Sathyanarayana for useful discussions. S.P.S.R. thanks the Department of Atomic Energy, Bombay, India, for financial assistance.

Registry No. $[Co(bpy)_2(PN\text{-}H)](ClO_4)_2$, 100229-36-5; $[Cu(bpy)(PN)Cl](ClO_4)\cdot H_2O$, 100229-39-8.

Supplementary Material Available: Listings of thermal parameters, positional parameters of the hydrogen atoms, selected torsion angles and asymmetry parameters, least-squares planes, bond lengths and angles in bpy moieties, and observed and calculated structure factors and packing diagrams (Figures 3 and 4) (48 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Reactivity of Phosphenium Ions toward 1,3- and 1,4-Dienes

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Received August 26, 1985

The phosphenium ions $[(i\text{-}Pr_2N)_2P]^+$ (**1**), $[(Me_2N)_2P]^+$ (**7**), and $[(i\text{-}Pr_2N)ClP]^+$ (**10**) react with a variety of 1,3-dienes to afford the corresponding 3-phospholenium (1-phosphacyclopent-3-enium) cations. The product of the reaction of **1** with 2,3-dimethyl-1,3-butadiene (**2**) was characterized by X-ray crystallography. Compound **2** crystallizes in the space group $P2_1/c$ (No. 14) with $Z = 4$, $a = 9.005$ (2) Å, $b = 16.134$ (4) Å, $c = 18.271$ (2) Å, and $\beta = 96.94$ (1)°. The product of the reaction of **7** with isoprene (**11**) was also characterized by X-ray crystallography. Compound **11** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 15.921$ (2) Å, $b = 7.903$ (12) Å, $c = 32.142$ (4) Å, and $\beta = 102.46$ (1)°. The reactivity of **10** toward the 1,4-dienes, penta-1,4-diene and cyclohexa-1,4-diene, was also investigated. The product of the penta-1,4-diene reaction (**15a**) was characterized by X-ray crystallography. Compound **15a** crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with $a = 8.309$ (4) Å, $b = 15.264$ (2) Å, and $c = 15.936$ (2) Å. Mechanistic aspects of these reactions are discussed from the standpoint of product distribution.

Introduction

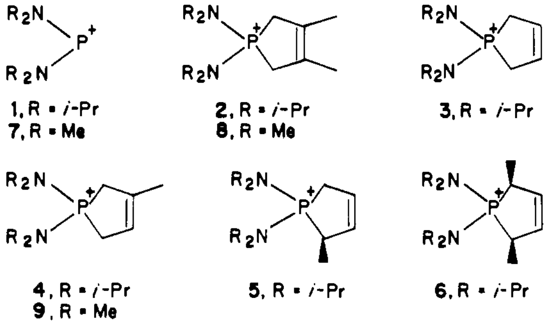
In the singlet state,[1] phosphenium ions (R_2P^+) feature two bond pairs and one lone pair of electrons at the cationic center. As a consequence, these six-electron species are expected to resemble electrophilic carbenoids in their chemical properties.[2] Bearing this parallel in mind, we are investigating the reactivity of phosphenium ions toward a variety of unsaturated organic substrates.

Phosphenium ions have, in fact, been postulated as intermediates in the McCormack reaction of dichlorophosphines with 1,3-dienes.[3] A somewhat stronger case for their intermediacy stems from the fact that complexes of the type $RPX_2\cdot AlX_3$ (R = Me, Ph; X = Cl, Br) are reactive toward 1,4-dienes.[4] In view of the foregoing, it was of interest to determine whether stabilized phosphenium ions would react with 1,3- and/or 1,4-dienes. Moreover, as recognized by SooHoo and Baxter[5] and ourselves,[6] the diene/phosphenium ion reaction represents a potentially useful and convenient synthetic route to phosphorus heterocycles.

Results and Discussion

(i) Reaction of Phosphenium Ions with 1,3-Dienes: Synthesis, Structure, and Spectroscopic Properties of 3-Phospholenium Ions.

Chart I



1, R = *i*-Pr
7, R = Me

2, R = *i*-Pr
8, R = Me

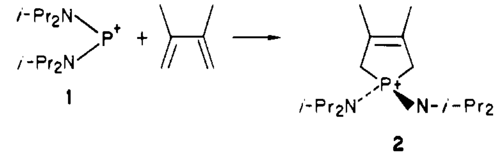
3, R = *i*-Pr

4, R = *i*-Pr
9, R = Me

5, R = *i*-Pr

6, R = *i*-Pr

Initial studies on the reactivity of phosphenium ions toward dienes centered on the reaction of $[(i\text{-}Pr_2N)_2P][AlCl_4]$ (**1**) with 2,3-dimethyl-1,3-butadiene. After a reaction time of 3 h at room temperature, a complete and quantitative conversion of **1** to **2** occurred as evidenced by ^{31}P NMR spectroscopy. The ^1H, ^{13}C, and ^{31}P NMR spectra of **2** (Table I) were consistent with its formulation as a 3-phospholenium (1-phosphacyclopent-3-enium) cation. This structure assignment was confirmed by an X-ray diffraction study of the tetrachloroaluminate salt of **2**, the results of which are illustrated in Figures 1 and 2 along with the atom-numbering schemes. Tables of bond lengths, bond angles, and atomic positional parameters are presented in Tables II–IV, while pertinent crystallographic data are collected in Table V.



1

2

The phosphacyclopentene ring of **2** adopts an envelope conformation for which the "hinge" is defined by the C1–C4 vector with the angle between the planes P1, C1, C4 and C1, C2, C3, C4 being 22.4°. The C–C bond lengths within the ring clearly demonstrate that the double bond is localized between C2 and C3 (1.319 (5) Å), which also carry the two methyl groups. The remaining carbon–carbon distances (average 1.512 (5) Å) cor-

---

(1) Molecular orbital calculations on $[H_2P]^+$, $[HFP]^+$, and $[F_2P]^+$ indicate that each model cation possesses a singlet ground state. Harrison, J. F.; Liedtke, R. C.; Liebmann, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 7162. Harrison, J. F. *Ibid.* **1981**, *103*, 7406.

(2) The parallels between phosphenium ions, carbenes, SO_2, NO, and other small molecules have been noted previously: Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994. Hutchins, L. D.; Deusler, E. N.; Paine, R. T. *Organometallics* **1982**, *1*, 1254.

(3) McCormack, W. B. U.S. Patents 2663736, 2663737, 1953; *Chem. Abstr.* **1955**, *49*, 7601. For reviews of this reaction, see: Quin, L. D. In "1,4-Cycloaddition Reactions"; Hamer, J., Ed.; Academic Press: New York, 1967; pp 47–96. Quin, L. D. In "The Heterocyclic Chemistry of Phosphorus"; Wiley-Interscience: New York, 1981; Chapter 2.

(4) Kashman, Y.; Menachem, Y.; Benary, E. *Tetrahedron* **1973**, *29*, 4279. Kashman, Y.; Rudi, A. *Tetrahedron Lett.* **1976**, 2819. Rudi, A.; Kashman, Y. *Ibid.* **1978**, 2209.

(5) SooHoo, C. K.; Baxter, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 7443.

(6) For preliminary accounts of this work, see: (a) Cowley, A. H.; Kemp, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A. *J. Am. Chem. Soc.* **1983**, *105*, 7444. (b) Cowley, A. H.; Stewart, C. A.; Whittlesey, B. R.; Wright, T. C. *Tetrahedron Lett.* **1984**, *25*, 815.

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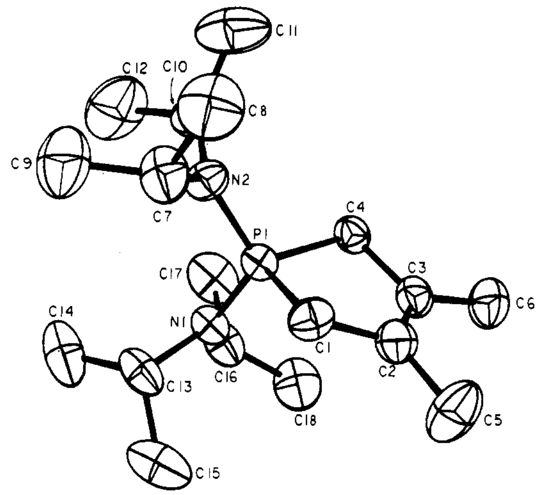
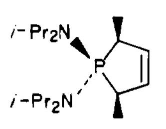


Figure 1. ORTEP plot of the 3-phospholenium cation $[(i\text{-}Pr_2N)_2\overline{PCH_2C(Me){=}C(Me)CH_2}][AlCl_4]$ (**2**) showing the atom-numbering scheme adopted.

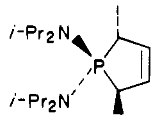
respond to single bonds. The phosphorus atom is four-coordinate and tetrahedral, the remaining two sites being occupied by $i\text{-}Pr_2N$ groups. As in the case of the parent phosphenium ion, $[(i\text{-}Pr_2N)_2P]^+$ (**1**) both amido groups possess a trigonal-planar nitrogen geometry.[7] Indeed the $[(i\text{-}Pr_2N)_2P]^+$ unit changes very little upon coordination: the P–N bond lengths increase by an average of 0.013 (4) Å while the N–P–N angles widen by 1.3 (2)°.

The ^1H NMR spectrum of **2** indicates that the ring methylene protons are equivalent, thus implying that the PC_4 envelope conformation is stereochemically nonrigid. The four *i*-Pr groups are also equivalent as a result of P–N bond rotation being rapid on the NMR time scale.

The reactivity of **1** toward 1,3-dienes was found to be quite general (Chart I). However, the reaction times vary significantly and depend on the electronic and steric demands of the diene. For example, the less activated dienes, 1,3-butadiene and isoprene, form the 3-phospholenium cations **3** and **4**, respectively, but the reactions require 24 h at room temperature to reach completion. Reaction times are still longer between **1** and *trans*-1,3-pentadiene and *trans*-2-*trans*-4-hexadiene, taking 3 and 9 days, respectively, to form **5** and **6**. These long reaction times are presumed due to increasing steric congestion at the reaction site. On the basis of ^1H, ^{13}C, and ^{31}P NMR data (Table I), it can be concluded that the structures of **3**–**6** are similar to that of **2**. The NMR spectra for **6** merit special comment because they indicate the presence of only one product. Since **6** can exist as cis (**6a**) and trans (**6b**)



6a, cis



6b, trans

isomers (with respect to the methyl group positions) this observation implies that the reaction of the diene with **1** is stereospecific. This aspect of the reaction is discussed later.

