-2-methylfuran (**5**) mp 38.5-39.5 °C, in 87% yield with 70% recovery of **3a**.<sup>6,7</sup> Irradiation of a mixture of **1a**



(1) For review articles, see: Davidson, R. S. *Mol. Assoc.* 1979, 1, 215-334. Mataga, N.; Ottolenghi, M. *Ibid.* 1979, 2, 1-78. Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* 1980, 13, 45. Lewis, F. D. *Ibid.* 1979, 12, 152.

(2) (a) Ledwith, A. *Acc. Chem. Res.* 1972, 5, 133. (b) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* 1973, 95, 4080. (c) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* 1973, 677. (d) Kuwata, S.; Shigemitsu, Y.; Odaira, Y. *J. Org. Chem.* 1973, 38, 3803. (e) Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* 1975, 53.

(3) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *J. Am. Chem. Soc.* 1978, 100, 535. Shigemitsu, Y.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* 1975, 407. Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* 1979, 101, 6458. Mizuno, K.; Ogawa, J.; Otsuji, Y. Annual Symposium on Photochemistry in Japan, Tokyo, Japan, 1979; pp 116.

(4) Farid, S.; Hartman, S. E.; Evans, F. R. "The Exciplex", Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; pp 327-343. Maroulis, A. J.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* 1979, 351. Arnold, D. R.; Borg, R. M.; Albini, A. *Ibid.* 1981, 138.

(5) Mizuno, K.; Kaji, R.; Otsuji, Y. *Chem. Lett.* 1977, 1027. Mizuno, K.; Kaji, R.; Okada, H.; Otsuji, Y. *J. Chem. Soc., Chem. Commun.* 1978, 594.

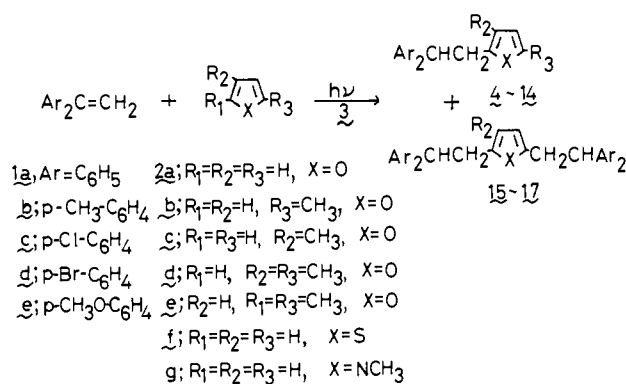
(6) Irradiation was carried out with a high-pressure mercury arc using a Pyrex filter (>280 nm) at ambient temperature.

Table I. Photoinduced Alkylation of 1,1-Diarylethylene with Five-Membered Heteroaromatic Compound<sup>a</sup>

1,1-diaryl-ethylene (D)	5-membered heteroaromatic compd (D')	electron acceptor (A)	conversion, %	product yield, <sup>b</sup> %	
1a	2a	3b	58	4, 49	15, 19
1a	2b	3a	100	5, 87	
1a	2c	3a	31	6, 34 <sup>c</sup>	16, 20
1a	2d	3a	37	7, 85	
1b	2a	3a	73	8, 54	17, 39
1b	2b	3b	53	9, 34	
1c	2b	3a	27	10, 49	
1d	2b	3a	30	11, 66	
1e	2a	3a	81 <sup>d</sup>		
1e	2b	3a	49	12, 80	
1e	2d	3a	25	13, 81	
1e	2g	3a	42	14, 61	

<sup>a</sup> Deaerated acetonitrile solutions; see text and ref 6. <sup>b</sup> Isolated yield based on 1,1-diarylethylene (1) consumed. <sup>c</sup> Two isomers are included. <sup>d</sup> See ref 8.