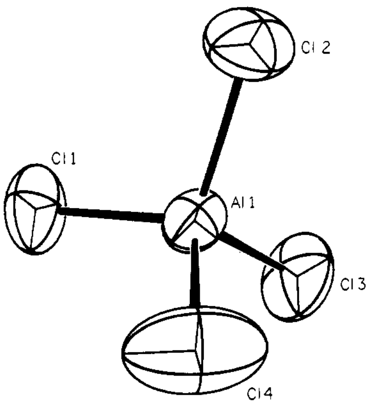


Figure 2. ORTEP plot of the $AlCl_4$ anion of $[(i\text{-}Pr_2N)_2\overline{PCH_2C(Me){=}C(Me)CH_2}][AlCl_4]$ (**2**).

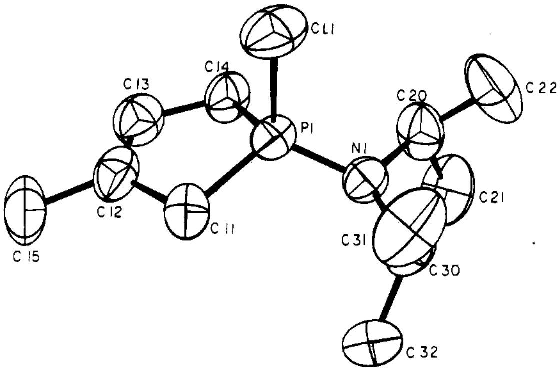
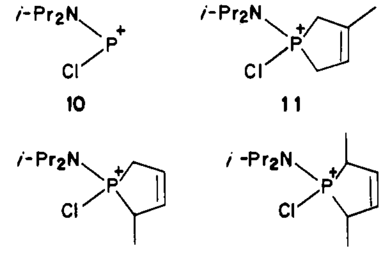


Figure 3. ORTEP plot of molecule A of the 3-phospholenium cation $[(i\text{-}Pr_2N)Cl\overline{PCH_2C(H){=}C(Me)CH_2}][AlCl_4]$ (**11**) showing the atom-numbering scheme adopted.

Chart II

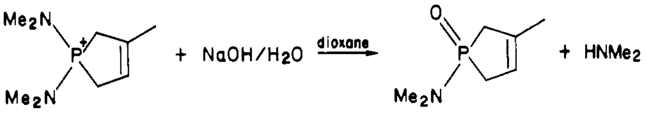


10 **11**

12a,b[a] **13a,b**[a]

[a] See text for a discussion of the stereochemistry of the methyl groups.

Attention is now turned to the less bulky and more reactive phosphenium ion $[(Me_2N)_2P][AlCl_4]$ (**7**).[8] For steric reasons, the reactivities of **7** toward dienes was expected to be greater than that of **1**. Thus the reactions of **7** with 2,3-dimethyl-1,3-butadiene and isoprene afforded the corresponding phospholenium cations, **8** and **9**, respectively, in approximately 1 h when the reaction mixture was warmed from −78 to 25 °C. NMR data are collected in Table I and are consistent with **8** and **9** having structures similar to those of **2** and **4**. However, while the NMR spectra of **9** were supportive of a 3-phospholenium cation formulation, the $AlCl_4^-$ salt was too reactive to permit isolation. Accordingly, **9** was converted into the anticipated phosphine oxide, **18**, by treatment with aqueous NaOH in dioxane. Pertinent NMR data for **18** are summarized in Table I.



9 **18**

A further increase in reactivity was apparent when the phosphenium ion $[(i\text{-}Pr_2N)ClP][AlCl_4]$ (**10**) was employed as the dienophile. Thus treatment of **10** with isoprene produced the phospholenium ion **11** in ~30 min (Chart II). Enhanced reactivity of **10** is also evident in the reactions with *trans*-1,3-pentadiene and *trans*-2-*trans*-4-hexadiene, both of which occur more rapidly than the corresponding reactions with **1**. The structure of **11**, based on NMR data, was confirmed by an X-ray crystal

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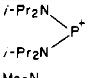
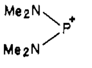
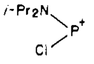
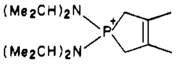
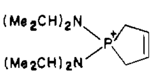
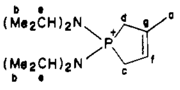
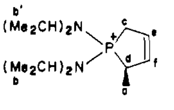
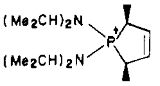
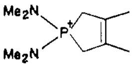
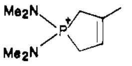
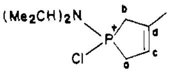
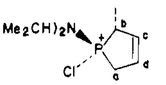
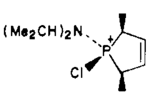
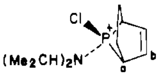
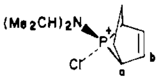
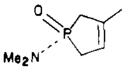
(7) Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.

(8) Kopp, R. W.; Bond, A. C.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3042. Schultz, C. W.; Parry, R. W. *Ibid.* **1976**, *15*, 3046. Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Ibid.* **1977**, *16*, 994.

Table I. NMR Data for the Phosphenium and 3-Phospholenium Cations Derived from 1,3-Dienes

compd	no.	$^{31}P\{^1H\}^a$	$^{13}C\{^1H\}^b$	$^1H^b$
	**1**	313		
	**7**	264		
	**10**	334		
	**2**	69.6	16.0 (d, $=CMe$, $^3J_{PC} = 14.5$ Hz); 22.6 ($CHMe_2$); 37.1 (d, CH_2, $^1J_{PC} = 76.5$ Hz); 47.9 (d, $CHMe_2$, $^2J_{PC} = 4.1$ Hz); 127.3 (d, $=C—Me$, $^2J_{PC} = 11.5$ Hz)	1.30 (d, 24 H, $CHMe_2$, $^3J_{HH} = 7.5$ Hz); 1.80 (br m, 6 H, $=CMe$); 3.10 (d, 4 H, CH_2, $^2J_{PH} = 11.1$ Hz); 3.7 (m, 4 H, CHMe)
	**3**	76.0	22.8 (CHMe); 32.2 (d, CH_2, $^1J_{PC} = 77$ Hz); 48.2 (d, $CHMe_2$, $^2J_{PC} = 3.9$ Hz); 125.6 (d, =CH, $^2J_{PC} = 14.4$ Hz)	1.20 (d, 24 H, CHMe, $^3J_{HH} = 7.5$ Hz); 3.10 (d, 4 H, CH_2, $^2J_{PH} = 10.5$ Hz); 3.7 (m, 4 H, $CHMe_2$); 5.9 (br m, 2 H, =CH)
	**4**	76.5	19.8(C_a); 22.9(C_b); 32.9 (d, C_c, $^1J_{PC} = 74.3$ Hz); 36.2 (d, C_d, $^1J_{PC} = 77.6$ Hz); 48.2 (d, C_e, $^2J_{PC} = 4.1$ Hz); 120.1 (d, C_f, $^2J_{PC} = 9.8$ Hz); 136.5 (d, C_g, $^2J_{PC} = 15.6$ Hz)	1.40 (d, 3 H, H_a, $^3J_{HH} = 7.5$ Hz); 2.0 (br s, 24 H, H_b); 3.2 (br m, 4 H, $H_c + H_d$); 3.8 (m, 4 H, C_e); 6.0 (br s, 1 H, C_f)
	**5**	79.7	19.5 (C_a); 23.6 ($C_b + C_{b'}$); 29.7 (d, C_c, $^1J_{PC} = 78.8$ Hz); 37.6 (d, C_d, $^1J_{PC} = 79.3$ Hz); 49.2 (d, $CHMe_2$, $^2J_{PC} = 9.1$ Hz); 49.3 (d, $CHMe_2$, $^2J_{PC} = 8.7$ Hz); 123.7 (d, C_e, $^2J_{PC} = 12.9$ Hz); 135.2 (d, C_f, $^2J_{PC} = 18.7$ Hz)	0.80 (s, 3 H, C_aH_3); 1.3 (m, 24 H, $CHMe_2$, $H_b + H_{b'}$); 3.1 (br s, 3 H, $C_cH_2 + C_dHMe$); 3.4 (br m, 4 H, $CHMe_2$); 6.1 (br s, 2 H, $H_e + H_f$)
	**6**	88.7	0.7 (CH_3); 19.4 ($CHMe_2$); 25.6 (d, $CHCH_3$ ring, $^1J_{PC} = 30.4$ Hz); 47.5 ($CHMe_2$); CH ring not observed	0.10 (s, 6 H, $CHCH_3$ ring); 1.30, 1.40 (d, 12 H, $CHMe_2$, $^3J_{HH} = 7.5$ Hz); 3.4 (m, 4 H, $CHMe_2$); 6.20 (s, 2 H, =CH ring)
	**8**	82.7	16.6 (d, CMe ring, $^3J_{PC} = 15.2$ Hz); 31.9 (d, CH_2, $^1J_{PC} = 80.4$ Hz); 36.9 (d, $CHMe_2$, $^2J_{PC} = 35.2$ Hz); 128.1 (d, =CMe, $^2J_{PC} = 12.6$ Hz)	1.9 (br s, 6 H, CMe ring); 2.80 (d, 12 H, NMe_2, $^3J_{PH} = 9.6$ Hz); 3.0 (br s, 4 H, CH_2)
	**9**	89.6		
	**11**	100.3	19.8 (Me ring); 22.2, 22.5 ($CHMe_2$); 38.4 (d, C_a, $^1J_{PC} = 71.8$ Hz); 41.4 (d, C_b, $^1J_{PC} = 76.3$ Hz); 53.3 ($CHMe_2$); 119.2 (d, C_c, $^2J_{PC} = 11.0$ Hz); 136.5 (d, C_d, $^2J_{PC} = 17.7$ Hz)	1.45 (d, 12 H, $CHMe_2$, $^3J_{HH} = 7.5$ Hz); 2.05 (br s, 3 H, Me ring); 3.65 (br s, 4 H, $C_aH_2 + C_bH_2$); 3.75 (m, 4 H, $CHMe_2$); 6.15 (br s, 1 H, C_cH)
	**12b**	107.5 (**12a**, 103.8)	14.9 (d, Me ring, $^2J_{PC} = 5.9$ Hz); 22.6 (d, $CHMe_2$, $^3J_{PC} = 5.1$ Hz); 22.0 (d, $CHMe_2$, $^3J_{PC} = 4.7$ Hz); 38.2 (d, C_a, $^1J_{PC} = 72.1$ Hz); 42.3 (d, C_b, $^1J_{PC} = 71.4$ Hz); 53.2 ($CHMe_2$); 123.8 (d, C_c, $^2J_{PC} = 15.1$ Hz); 133.0 (d, C_d, $^2J_{PC} = 22.2$ Hz)	
	**13a**	115.5 (**13b**, 97.4)	16.3 (d, Me ring, $^2J_{PC} = 5.0$ Hz); 22.3, 22.5 ($CHMe_2$); 42.3 (d, CHMe ring, $^1J_{PC} = 68.1$ Hz); 53.1 ($CHMe_2$); 130.8 (d, =CH ring, $^2J_{PC} = 21.3$ Hz)	
	**14b**	98.7	21.6, 21.8 ($CHMe_2$); 22.0 (d, CH_2, $^2J_{PC} = 25.4$ Hz); 45.1 (d, C_aH, $^1J_{PC} = 65.4$ Hz); 53.0 ($CHMe_2$); 132.0 (d, C_bH, $^2J_{PC} = 10.5$ Hz)	
	**14a**	117.2	23.2, 23.0 ($CHMe_2$); 21.8 (d, CH_2, $^2J_{PC} = 49.0$ Hz); 45.6 (d, C_aH, $^1J_{PC} = 66.8$ Hz); 52.8 ($CHMe_2$); 133.0 (d, C_bH, $^2J_{PC} = 14.8$ Hz)	
	**18**	66.7		

[a] ^{31}P chemical shifts (ppm) are reported relative to 85% H_3PO_4 (0.0 ppm). [b] ^{13}C and ^1H chemical shifts (ppm) are reported relative to Me_4Si (0.0 ppm).

structure determination, the results of which are shown in Figure 3. Tables of bond lengths, bond angles, and atomic positional parameters are given in Tables VI–VIII, respectively, while pertinent crystallographic data are presented in Table V. Compound **11** crystallizes in the monoclinic space group $P2_1/c$ with two molecules per asymmetric unit. Molecule A is illustrated in Figure 3. The five-membered 3-phospholenium ring of molecule A comprises P1, C11, C12, C13, and C14 and adopts an envelope conformation analogous to that of **2**. The "hinge" is defined by the C11–C14 vector while the angle between the planes P1, C11, C14 and C11, C12, C13, C14 is 18.5° (16.7° in molecule B). The C–C ring bond lengths confirm the location of the double bond in the 3-positions; C12–C13 = 1.306 (5) Å compared with single bonds C11–C12 = 1.498 (5) Å and C13–C14 = 1.483 (6) Å. The four-coordinate phosphorus atom adopts a tetrahedral configuration, being additionally bonded to *i*-Pr_2N and Cl groups, the geometries of which deserve no special comment. We note however that the chlorine is on the same side of the P1, C11, C14 plane as the C12, C13, and C15 carbons, presumably as a result of steric effects. The conformations of molecules A and B do not differ in a fundamental manner; however, there are some variations in the bond lengths (~0.05 Å) and bond angles (~2°). The largest differences generally occur in the *i*-Pr_2N groups, particularly in some of the C–C bond lengths. However, these are not

Table II. Bond Distances (Å) for $[(i\text{-}Pr_2N)_2\overline{PCH_2C(Me){=}C(Me)C}H_2][AlCl_4]$ (**2**)[a]

atom 1	atom 2	dist	atom 1	atom 2	dist
P1	N1	1.624 (3)	C7	C8	1.500 (6)
P1	N2	1.627 (3)	C7	C9	1.495 (6)
P1	C1	1.812 (3)	C10	C11	1.485 (7)
P1	C4	1.809 (3)	C10	C12	1.482 (7)
N1	C13	1.494 (4)	C13	C14	1.512 (6)
N1	C16	1.503 (4)	C13	C15	1.507 (6)
N2	C7	1.488 (4)	C16	C17	1.492 (6)
N2	C10	1.528 (4)	C16	C18	1.515 (6)
C1	C2	1.505 (5)	Al1	Cl1	2.119 (2)
C2	C3	1.319 (5)	Al1	Cl2	2.118 (2)
C2	C5	1.495 (5)	Al1	Cl3	2.111 (2)
C3	C4	1.519 (4)	Al1	Cl4	2.116 (2)
C3	C6	1.489 (5)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table III. Bond Angles (deg) for $[(i\text{-}Pr_2N)_2\overline{PCH_2C(Me){=}C(Me)C}H_2][AlCl_4]$ (**2**)[a]

atom 1	atom 2	atom 3	angle
N1	P1	N2	116.1 (2)
N1	P1	C4	109.9 (1)
N1	P1	C1	110.6 (2)
N2	P1	C4	113.0 (2)
N2	P1	C1	109.4 (2)
C1	P1	C4	95.9 (3)
P1	N1	C13	115.2 (2)
P1	N1	C16	129.9 (2)
C13	N1	C16	114.8 (3)
P1	N2	C7	121.0 (2)
P1	N2	C10	114.0 (2)
C7	N2	C10	124.9 (3)
P1	C1	C2	101.8 (2)
C1	C2	C3	117.0 (3)
C1	C2	C5	115.8 (3)
C3	C2	C5	126.9 (4)
C2	C3	C4	116.7 (3)
C2	C3	C6	126.7 (3)
C4	C3	C6	116.6 (3)
P1	C4	C3	101.9 (2)
N2	C7	C8	113.6 (3)
N2	C7	C9	114.5 (3)
C8	C7	C9	113.5 (4)
N2	C10	C11	110.9 (4)
N2	C10	C12	115.4 (4)
C11	C10	C12	112.6 (4)
N1	C13	C14	111.7 (3)
N1	C13	C15	112.0 (3)
C14	C13	C15	113.1 (4)
N1	C16	C17	112.1 (3)
N1	C16	C18	113.9 (3)
C17	C16	C18	113.0 (4)
Cl1	Al1	Cl2	108.79 (7)
Cl1	Al1	Cl3	108.30 (7)
Cl1	Al1	Cl4	110.3 (1)
Cl2	Al1	Cl3	110.40 (9)
Cl2	Al1	Cl4	108.57 (8)
Cl3	Al1	Cl4	110.43 (9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Positional Parameters and Their Estimated Standard Deviations for $[(i\text{-}Pr_2N)_2\overline{PCH_2C(Me){=}C(Me)C}H_2][AlCl_4]$ (**2**)[a]

atom	*x*	*y*	*z*	$B/\text{Å}^2$
P1	0.7525 (1)	0.22019 (7)	0.87528 (6)	2.60 (2)
N1	0.3537 (4)	−0.1730 (2)	0.0722 (2)	3.01 (8)
N2	0.7935 (4)	0.3162 (2)	0.8962 (2)	3.42 (8)
C1	1.0766 (5)	−0.1623 (3)	0.1297 (3)	3.4 (1)
C2	0.1197 (5)	−0.1073 (3)	0.1954 (3)	3.6 (1)
C3	0.2374 (5)	−0.1298 (3)	0.2412 (3)	3.29 (9)
C4	0.6789 (5)	0.2063 (3)	0.7795 (2)	2.98 (9)
C5	0.0153 (7)	−0.0372 (4)	0.2051 (4)	6.1 (2)
C6	0.2946 (7)	−0.0888 (4)	0.3120 (3)	5.0 (1)
C7	1.0628 (6)	−0.3382 (4)	0.0590 (3)	4.7 (1)
C8	0.9523 (7)	−0.3790 (4)	0.1028 (4)	6.2 (2)
C9	1.0795 (8)	−0.3818 (5)	−0.0118 (4)	6.9 (2)
C10	0.3311 (6)	−0.3776 (3)	0.1294 (3)	4.8 (1)
C11	0.279 (1)	−0.4402 (4)	0.1802 (5)	7.9 (2)
C12	0.4072 (8)	−0.4154 (5)	0.0699 (5)	8.1 (2)
C13	0.2861 (6)	−0.1603 (4)	−0.0058 (3)	4.1 (1)
C14	0.3779 (8)	−0.2011 (5)	−0.0597 (3)	6.6 (2)
C15	0.2537 (8)	−0.0702 (5)	−0.0228 (4)	6.5 (2)
C16	0.5077 (5)	−0.1371 (3)	0.0906 (3)	3.9 (1)
C17	0.6214 (7)	−0.2022 (4)	0.1138 (4)	5.8 (2)
C18	0.5144 (6)	−0.0645 (4)	0.1435 (4)	5.7 (1)
Al1	0.2042 (2)	0.2057 (1)	0.1512 (1)	4.22 (3)
Cl1	0.1725 (2)	0.3539 (1)	0.54715 (9)	6.84 (4)
Cl2	0.3506 (2)	0.3670 (1)	0.7246 (1)	7.17 (4)
Cl3	0.9940 (2)	0.2829 (2)	0.6903 (1)	8.48 (5)
Cl4	0.3020 (3)	0.1761 (1)	0.6415 (2)	10.16 (8)

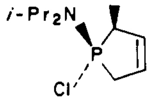
[a] Thermal parameters for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table V. Crystallographic and Intensity Data Collection Parameters for **2**, **11**, and **15a**

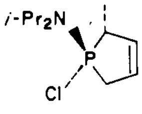
	2	**11**	**15a**
formula	$AlC_{18}Cl_4H_{38}N_2P$	$AlC_{11}Cl_5H_{22}NP$	$AlC_{11}Cl_5H_{22}NP$
fw	482.15	502.60	502.60
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a/Å	9.005 (2)	15.921 (2)	8.309 (4)
b/Å	16.134 (4)	7.903 (12)	15.264 (2)
c/Å	18.271 (2)	32.142 (4)	15.936 (2)
β/deg	96.94 (1)	102.46 (1)	
$V/\text{Å}^3$	2633 (1)	3949 (3)	2021 (2)
Z	4	8	4
ρ(calcd)/g cm^{-3}	1.216	1.357	1.223
μ(Mo Kα)/cm^{-1}	5.5	8.5	7.5
λ(Mo Kα)/Å	0.71069	0.71069	0.71069
cryst size/mm	0.6 × 0.6 × 0.4	0.5 × 0.4 × 0.4	0.5 × 0.5 × 0.3
ω scan angle/deg	$0.8 + 0.35 \tan\theta$	$0.8 + 0.35 \tan\theta$	$0.8 + 0.35 \tan\theta$
2θ limits/deg	$2.0 \leqslant 2\theta \leqslant 50.0$	$4.0 \leqslant 2\theta \leqslant 50.0$	$2.0 \leqslant 2\theta \leqslant 50.0$
ω scan speed/deg min^{-1}	2–10	2–10	1.8–10
collecn mode	ω–2θ	ω–2θ	ω–2θ
total no. of unique measd data	5869	7184	2063
no. of data obsd	3309	3588	1014
data omission factor	$I > 2.5\sigma(I)$	$I > 3.0\sigma(I)$	$I > 2.0\sigma(I)$
no. of params refined	236	519	172
R	0.0635	0.0487	0.0664
R_w	0.0963	0.0635	0.0841
GOF	1.853	2.581	2.385

considered to be chemically significant.