Scheme I



and furan (2a) or methylfurans (2c,d) in the presence of 3a afforded the corresponding 1:1 and 2:1 adducts in moderate yields. However, irradiation of a mixture of 1a and 2,5-dimethylfuran (2e), thiophen (2f), or 1-methylpyrrole (2g) in the presence of 3a gave no crossed adducts at all, with quantitative recovery of starting materials.<sup>7</sup> No photocrossed addition also took place between 1,1-bis(4-methoxyphenyl)ethylene (1e) and 2a,<sup>8</sup> whereas irradiation of 1e and 2g in the presence of 3a gave 2-[2,2-bis(4-methoxyphenyl)ethyl]-1-methylpyrrole (14) in 61% yield. Table I summarizes the results of the photoinduced crossed additions so far accumulated.<sup>9</sup> The results indicate that diarylethylenes D react with heteroaromatic compounds D' to give crossed adducts only if they have similar oxidation potentials.<sup>10</sup>

From a mechanistic viewpoint, some sensitized and quenching experiments were performed for the 1a-2b system. The photo-reaction of this system was not sensitized by triplet sensitizers such as Michler's ketone ( $E_T = 62$  kcal/mol) and benzophenone ( $E_T = 69.2$  kcal/mol).<sup>11</sup> But, it was sensitized by various aromatic

(7) A slight amount of 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene was detected by GC analyses, but the yield was very low.<sup>2b</sup>

(8) In this photoreaction, two dimers, 1,1,4,4-tetraanisyl-1,3-butadiene, mp 199-200 °C and 1,1,4,4-tetraanisyl-1-butene, mp 102-104 °C, were obtained in 23% and 67% yield, respectively. See: Sket, B.; Zupan, M. *Synth. Commun.* 1976, 6, 309.

(9) All new compounds obtained here afforded satisfactory spectral data (NMR, IR, and mass) and elemental analyses.

(10) The oxidation potentials of the olefins vs. Ag/Ag<sup>+</sup> in acetonitrile using a Pt electrode are 1.40 for 1a, 1.12 for 1b, 1.20 for 1c, 1.15 for 1d, and 0.78 V for 1e. The oxidation potentials of the heteroaromatic compounds under similar conditions are 1.46 for 2a, 1.18 for 2b, 1.23 for 2c, 0.90 for 2d, 0.95 for 2e, and 0.74 V for 2f. The pairs listed in Table I, which reacted with each other to give the crossed adducts, have similar oxidation potentials with respect to one another. On the other hand, the pairs which gave no crossed adducts greatly differ from one another in their oxidation potentials. The necessary conditions for the formation of crossed adducts will be discussed in a separate paper.

(11) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

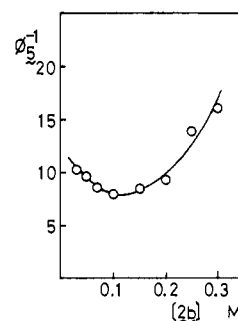
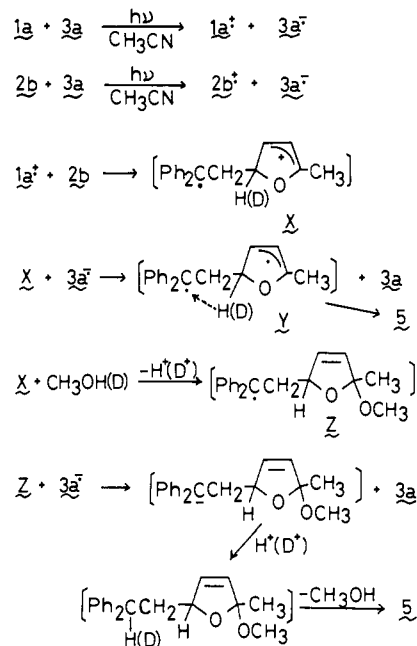


Figure 1. Plot of reciprocal quantum yield for the formation of 5 ( $\phi_5^{-1}$ ) vs. the concentration of 2b ([2b]) in deaerated acetonitrile solution, 313-nm irradiation; [1a] = 0.05 M, [2b] = 0.03-0.3 M, [3a] = 0.05 M.

Scheme II



nitriles such as 1,4-dicyanobenzene (3b), 1,4-dicyanonaphthalene (3c), and 9,10-dicyanoanthracene (3d), besides 3a.<sup>12</sup> The efficiency of the sensitizers decreased with decreasing reduction potentials.<sup>10</sup> In the photoreaction using 3a as a sensitizer, formation of 5 was quenched by addition of methanol; instead,

(12) The reduction potentials of electron acceptors vs. Ag/Ag<sup>+</sup> in acetonitrile using a Pt electrode are -2.25 for 3a, -1.92 for 3b, -1.59 for 3c, and -1.13 V for 3d. See: Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* 1976, 98, 5931. See also ref 4.