The NMR data for the reactions of **10** with 1,3-dienes are consistent with the production of 3-phospholenium cations. However, in two of the reactions two products, **12a,b** and **13a,b**, were formed. In the former case the observation can be rationalized on the basis of syn and anti isomers (**12a** and **12b**). (In each case syn and anti are chosen on the basis of the relative orientations of the Me and *i*-Pr$_2$N groups.) Measurement of the ^{31}P NMR peak areas indicates that the two isomers are produced in the ratio of 37:13. It is proposed that the more abundant isomer



12a, syn



12b, anti

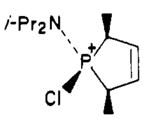
Table VI. Bond Distances (Å) for $[(i\text{-Pr}_2N)Cl\overline{PCH_2C(H)=C(Me)CH_2}][AlCl_4]$ (**11**)[a]

molecule A			molecule B		
atom 1	atom 2	dist	atom 1	atom 2	dist
Cl1	P1	2.001 (1)	Cl2	P2	2.007 (2)
P1	N1	1.589 (3)	P2	N2	1.585 (3)
P1	C11	1.771 (4)	P2	C51	1.784 (4)
P1	C14	1.778 (4)	P2	C54	1.778 (6)
N1	C20	1.494 (5)	N2	C60	1.540 (6)
N1	C30	1.498 (4)	N2	C70	1.498 (8)
C11	C12	1.498 (5)	C51	C52	1.487 (6)
C12	C13	1.306 (5)	C52	C53	1.279 (6)
C12	C15	1.499 (6)	C52	C55	1.489 (6)
C13	C14	1.483 (6)	C53	C54	1.487 (7)
C20	C21	1.495 (7)	C60	C61	1.413 (7)
C20	C22	1.514 (7)	C60	C62	1.447 (9)
C30	C31	1.524 (6)	C70	C71	1.401 (10)
C30	C32	1.488 (7)	C70	C72	1.433 (9)
Cl11	Al1	2.108 (2)	Cl21	Al2	2.117 (2)
Cl12	Al1	2.110 (2)	Cl22	Al2	2.125 (2)
Cl13	Al1	2.114 (2)	Cl23	Al2	2.115 (2)
Cl14	Al1	2.104 (2)	Cl24	Al2	2.105 (2)

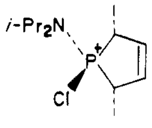
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

is **12b**, the anti form, which minimizes the steric interaction between substituents.

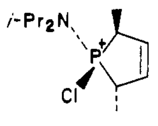
The reactions of **10** with *trans*-2-*trans*-4-hexadiene yields only two of three possible phospholenium cations **13a–c**. The cations are produced in the ratio 89:11 and are assigned the structures **13a** and **13b**, respectively. The reason for this assignment is discussed in the next section.



13a, anti, anti

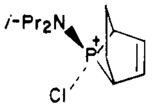


13b, syn, syn

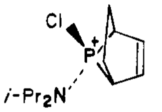


13c, syn, anti

The reaction of **10** with cyclohexa-1,3-diene was also investigated. ^{31}P NMR spectroscopy revealed the presence of two products, **14a,b**, formed in approximate ratio 3:2. On the basis of the reactivity of **10** toward other 1,3-dienes, it is assumed that 1,4-addition occurs. Since the phosphorus carries two different groups, i.e. *i*-Pr$_2$N and Cl, this can result in the two isomers



14a



14b

It is suggested that the predominant isomer is that which places the Cl atom on the same side of the PC$_4$ ring as the C$_2$H$_4$ bridge, i.e. **14b**, as this would be the sterically least encumbered configuration.

(ii) Stereochemical Aspects of the Reaction of Phosphenium Ions with 1,3-Dienes. Phosphenium ions are isolobal[9] with carbenes and are computed to be ground-state singlets.[1] This is confirmed by the observation of sharp signals in the ^{31}P NMR spectra.[10] As such, it is expected that phosphenium ions will behave in a fashion similar to singlet carbenes.

Three mechanisms are possible for the addition of $[R_2P]^+$ species to dienes. First, a two-step process involving radical intermediates may occur as shown in Scheme I. This type of process is anticipated for triplet phosphenium cations but cannot be excluded for such species in the singlet ground state. The remaining two mechanisms are chelotropic cycloadditions but differ in the location of initial attack, being either [2 + 2] or [2 + 4]. The former is a two-step process involving initial addition to only one double bond followed by a rearrangement as illustrated in Scheme II. This type of process is known to occur for carbene addition to 1,3-dienes.[11] The latter is a single-step process which is symmetry-allowed and has been observed for the reaction of SO$_2$ with 1,3-dienes.[12] The orbital interactions of consequence for the [2 + 4] process are shown in Figure 4. For most of the 1,3-dienes examined it is not possible to decide on a particular mechanism on the basis of the product distribution. However, in the case of *trans*-2-*trans*-4-hexadiene a difference in products would be expected for each process. Thus in the reaction of **1** to form **6**, two products, **6a** and **6b**, are possible. However, only one product is observed, and it is assigned structure **6a** (i.e. with the methyl groups on a common side of the PC$_4$ ring, a cis configuration). This is the predicted structure for a concerted disrotatory [2 + 4] cheletropic reaction and has been discussed for the corresponding SO$_2$/diene reaction.[12] In contrast, two products would be expected if this reaction proceeded via a free-radical pathway or the [2 + 2] chelotropic process since these should involve loss of stereochemical information at least one methyl-carrying carbon.

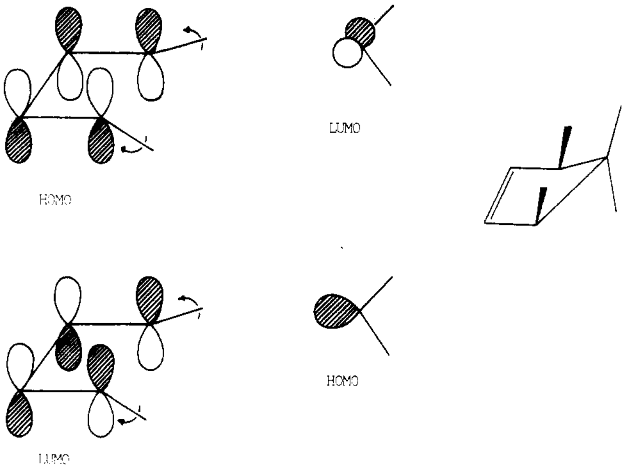
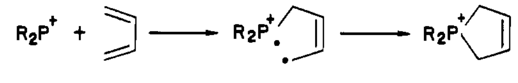
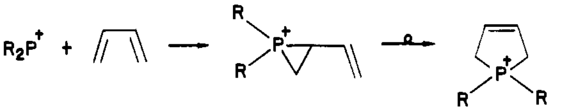


Figure 4. Orbital interactions for the [2 + 4] cheletropic reaction of a phosphenium ion with *trans*-2-*trans*-4-hexadiene.

Scheme I



Scheme II



The second reaction of mechanistic importance occurs with the phosphenium ion **10** to form **13**. For a concerted [2 + 4] chelotropic reaction, the methyl groups are expected to be cis. However, since the two groups on the phosphenium ion are different, this can result in the anti,anti (**13a**) and *syn,syn* (**13b**) structures. If a radical mechanism or [2 + 2] chelotropic process were in operation, structures **13a–c** all would be possible. Moreover, if a process occurred whereby the PC$_4$ ring methyl groups were trans as in **13c**, only a single product would be obtained. The observation of one product with **1** and two with

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(9) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148. Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711. Stone, F. G. A. *Ibid.* **1984**, *23*, 89.

(10) For a review see: Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. Cowley, A. H.; Norman, N. C. In "^{31}P NMR Spectroscopy"; Verlag Chemie: Weinheim, West Germany, in press.

(11) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley-Interscience: New York, 1976.

(12) Mock, W. L. *J. Am. Chem. Soc.* **1966**, *88*, 2857. McGregor, S. D.; Lemal, D. M. *Ibid.* **1966**, *88*, 2858.

Table VII. Bond Angles (deg) for $[(i\text{-Pr}_2N)Cl\overline{PCH_2C(H)=C(Me)CH_2}][AlCl_4]$ (**11**)[a]

molecule A				molecule B			
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl1	P1	N1	113.5 (1)	Cl2	P2	N2	113.8 (1)
Cl1	P1	C11	107.0 (2)	Cl2	P2	C51	104.7 (2)
Cl1	P1	C14	104.2 (2)	Cl2	P2	C54	105.5 (3)
N1	P1	C11	116.8 (2)	N2	P2	C51	118.9 (2)
N1	P1	C14	115.7 (2)	N2	P2	C54	114.3 (3)
C11	P1	C14	97.8 (2)	C51	P2	C54	97.5 (3)
P1	N1	C20	117.5 (3)	P2	N2	C60	117.4 (3)
P1	N1	C30	124.4 (2)	P2	N2	C70	119.1 (6)
C20	N1	C30	115.2 (3)	C60	N2	C70	122.1 (6)
P1	C11	C12	102.6 (3)	P2	C51	C52	102.5 (3)
C11	C12	C13	115.8 (4)	C51	C52	C53	116.0 (4)
C11	C12	C15	117.9 (5)	C51	C52	C55	118.8 (4)
C13	C12	C15	126.3 (4)	C53	C52	C55	125.2 (5)
C12	C13	C14	118.9 (4)	C52	C53	C54	120.5 (5)
P1	C14	C13	101.4 (3)	P2	C54	C53	100.0 (4)
N1	C20	C21	110.0 (5)	N2	C60	C61	114.9 (4)
N1	C20	C22	112.7 (4)	N2	C60	C62	111.3 (6)
C21	C20	C22	112.3 (6)	C61	C60	C62	124.2 (6)
N1	C30	C31	112.6 (4)	N2	C70	C71	120.1 (6)
N1	C30	C32	112.4 (4)	N2	C70	C72	114.7 (6)
C31	C30	C32	111.4 (6)	C71	C70	C72	123.1 (9)
Cl11	Al1	Cl12	108.81 (8)	Cl21	Al2	Cl22	110.74 (7)
Cl11	Al1	Cl13	108.99 (8)	Cl21	Al2	Cl23	107.04 (7)
Cl11	Al1	Cl14	111.18 (7)	Cl21	Al2	Cl24	109.05 (7)
Cl12	Al1	Cl13	109.21 (8)	Cl22	Al2	Cl23	109.61 (7)
Cl12	Al1	Cl14	108.10 (8)	Cl22	Al2	Cl24	109.21 (7)
Cl13	Al1	Cl14	110.50 (8)	Cl23	Al2	Cl24	111.18 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

10 and *trans*-2-*trans*-4-hexadiene is thus consistent with the proposed disrotatory [2 + 4] chelotropic reaction mechanism. The absence of products in discord with this mechanism is in keeping with its anticipated stereospecificity.

(iii) Reaction of Phosphenium Ions with 1,4-Dienes. Having established the generality of the reaction of phosphenium ions toward 1,3-dienes, we next focused attention on their reaction with 1,4-dienes. Treatment of **10** with an equimolar quantity of 1,4-pentadiene produced, after workup, a white crystalline material, **15**. A ^{31}P NMR spectrum of **15** comprised one resonance at +118 ppm. However, the presence of two isomers, **15a** and **15b** in a 10:3 ratio, was apparent from the $^{13}C\{^1H\}$ NMR spectrum. Further recrystallization produced pure **15a** in a form suitable for X-ray diffraction experiments. The results of the X-ray study are illustrated in Figure 5 along with the atom-numbering scheme. Tables of bond lengths, bond angles, and atomic positional parameters are given in Tables IX–XI while pertinent crystallographic data are collected in Table V.

The structure of **15a** involves a five-membered, phosphacyclopentane ring containing P1, C1, C2, C4, and C5. This ring adopts an envelope conformation with the C1–C5 vector as the hinge. The angle between the planes defined by P1, C1, C5 and C1, C2, C4, C5 is 30.4°. In addition carbons C2 and C4 constitute part of a cyclopropane ring system together with C3. The plane of the cyclopropane ring forms an angle of 110.7° with that defined by C1, C2, C4, and C5 and is disposed in the opposite sense to that of the P1–C1–C5 plane. The C–C bond lengths in the PC_4 ring show that C2–C4 (1.568 (15) Å) is significantly longer than either C1–C2 (1.427 (14) Å) or C4–C5 (1.413 (15) Å). The remaining cyclopropane bond lengths are C2–C3 = 1.481 (15) Å and C3–C4 = 1.54 (2) Å. Due to the relatively high esds associated with the latter distances, these differences should not be regarded as significant. The phosphorus atom is tetrahedrally coordinated, the remaining two sites being occupied by chlorine and $i\text{-Pr}_2N$ groups. These are oriented such that the $i\text{-Pr}_2N$ group adopts a proximal position with respect to the cyclopropane function. In addition, the $i\text{-Pr}_2N$ group nitrogen is trigonal-planar, a feature in common with the structures of **1** and **3**. The NMR data for **15a** and **15b** are presented in Table XII. The $^{13}C\{^1H\}$ NMR data for **15b** deserve no special comment except they indicate the presence of a cyclopropane ring. We therefore propose a structure analogous to **15a** but with the Cl and $i\text{-Pr}_2N$ positions reversed.

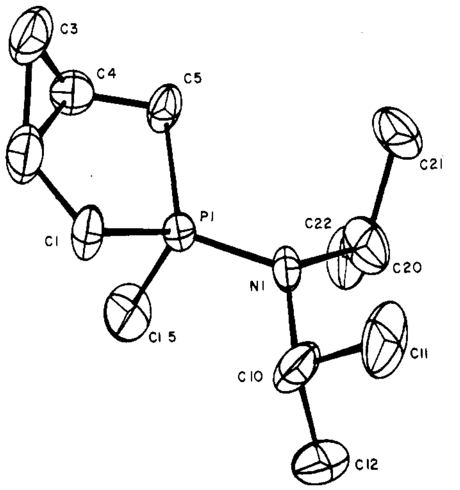
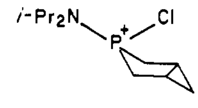
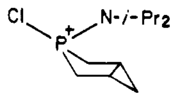


Figure 5. ORTEP plot of the cation of $[(i\text{-Pr}_2N)Cl\overline{PCH_2\underline{C(H)CH_2C}}(H)CH_2][AlCl_4]$ (**15a**) showing the atom-numbering scheme adopted.

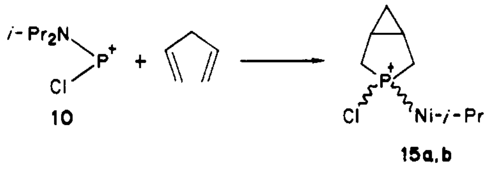


15a



15b

This observation is of interest since it indicates that addition of the phosphenium ion **10** has occurred 1,5 across the diene:



An alternative possibility is 2,4-addition, which would lead to the

Table VIII. Positional Parameters and their Estimated Standard Deviations for $[(i\text{-}Pr_2N)Cl\overline{CH_2C(H)=C(Me)CH_2}][AlCl_4]$ (**11**)[a]

atom	*x*	*y*	*z*	$B/Å^2$
		Molecule A		
Cl1	0.2176 (1)	0.0504 (2)	0.27209 (5)	6.54 (4)
P1	0.20068 (8)	0.2530 (2)	0.23387 (4)	4.02 (3)
N1	0.2872 (2)	0.3203 (5)	0.2227 (1)	4.06 (9)
C11	0.1149 (3)	0.2052 (7)	0.1904 (2)	5.1 (1)
C12	0.0379 (3)	0.2683 (7)	0.2056 (2)	5.2 (1)
C13	0.0543 (3)	0.3623 (8)	0.2398 (2)	5.9 (1)
C14	0.1452 (3)	0.3998 (8)	0.2601 (2)	5.1 (1)
C15	−0.0493 (4)	0.2252 (9)	0.1795 (2)	7.1 (2)
C20	0.3469 (3)	0.4196 (8)	0.2560 (2)	5.7 (1)
C21	0.3708 (4)	0.5818 (9)	0.2376 (2)	8.3 (2)
C22	0.4251 (5)	0.319 (1)	0.2776 (2)	9.3 (2)
C30	0.3266 (3)	0.2491 (7)	0.1881 (2)	4.8 (1)
C31	0.3311 (4)	0.0565 (9)	0.1892 (2)	7.5 (2)
C32	0.2838 (4)	0.312 (1)	0.1452 (2)	8.0 (2)
Al1	0.0395 (1)	−0.2858 (2)	0.12812 (6)	5.53 (4)
Cl11	0.0657 (1)	−0.0582 (2)	0.09356 (6)	8.68 (5)
Cl12	0.1409 (1)	−0.2721 (2)	0.18247 (6)	8.60 (5)
Cl13	−0.0782 (1)	−0.3159 (3)	0.14765 (6)	9.17 (6)
Cl14	0.0623 (1)	−0.4943 (2)	0.09139 (6)	8.18 (5)
		Molecule B		
Cl2	0.2008 (2)	0.3205 (2)	0.52031 (6)	9.65 (6)
P2	0.2655 (1)	0.4924 (2)	0.49352 (5)	5.10 (4)
N2	0.2518 (3)	0.6813 (6)	0.5072 (1)	6.0 (1)
C51	0.2422 (4)	0.4399 (8)	0.4382 (2)	5.5 (2)
C52	0.3144 (4)	0.3252 (7)	0.4348 (2)	5.2 (1)
C53	0.3760 (4)	0.3169 (8)	0.4677 (2)	6.8 (2)
C54	0.3751 (4)	0.4238 (9)	0.5057 (2)	7.6 (2)
C55	0.3117 (4)	0.2346 (9)	0.3939 (2)	7.8 (2)
C60	0.3084 (7)	0.744 (1)	0.5494 (2)	11.6 (3)
C61	0.3563 (5)	0.892 (1)	0.5458 (2)	8.5 (2)
C62	0.2695 (5)	0.707 (1)	0.5851 (2)	9.6 (2)
C70	0.1737 (5)	0.776 (1)	0.4845 (3)	13.5 (2)
C71	0.0915 (5)	0.721 (1)	0.4875 (3)	10.7 (3)
C72	0.1885 (5)	0.8903 (9)	0.4522 (2)	8.7 (2)
Al2	0.4255 (1)	0.7420 (2)	0.37963 (5)	4.98 (4)
Cl21	0.5015 (1)	0.5208 (2)	0.38266 (5)	7.20 (4)
Cl22	0.2962 (1)	0.6923 (3)	0.34807 (6)	7.20 (5)
Cl23	0.4292 (1)	0.8179 (3)	0.44310 (5)	7.75 (5)
Cl24	0.4768 (1)	0.9304 (3)	0.34601 (6)	8.78 (5)

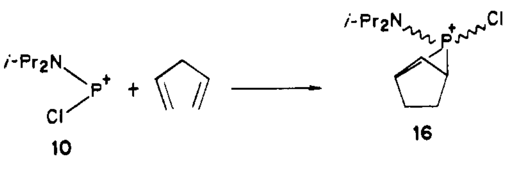
[a] Thermal parameters for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as in Table IV.

Table IX. Bond Distances (Å) for $[(i\text{-}Pr_2N)Cl\overline{PCH_2\underline{C(H)CH_2C}(H)CH_2}][AlCl_4]$ (**15a**)[a]

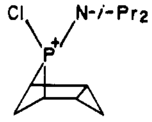
atom 1	atom 2	dist	atom 1	atom 2	dist
P1	Cl5	1.970 (3)	C4	C5	1.413 (13)
P1	N1	1.636 (7)	C10	C11	1.57 (2)
P1	C1	1.805 (9)	C10	C12	1.53 (2)
P1	C5	1.803 (9)	C20	C21	1.58 (2)
N1	C10	1.528 (12)	C20	C22	1.52 (2)
N1	C20	1.492 (12)	Al1	Cl1	2.116 (4)
C1	C2	1.427 (14)	Al1	Cl2	2.127 (4)
C2	C3	1.481 (15)	Al1	Cl3	2.117 (4)
C2	C4	1.568 (15)	Al1	Cl4	2.120 (4)
C3	C4	1.54 (2)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

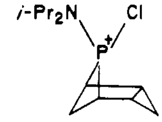
phosphabicyclo[2,1,1]hexane structure **16**. However the absence of **16** from the products indicates a preferred 1,5-addition mechansim:



A similar reaction between **10** and 1,4-cyclohexadiene affords, after workup, a white crystalline material, **17**. A ^{31}P NMR spectrum reveals two resonances of equal intensity at δ 54.3 and 53.4. The $^{13}C\{^1H\}$ NMR spectra are indicative of a cyclopropane ring in these products, thus leading to the following structure assignments:



17a



17b

Conclusions

The results of this study indicate that the reactivity of phosphenium ions toward dienes is a general process. For the case of 1,3-dienes, X-ray crystallography and ^{31}P NMR spectroscopy reveal that 1,4-addition occurs, resulting in a 3-phospholenium cations. Moreover the number of isomers observed when the diene is *trans*-2-*trans*-4-hexadiene is consistent with a [2 + 4] cheletropic reaction mechanism, as opposed to an alternative [2 + 2] or radical process. The reactivity of phosphenium ions toward 1,4-dienes has also been demonstrated and represents a potentially useful synthetic route to phosphorus-containing heterocycles.