Table II. Deuterium Incorporation<sup>a</sup>

solvent	D	D'	A	5-d <sub>1</sub> , <sup>b</sup> %
CH <sub>3</sub> CN	1a	2b-d <sub>1</sub> <sup>c</sup>	3a	20
CH <sub>3</sub> CN	1a	2b-d <sub>1</sub> <sup>d</sup>	3a	30
CH <sub>3</sub> CN	1a	2b-d <sub>1</sub> <sup>d</sup>	3b	30
CD <sub>3</sub> CN	1a	2b	3a	30
CD <sub>3</sub> CN	1a	2b-d <sub>1</sub> <sup>d</sup>	3a	65
CH <sub>3</sub> CN-CH <sub>3</sub> OD (9:1)	1a	2b	3a	94

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

1,1-diphenyl-2-methoxyethane was produced.<sup>2b</sup> 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**.<sup>13</sup>

On the basis of these results, we propose the mechanism involving heterodimer cation radical (DD<sup>•+</sup>) (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<sup>•+</sup>**) and the anion radical (**3a<sup>•-</sup>**). Negative Δ*G* value (-6.3 kcal/mol) estimated from Weller's equation<sup>14</sup> and a near diffusion controlled rate (1.6 × 10<sup>10</sup> s<sup>-1</sup> M<sup>-1</sup>) for the fluorescence quenching of **3a** by **1a** in acetonitrile ensure the efficient photoinduced electron transfer. If the cation radical **2b<sup>•+</sup>** is formed, it would be quenched without formation of a crossed adduct; the nucleophilic reactivity of **1a** is too low to react with **2b<sup>•+</sup>**; hence **2b<sup>•+</sup>** is quenched by a back electron transfer from **3a<sup>•-</sup>**.<sup>15</sup>

The second step is the formation of heterodimer cation radical (DD<sup>•+</sup>). The third step is the back electron transfer from **3a<sup>•-</sup>** to DD<sup>•+</sup>, giving crossed adducts DD' and **3a**. A support for the intermediacy of DD<sup>•+</sup> was obtained from the results of the photoreaction of **1a** and 2-methylfuran-5-*d* (**2b-d<sub>1</sub>**) 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<sup>+</sup> 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) Δ*G* (kcal/mol) = 23.06[E(D/D<sup>•+</sup>)<sub>v</sub> - E(A<sup>-</sup>/A)<sub>v</sub> - e<sup>2</sup>o/(εa)] - E<sub>0-0</sub>. Rehm, D.; Weller, A. *Israel J. Chem.* 1970, 8, 259.

(15) There is a high possibility that **2b<sup>•+</sup>** 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 Δ*G* value (-11.3 kcal/mol) and a near diffusion controlled rate (7.4 × 10<sup>9</sup> s<sup>-1</sup> M<sup>-1</sup>) 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<sup>•+</sup>** + **2b** ⇌ **1a** + **2b<sup>•+</sup>**. However, the unreactivity of **2b<sup>•+</sup>** prohibits the possibility of the reaction of **2b<sup>•+</sup>** with **1a** to give the crossed addition product. The most probable fate of **2b<sup>•+</sup>** is the quenching by a back electron transfer from **3a<sup>•-</sup>** to **2b<sup>•+</sup>**.

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

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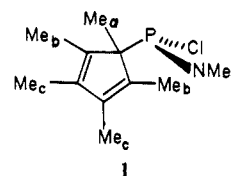
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Cyclopentadienyl- and pentamethylcyclopentadienyl-substituted cations of the group 5A elements, (R<sub>5</sub>C<sub>5</sub>)<sub>2</sub>E<sup>+</sup>, E = P, As, Sb, Bi; R = H, Me, are isoelectronic with the corresponding neutral compounds of the group 4A elements, viz., (R<sub>5</sub>C<sub>5</sub>)<sub>2</sub>M, M = Si, Ge, Sn, Pb. Since (R<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Sn,<sup>1</sup> (R<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Pb,<sup>2</sup> and (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Ge<sup>3</sup> feature pentahapto bonding of the cyclopentadienyl ligands, it seemed possible that the group 5A cations might also exhibit multihapto bonding.