Experimental Section

Materials. The compounds $HSiCl_3$, PCl_3, 1,3-butadiene, isoprene, *trans*-1,3-pentadiene (piperylene), *trans*-2-*trans*-4-hexadiene, 2,3-dimethyl-2,3-butadiene, 1,3-cyclohexadiene, 1,4-pentadiene, and 1,4-cyclohexadiene were obtained commercially and used without purification. The Al_2Cl_6 was freshly sublimed in a thermal gradient tube oven. The diisopropylamine was distilled from BaO under an atmosphere of dry nitrogen.

Solvents, such as Et_2O, *n*-hexane, and THF, were dried by refluxing over potassium benzophenone ketyl. Methylene chloride was dried by refluxing over CaH_2. All solvents were collected and stored under an atmosphere of dry, oxygen-free nitrogen.

General Considerations. All experiments were conducted under an atmosphere of dry oxygen-free nitrogen using standard Schlenk line techniques. All phospholenium salts were recrystallized by using the following procedure. After removal of all volatiles by vacuum pumping, the resulting solid or oil product was dissolved in the minimum volume of CH_2Cl_2. Two to three times this volume of *n*-hexane was layered gently over the CH_2Cl_2 solution, and the two-phase solution was placed carefully in a freezer at −16 to −20 °C. Crystallization took place upon slow diffusion of the *n*-hexane into the CH_2Cl_2/phospholenium salt solution.

Spectroscopic Measurements. ^1H NMR spectra were recorded on Varian EM390 and Nicolet NT200 spectrometers operating at 90 and 200 MHz, respectively. ^{13}C and ^{31}P NMR spectra were recorded on Varian FT80A and Nicolet NT200 instruments operating at 20 and 50 MHz for ^{13}C and 32.384 and 80.988 MHz for ^{31}P. ^1H and ^{13}C spectra were referenced to internal Me_4Si (0.0 ppm) and ^{31}P spectra were referenced to external 85% H_3PO_4 (0.0 ppm). Positive values are to high frequency in all cases.

Mass spectral data were obtained on a DuPont-Consolidated Electrodynamics Corp. Model 21-491 spectrometer operating at an ionizing voltage of 70 eV.

Preparation of $(i\text{-}Pr_2N)_2PCl$. A 25-mL (177.5-mmol) sample of $i\text{-}Pr_2NH$ in 250 mL of Et_2O was lithiated with 111 mL (177.6 mmol) of a 1.6 *m* *n*-BuLi/*n*-hexane solution at 0 °C. Lithiation was completed by allowing the reaction mixture to warm to room temperature and stir for 1 h. The solution was recooled to −78 °C, and 7 mL (80.2 mmol) of PCl_3 was added dropwise with rapid stirring. The reaction mixture was allowed to warm to room temperature overnight, and then the Et_2O was removed by evacuation. Filtration, followed by two recrystallizations from *n*-hexane, afforded an 80% yield of pure $(i\text{-}Pr_2N)_2PCl$ (mp 102–103 °C). Anal. Calcd for $C_{12}H_{28}ClN_2P$: C, 54.02; H, 10.58; N, 10.50. Found: C, 54.18; H, 10.86; N, 10.73.

Preparation of $(i\text{-}Pr_2N)PCl_2$. A 28-mL (200.0-mmol) sample of freshly distilled $(i\text{-}Pr_2N)PH_2$ in 50 mL of Et_2O was added to a stirred solution of PCl_3 (10 mL, 115.0 mmol) in 250 mL of Et_2O. The cloudy white solution was stirred overnight and filtered through a medium-porosity frit. All volatiles were removed. The clear, slightly yellow oil was purified by distillation (bp 48–52 °C (0.005 torr)). Anal. Calcd for $C_6H_{14}Cl_2NP$: C, 35.66; H, 6.98. Found: C, 35.42; H, 6.92.

Table X. Bond Angles (deg) for $[(i\text{-}Pr_2N)ClPCH_2C(H)CH_2C(H)CH_2][AlCl_4]$ (**15a**)[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
N1	P1	Cl5	112.6 (3)	C2	C4	C5	114.9 (9)
C1	P1	Cl5	103.4 (4)	C3	C4	C5	120 (1)
Cl5	P1	C5	104.3 (4)	P1	C5	C4	100.0 (7)
N1	P1	C1	116.9 (4)	N1	C10	C12	110 (1)
N1	P1	C5	118.0 (4)	N1	C10	C11	106 (1)
C1	P1	C5	99.7 (5)	C11	C10	C12	115 (1)
P1	N1	C10	114.2 (6)	N1	C20	C21	108 (1)
P1	N1	C20	125.5 (7)	N1	C20	C22	117 (1)
C10	N1	C20	117.2 (8)	C21	C20	C22	108 (1)
P1	C1	C2	101.2 (7)	Cl1	Al1	Cl2	108.5 (2)
C1	C2	C4	114.3 (9)	Cl1	Al1	Cl3	110.6 (2)
C3	C2	C4	60.7 (9)	Cl1	Al1	Cl4	108.5 (2)
C1	C2	C3	126 (1)	Cl2	Al1	Cl3	107.2 (2)
C2	C3	C4	62.4 (8)	Cl3	Al1	Cl4	111.6 (2)
C2	C4	C3	56.8 (7)	Cl2	Al1	Cl4	110.4 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table XI. Positional Parameters and Their Estimated Standard Deviations for $[(i\text{-}Pr_2N)ClPCH_2C(H)CH_2C(H)CH_2][AlCl_4]$ (**15a**)[a]

atom	x	y	z	B/Å^2
P1	0.6539 (4)	0.5102 (2)	0.4771 (2)	4.75 (6)
N1	0.479 (1)	0.4677 (6)	0.5000 (6)	5.1 (2)
Cl5	0.8342 (5)	0.4410 (3)	0.5222 (4)	11.2 (1)
C1	0.703 (1)	0.5211 (9)	0.3673 (8)	6.4 (3)
C2	0.814 (2)	0.592 (1)	0.369 (1)	8.8 (4)
C3	0.773 (2)	0.6866 (9)	0.370 (1)	9.6 (4)
C4	0.817 (2)	0.6439 (8)	0.4543 (9)	8.0 (4)
C5	0.694 (2)	0.6205 (8)	0.5116 (8)	6.8 (3)
C10	0.429 (2)	0.3920 (8)	0.4430 (9)	8.2 (4)
C11	0.252 (2)	0.413 (1)	0.414 (1)	11.0 (5)
C12	0.448 (2)	0.3052 (8)	0.490 (1)	11.9 (6)
C20	0.394 (2)	0.476 (1)	0.5821 (9)	9.6 (5)
C21	0.317 (2)	0.570 (1)	0.586 (1)	12.4 (5)
C22	0.496 (2)	0.463 (1)	0.660 (1)	10.3 (5)
Al1	0.6868 (5)	0.2445 (2)	0.2346 (2)	5.49 (9)
Cl1	0.5361 (5)	0.3535 (2)	0.2110 (3)	8.26 (9)
Cl3	0.5693 (5)	0.1530 (3)	0.3135 (3)	9.7 (1)
Cl4	0.9039 (5)	0.2903 (3)	0.2888 (3)	10.4 (1)
Cl2	0.7337 (5)	0.1802 (2)	0.1188 (2)	8.5 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as in Table IV.

Preparation of $[(i\text{-}Pr_2N)_2P]^+[AlCl_4]^-$ **(1).** This phosphenium salt was prepared as described in the literature[7] by mixing $(i\text{-}Pr_2N)_2PCl$ with a 10% molar excess of $AlCl_3$ units in CH_2Cl_2 solution at −78 °C.

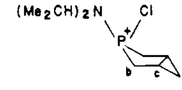
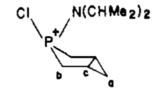
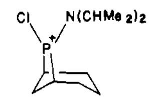
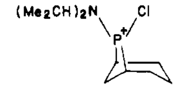
Preparation of $[(i\text{-}Pr_2N)ClP]^+[AlCl_4]^-$ **(10).** In a typical preparation, 1.007 g (4.98 mmol) of $i\text{-}Pr_2NPCl_2$ was added to 50 mL of CH_2Cl_2 and the resulting solution cooled to −78 °C. To this rapidly stirred solution was added 0.740 g of Al_2Cl_6 (5.48 mmol, 10% molar excess of $AlCl_3$ units), and the solution was allowed to warm to room temperature. The phosphenium salt was too moisture-sensitive to obtain a satisfactory chemical analysis. However, the quantitative formation of (**10**) was apparent (i) from the ^{31}P chemical shift (δ 334),[6b] which is in the region typical for phosphenium cations,[10] and (ii) from its subsequent reaction chemistry.

Preparation of $[(i\text{-}Pr_2N)_2PCH_2C(Me){=}C(Me)CH_2][AlCl_4]$ **(2).** 2,3-Dimethyl-1,3-butadiene (0.5 mL, 4.4 mmol) was added to a solution of **1** (3.0 mmol) in 50 mL of CH_2Cl_2 at 0 °C. The solution turned from bright yellow to darker yellow immediately. The reaction mixture was allowed to warm to room temperature and stir for 8 h. All volatiles were removed, and the yellow solid was dissolved in minimum volume of CH_2Cl_2. Total conversion to the phospholenium salt was confirmed by ^{31}P NMR spectroscopy (Table I). Clear, colorless crystals of **2** (mp 132–36 °C) were formed after 6 days with the *n*-hexane/CH_2Cl_2 layering technique. The yield of **2** was 93%. Anal. Calcd for $C_{18}H_{38}AlCl_4PN_2$: C, 44.82; H, 7.96; N, 5.81. Found: C, 44.45; H, 7.94; N, 5.81.

Preparation of $[(i\text{-}Pr_2N)_2PCH_2C(H){=}C(H)CH_2][AlCl_4]$ **(3).** A solution of 3.05 mmol of $[(i\text{-}Pr_2N)_2P][AlCl_4]$ (**1**) in 50 mL of CH_2Cl_2 in a 100-mL Schlenk vessel was cooled to −78 °C. The Schlenk flask was equipped with a condenser capable of being maintained at −78 °C. After 2.5 mL of 1,3-butadiene was condensed into the reactor, the reaction mixture was allowed to assume ambient temperature over a period of several hours. All volatiles were removed by evacuation, and the resulting white solid was recrystallizes twice from a mixture of CH_2Cl_2 and *n*-hexane. The yield was 78% after two crystallizations; mp 153 °C. Anal. Calcd for $C_{16}H_{34}AlCl_4N_2P$: C, 42.3; H, 6.7. Found: C, 42.1; H, 7.7.

Preparation of $[(i\text{-}Pr_2N)_2PCH_2C(Me){=}C(H)CH_2][AlCl_4]$ **(4).** A 0.6-mL (6.00-mmol) aliquot of 2-methyl-1,3-butadiene (isoprene) was added to a solution of 4.23 mmol of **1** in 50 mL of CH_2Cl_2 at 0 °C. The reaction mixture was allowed to warm to room temperature and stir overnight. All volatiles were removed by evacuation, and the yellowish solid was recrystallized from CH_2Cl_2/*n*-hexane solution at −20 °C over a period of several weeks. The yield was 92%; mp 144 °C. Anal. Calcd

Table XII. NMR Data for Compounds Obtained from the Reaction of the Phosphenium Ion **10** with 1,4-Dienes

compd	no.	$^{31}P\{^1H\}$[a]	$^{13}C\{^1H\}$[b]
	**15a**	117.6	16.0 (d, C_aH_2, $^3J_{PC}$ = 10.4 Hz); 21.2, 21.5 (CH*Me*$_2$); 35.4 (d, C_bH_2, $^1J_{PC}$ = 69.1 Hz); 49.8 (d, C_cH, $^2J_{PC}$ = 32.6 Hz); 52.8 (*C*HMe$_2$)
	**15b**	117.6	14.1 (d, C_aH_2, $^3J_{PC}$ = 14.5 Hz); 22.2, 22.5 (CH*Me*$_2$); 34.9 (d, C_bH_2, $^1J_{PC}$ = 69.1 Hz); 49.8 (d, C_cH, $^2J_{PC}$ = 32.6 Hz); 53.2 (*C*HMe$_2$)
	**17a**	54.3, 53.4	
	**17b**		

[a] ^{31}P NMR chemical shifts (ppm) are reported relative to 85% H_3PO_4 (0.0 ppm). [b] ^{13}C NMR chemical shifts (ppm) are reported relative to Me_4Si (0.0 ppm).

for $C_{17}H_{36}AlCl_4N_2P$: C, 43.6; H, 7.7. Found: C, 42.9; H, 7.4.

Preparation of $[(i\text{-}Pr_2N)_2PCHMeC(H){=}C(H)CH_2][AlCl_4]$ (5). A 0.2-mL (1.0-mmol) aliquot of *trans*-piperylene was added slowly to a solution of 1.88 mmol of **1** in 50 mL of CH_2Cl_2 at 0 °C. The reaction mixture was allowed to stir for 3 days at room temperature. Monitoring of the reaction by ^{31}P NMR spectroscopy revealed that small amounts of **1** were present. A further 0.2 mL of *trans*-piperylene was therefore added, and the reaction was completed by refluxing the solution for 3 h, followed by stirring overnight at room temperature. Recrystallization from CH_2Cl_2/n-hexane afforded microfine crystals of **5** in ~64% yield, mp 175° C. Anal. Calcd for $C_{17}H_{36}AlCl_4N_2P$: C, 43.6; H, 7.7. Found: C, 43.3; H, 7.3.

Preparation of $[(i\text{-}Pr_2N)_2PCHMeC(H){=}C(H)CHMe][AlCl_4]$ (6). **1** (2.91 mmol) in 50 mL of CH_2Cl_2 was treated with 0.35 mL (3.07 mmol) of *trans*-2-*trans*-4-hexadiene at ambient temperature. The reaction flask was fitted with a reflux condenser, and the reaction mixture was heated to 50 °C for 9 days. ^{31}P NMR spectroscpy indicated that the crude reaction mixture contained several products. Crystallization from CH_2Cl_2/n-hexane gave **6** in 55% yield; mp 167 °C. Anal. Calcd for $C_{18}H_{38}AlCl_4N_2P$: C, 44.8; H, 7.9. Found, C, 44.1; H, 8.1.

Preparation of $[(Me_2N)_2PCH_2C(Me){=}C(Me)CH_2][AlCl_4]$ (8). 2,3-Dimethyl-1,3-butadiene (1 mL, 8.84 mmol) was added to a stirred solution of 6.9 mmol of $[(Me_2N)_2P][AlCl_4]$ (**7**)[8] in 50 mL of CH_2Cl_2 at 0 °C. ^{31}P NMR monitoring of the reaction mixture showed an equal amount of the phosphenium and phospholenium cations. The solution was therefore recooled to 0 °C, and an additional 0.5 mL (6.9 mmol) of 2,3-dimethyl-1,3-butadiene was added. Completion of the reaction was confirmed by ^{31}P NMR spectroscopy. The amber solution was filtered from the rubbery polymer. Long needlelike crystals of **8** were grown by recrystallization from CH_2Cl_2/n-hexane. Anal. Calcd for $C_{10}H_{22}AlCl_4N_2P$: C, 32.5; H, 6.0. Found: C, 32.7; H, 5.9.

Preparation of $[(Me_2N)_2PCH_2C(Me){=}C(H)CH_2][AlCl_4]$ (9). Isoprene (0.5 mL, 5.00 mmol) was added to a solution of **7** (4.18 mmol) in ~50 mL of CH_2Cl_2 at -78 °C. The reaction mixture was allowed to warm to room temperature slowly and stirred for an additional 1.5 h. The thick orange solution was filtered through a Celite 545 filter aid supported on a medium-porosity frit. ^{31}P NMR spectroscopy indicated the presence of a small amount of unreacted **7**. An additional 0.5 mL of isoprene was therefore added to the reaction mixture, and stirring was continued overnight. This compound was not isolated but was hydrolyzed to **18**.

Preparation of $[Me_2NP(O)CH_2C(Me){=}C(H)CH_2]$ (18). Approximately 2.64 mmol of **9** was suspended in 20 mL of dioxane. A 7-mL aliquot of 0.6 M NaOH in H_2O/dioxane was added to this stirred suspension, and the reaction mixture was refluxed overnight at 100 °C. Upon removal of the reflux condenser, a slight smell of amine was detected. The solution was cooled to ambient temperature and transferred to a separatory funnel where the aqueous layer was extracted with three 10-mL aliquots of CH_2Cl_2. The organic layer was dried of $MgSO_4$ and then filtered. The solvents were removed from the phospholene oxide by heating the mixture to 60 °C in a dynamic vacuum for several hours. A white powdery product remained. The yield of **18** was 72%. Anal. Calcd for $C_7H_{14}NOP$: C, 52.8; H, 8.8. Found: C, 52.5; H, 8.4.

Preparation of $[(i\text{-}Pr_2N)ClPCH_2C(Me){=}C(H)CH_2][AlCl_4]$ (11). A solution of isoprene (0.8 mL, 8.77 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of **10** (4.48 mmol) in 40 mL of CH_2Cl_2 at 0 °C. The stirred reaction mixture was allowed to warm to room temperature over a period of 2 h. Monitoring by ^{31}P NMR spectroscopy indicated that **11** (mp 144 °C) had been produced in quantitative yield (yield after purification was 92%). Compound **11** was characterized by X-ray crystallography.

Preparation of $[(i\text{-}Pr_2N)ClPCHMeC(H){=}C(H)CH_2][AlCl_4]$ (12a,b). A solution of *trans*-piperylene (*trans*-1,3-pentadiene) (0.42 mL, 4.2 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of **10** (3.9 mmol) in 50 mL of CH_2Cl_2 at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for ~2 h. All volatiles were removed by evacuation. The slightly yellowish solid product was redissolved in a minimum amount of CH_2Cl_2. ^{31}P NMR spectroscopy indicated the presence of two isomers in an ~1:4 ratio (see text). The yield of the combined isomers was 90%. Anal. Calcd for $C_{11}H_{22}AlCl_5NP$: C, 32.7; H, 5.5. Found: C, 32.4; H, 5.1.

Preparation of $[(i\text{-}Pr_2N)ClPCHMeC(H){=}C(H)CHMe][AlCl_4]$ (13a,b). A solution of 0.7 mL (6.1 mmol) of *trans*-2-*trans*-4-hexadiene in 20 mL of CH_2Cl_2 was added dropwise to a solution of **10** (5.1 mmol) in 50 mL of CH_2Cl_2 at 0 °C. About halfway through the addition, the solution turned lemon yellow. After the addition was complete, a dark yellow solution was formed. The reaction mixture was allowed to warm to room temperature and stirred for 5 h. ^{31}P NMR spectroscopy indicated the presence of two major products, **13a** with δ 115.5 (89%) and **13b** with δ 97.4 (11%), and a minor impurity at δ 15.8. All volatiles were then removed and **13a** was crystallized in 70% yield from CH_2Cl_2/n-hexane. Anal. Calcd for $C_{12}H_{24}AlCl_5NP$: C, 34.5; H, 5.7. Found: C, 34.0; H, 5.8.

Preparation of $[(i\text{-}Pr_2N)ClPCH(CH_2CH_2)C(H){=}C(H)CH][AlCl_4]$ (14a,b). A 0.4-mL (2.4-mmol) sample of 1,3-cyclohexadiene was added dropwise to a solution of **10** (3.74 mmol) in 35 mL of CH_2Cl_2 at 0 °C. The solution changed color from pale yellow to clear amber. After the reaction mixture was stirred overnight, the volatiles were removed by evacuation and the resulting residue was redissolved in a minimum volume of CH_2Cl_2. ^{31}P NMR spectroscopy indicated the presence of two products, **14a** with δ 117.2 (40%) and **14b** with δ 98.7 (60%). Repeated attempts at crystallization were unsuccessful, and only an oily product could be obtained.