Treatment of (Me<sub>5</sub>C<sub>5</sub>)ECl<sub>2</sub>, E = P, As,<sup>4</sup> with Me<sub>3</sub>SiNMe<sub>2</sub> affords (Me<sub>5</sub>C<sub>5</sub>)(Me<sub>2</sub>N)PCl (**1**) and (Me<sub>5</sub>C<sub>5</sub>)(Me<sub>2</sub>N)AsCl (**2**). Compound **1** was characterized by elemental analysis, mass spectroscopy (parent peak, *m/e* 245), and NMR spectroscopy. <sup>1</sup>H NMR (60 MHz) Me<sub>2</sub>N (d, δ 2.58, *J*<sub>PNC</sub> = 11.3 Hz), Me<sub>5</sub>C<sub>5</sub> (br s, δ 1.9); <sup>13</sup>C {<sup>1</sup>H} NMR (20.0 MHz) (Me<sub>4</sub>Si) Me<sub>2</sub>N (d, δ 41.51, *J*<sub>PNC</sub> = 17.5 Hz), C<sub>5</sub>Me<sub>5</sub> (s, δ 11.8), C<sub>5</sub>Me<sub>5</sub> (br, δ 138.6); <sup>31</sup>P {<sup>1</sup>H} NMR (36.43 MHz) (s, δ 144.8).<sup>5</sup> The Me<sub>5</sub>C<sub>5</sub> ring of **1** is bonded in the monohapto manner, since on cooling to -40 °C, the 200-MHz <sup>1</sup>H NMR spectrum of the pentamethylcyclopentadienyl methyl protons exhibits three resonances: Me<sub>a</sub> (d, 3 H, δ 1.37, *J*<sub>PCC<sub>H</sub></sub> = 6.65 Hz), Me<sub>b</sub> (d, 6 H, δ 1.77, *J*<sub>PCC<sub>H</sub></sub> = 6.3 Hz), Me<sub>c</sub> (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: <sup>1</sup>H NMR (200 MHz) Me<sub>2</sub>N (s, 6 H, δ 2.75), Me<sub>5</sub>C<sub>5</sub> (s, 15 H, δ 1.84); <sup>13</sup>C {<sup>1</sup>H} NMR (20.0 MHz) (Me<sub>4</sub>Si) Me<sub>2</sub>N (s, δ 42.45), Me<sub>5</sub>C<sub>5</sub> (s, δ 11.59), Me<sub>5</sub>C<sub>5</sub> (s, δ 125.16).

Treatment of **1** with a stoichiometric quantity of Al<sub>2</sub>Cl<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution at -78 °C, followed by warming to room temperature, affords a red-brown solution. The presence of the AlCl<sub>4</sub><sup>-</sup> anion as the sole aluminum-containing species was evidenced by the presence of a sharp singlet (*w*<sub>h</sub> ~ 9 Hz, δ 103)<sup>6</sup> in the <sup>27</sup>Al NMR, thus indicating the formation of the phosphonium ion [(Me<sub>5</sub>C<sub>5</sub>)(Me<sub>2</sub>N)P]<sup>+</sup> (**3**). <sup>1</sup>H NMR (60.0 MHz) Me<sub>2</sub>N (d, 6 H, δ 3.18, *J*<sub>PNC</sub> = 9.1 Hz), C<sub>5</sub>Me<sub>5</sub> (d, 15 H, δ 2.14, *J*<sub>PCC<sub>H</sub></sub> = 2.6

(1) (a) For the X-ray crystal structure of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Sn, 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<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Sn 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<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Sn, 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<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Pb comprises a polymeric zigzag chain with alternating bridging and terminal η<sup>5</sup>-cyclopentadienyl groups: Panattoni, C.; Bombieri, G.; Croatto, U. *Acta Crystallogr.* 1966, 21, 823-826. In the vapor state, however, (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Pb is monomeric.<sup>1b</sup> We have synthesized (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Pb recently and found that this compound is monomeric in the solid state.<sup>1a</sup>

(3) The structure of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ge 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<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Ge, has been determined recently by electron diffraction and found to involve pentahapto bonding by both Me<sub>5</sub>C<sub>5</sub> 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 <sup>31</sup>P chemical shifts are downfield from external 85% H<sub>3</sub>PO<sub>4</sub>.

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