Preparation of $[(i\text{-}Pr_2N)ClPCH_2CH(CH_2)CHCH_2][AlCl_4]$ (15a,b). A solution of 0.5 mL (4.84 mmol) of 1,4-pentadiene in 10 mL of CH_2Cl_2 was added dropwise to a solution of **10** (2.25 mmol) in 40 mL of CH_2Cl_2 at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 20 h. ^{31}P NMR spectroscopy indicated the presence of only one compound. However, $^{13}C\{^1H\}$ NMR spectroscopy indicated that conformers **15a** and **15b** had been formed (see text). After removal of the volatiles, **15a** was recrystallized from CH_2Cl_2/n-hexane solution at - 20 °C. Compound **15a** was characterized by X-ray crystallography.

X-ray Structure Analysis of $[(i\text{-}Pr_2N)_2PCH_2C(Me){=}C(Me)CH_2][AlCl_4]$ (2). A suitable crystal of **2** was obtained from CH_2Cl_2/n-hexane at -20 °C and sealed in a Lindemann capillary under nitrogen. Initial lattice parameters were obtained from a least-squares fit to 25 reflections, $15° \leq 2\theta \leq 20°$, accurately centered on an Enraf-Nonius CAD-4F diffractometer and subsequently refined by using higher angle data. Data were collected for one independent quadrant $+h,+k,+l$, in the ω-2θ scan mode over the range $2.0° \leq 2\theta \leq 50.0°$ at ambient temperature. The final scan speed was determined from the net intensity gathered in an initial pre-scan at 10° min^{-1} and ranged from 2–10° min^{-1}. Two check reflections were measured every 30 min throughout data collection but showed no significant drop in intensity. Systematic absences uniquely defined the space group as $P2_1/c$.

Data were corrected for Lorentz and polarization effects but not absorption (μ = 5.5 cm^{-1}). After equivalent and duplicate reflections were averaged, 5869 unique data were used to solve the structure with MULTAN,[13] which located the phosphorus, aluminum, and chlorine atoms. A difference Fourier map revealed the positions of all non-hydrogen atoms, which were refined with anisotropic thermal parameters. Hydrogen atoms were not refined but were placed in calculated positions 0.95 Å from their respective carbon atom and included in the structure factor calculation. Final full-matrix least-squares refinement using 3309 reflections, $I > 2.5\sigma(I)$, with a weighting scheme and extinction correction converged smoothly to give the final residuals shown in Table V. There were no peaks in the final difference map greater than 0.6 e Å^3. Most peaks were associated with the $AlCl_4^-$ anion. However, attempts to model the apparent disorder was unsuccessful, and in the final cycles only the four main chlorine atoms were included. The $AlCl_4^-$ anion is shown in Figure 2. The structures of **11** and **15a** were collected in a manner similar to that used for **2**. Data for both compounds are presented in Table V.

The structure of **11** comprised two molecules (or ion pairs) per asymmetric unit. Data collection and reduction were essentially the same as described for **2** except that most hydrogen atoms were directly located and refined, all for molecule A and some for molecule B. Bond lengths, bond angles, and atomic positional parameters are given in the text. Hydrogen positions, thermal parameters and tables of observed and calculated structure factors are available as supplementary material for all three structures. The data for **15a** were collected in the orthorhombic space group $P2_12_12_1$, which was deduced from systematic absences. Data collection and reduction were as described for **2**, details of which are given in Table V. The hydrogen atoms were neither located nor refined in this structure.

Registry No. **1**, 68880-45-5; **2**, 87712-41-2; **3**, 87712-45-6; **4**, 87712-43-4; **5**, 87712-47-8; **6**, 100084-29-5; **7**, 100084-30-8; **8**, 87712-51-4; **9**, 87712-53-6; **10**, 92416-17-6; **11**, 100084-32-0; **12a**, 100084-34-2; **12b**, 100084-36-4; **13a**, 100084-38-6; **13b**, 100164-71-4; **14a**, 100084-40-0; **14b**, 100084-42-2; **15a**, 92392-03-5; **15b**, 92470-18-3; **18**, 92063-25-7; $(i\text{-}Pr_2N)_2PCl$, 56183-63-2; $(i\text{-}Pr_2N)PCl_2$, 921-26-6; $(i\text{-}Pr_2N)PH_2$,

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(13) Main, P. "MULTAN 82", University of York, York, England, 1982.

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93583-25-6; *i*-Pr_2NH, 108-18-9; PCl_3, 7719-12-2; $AlCl_3$, 7446-70-0; 1,3-butadiene, 106-99-0; 2,3-dimethyl-1,3-butadiene, 513-81-5; isoprene, 78-79-5; *trans*-piperylene, 2004-70-8; *trans*-2-*trans*-4-hexadiene, 5194-51-4; 1,3-cyclohexadiene, 592-57-4; 1,4-pentadiene, 591-93-5.

Supplementary Material Available: Tables of positional and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and observed and calculated structure factors (89 pages). Ordering information is given on any current masthead page.

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Redox Reactions of Chromium Tetracarbonyl and Tricarbonyl Complexes: Thermodynamic, Kinetic, and Catalytic Aspects of Isomerization in the *fac*/*mer*-Tricarbonyltris(trimethyl phosphite)chromium(1+/0) System

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Electrochemical studies have been undertaken on mixtures of *cis*- and *trans*-$[Cr(CO)_4P_2]^{+/0}$ systems (where P = P(*m*-tol)$_3$, P(*p*-tol)$_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$). In accordance with theoretical predictions, redox potentials for both *cis*- and *trans*-$[Cr(CO)_4P_2]^{+/0}$ are similar and oxidation involves the formation of *trans*-$[Cr(CO)_4P_2]^+$ via either direct electron transfer or *cis*-$[Cr(CO)_4P_2]^+$ to *trans*-$[Cr(CO)_4P_2]^+$ isomerization after electron transfer. The *trans*-$[Cr(CO)_4P_2]^+$ species have all been identified by infrared spectroscopy. *trans*-$[Cr(CO)_4(P(OPh)_3)_2]^+$ is a very strong oxidant and can be used to oxidize all the other $[Cr(CO)_4P_2]$ complexes: *trans*-$[Cr(CO)_4(P(OPh)_3)_2]^+$ + *cis*/*trans*-$[Cr(CO)_4P_2]$ → *cis*/*trans*-$[Cr(CO)_4(P(OPh)_3)_2]$ + *trans*-$[Cr(CO)_4P_2]^+$. Tricarbonyltris(phosphorus ligand)chromium complexes, $Cr(CO)_3P_3$, can exist in *fac* or *mer* isomeric forms. In contrast to those of the tetracarbonyl complexes, the oxidation potentials of the *fac* and *mer* isomers of the tricarbonyls occur at considerably different potentials, enabling detailed electrochemical studies to be made. In this work it is shown that isomerization of *fac*-$[Cr(CO)_3(P(OMe)_3)_3]$ → *mer*-$[Cr(CO)_3(P(OMe)_3)_3]$ occurs either slowly by an intramolecular twist mechanism or via an alternative redox-catalyzed pathway. Variable-temperature electrochemical studies at platinum electrodes (cyclic voltammetry and differential-pulse voltammetry at a stationary electrode, rotating-disk voltammetry, and controlled-potential electrolysis) of the redox properties of both *fac*- and *mer*-$[Cr(CO)_3(P(OMe)_3)_3]$ provide a complete thermodynamic and kinetic description of the catalytic scheme, which involves the following reactions:

$$fac\text{-}[Cr(CO)_3(P(OMe)_3)_3] \xrightarrow{\text{oxidant}} fac\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ \qquad \text{(i)}$$

where oxidant = e^-, $NOPF_6$, or *trans*-$[Cr(CO)_4(P(OPh)_3)_2]^+$

$$fac\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ \rightleftarrows mer\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ \qquad \text{(ii)}$$

$$mer\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ + fac\text{-}[Cr(CO)_3(P(OMe)_3)_3] \xrightarrow{\text{fast}} fac\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ + mer\text{-}[Cr(CO)_3(P(OMe)_3)_3] \qquad \text{(iii)}$$

where *fac*/*mer*-$[Cr(CO)_3(P(OMe)_3)_3]^+$ is the catalyst. Data at 22 °C in dichloromethane:

$$fac\text{-}[Cr(CO)_3(P(OMe)_3)_3] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} mer\text{-}[Cr(CO)_3(P(OMe)_3)_3]$$

$$k_1 = (1.8 \pm 0.3) \times 10^{-4}\ s^{-1} \qquad k_{-1} = (4.5 \pm 1.3) \times 10^{-5}\ s^{-1} \qquad K_1 = 4 \pm 0.5$$

$$fac\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ \xrightarrow[k_{-2}]{k_2} mer\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+$$

$$k_2 = 0.11 \pm 0.01 \qquad k_{-2} = (1.7 \pm 0.8) \times 10^{-4}\ s^{-1} \qquad K_2 = 640 \pm 130$$

The activation parameters for *fac*-$[Cr(CO)_3(P(OMe)_3)_3]^+$ ⇄ *mer*-$[Cr(CO)_3(P(OMe)_3)_3]^+$ are consistent with those expected for an intramolecular twist mechanism ($E_A = 15.9 \pm 0.7$ kJ/mol; $\Delta S^* = -17.0 \pm 1.0$ J/(K mol)). The equilibrium constant, K_3, for the redox cross-reaction

$$fac\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ + mer\text{-}[Cr(CO)_3(P(OMe)_3)_3] \underset{}{\overset{K_3}{\rightleftharpoons}} fac\text{-}[Cr(CO)_3(P(OMe)_3)_3] + mer\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+$$

has a value of 160 ± 13. The electrochemical properties of *fac*/*mer*-$[Cr(CO)_3(P(OEt)_3)_3]$ are similar.

Introduction

There is a considerable interest in the interplay between steric and electronic effects determining the isomeric form of octahedral carbonyl complexes.[3,4] In addition, extensive studies have been made of the substituent effects of the groups attached to the donor atom on the thermodynamic aspects of the electrochemical oxidation or reduction of these complexes.[3,5,6]

In the particular case of the group VI (group 6[22]) tetracarbonyl and tricarbonyl species, $M(CO)_4P_2$ and $M(CO)_3P_3$ (M = Cr, Mo,

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[1] Deakin University.

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[3] Bursten, B. E. *J. Am. Chem. Soc.* **1982**, *104*, 1299 and references cited therein.

[4] Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29.

[5] (a) Butler, G.; Chatt, J.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1979**, 113. (b) Chatt, J.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 121. (c) Crichton, B. A. L.; Dilworth, J. R.; Pickett, C. J.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 419. (d) Leigh, G. J.; Morris, R. H.; Pickett, C. J.; Stanley, D. R.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 800.

[6] Pombeiro, A. J. L. *Port. Electrochim. Acta* **1983**, *1*, 19.

0020-1669/86/1325-0749$01.50/0 © 1986 American Chemical Society