

can-9-one (**12**) was produced in a 70% yield. The structure assignment of **12** is based upon elemental analysis and IR, ^1H NMR, and ^{13}C NMR spectra.¹⁷ The structure is also consistent with a finding that **12** is treated with HCl in chloroform¹⁸ to afford 1-methylbicyclo[5.3.0]-7-decen-9-one (**7**).¹²

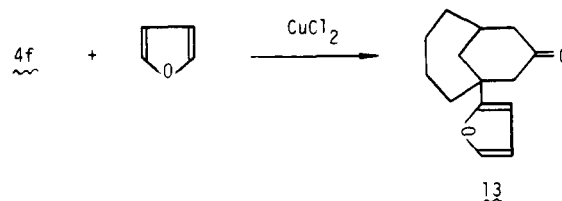
At the present moment it is very difficult to explain the reason why the oxidation of σ -1-(trans-fused bicyclo[5.3.0]-decan-9-one)methylpalladium(II) complex (**4g**) takes a different reaction course from that of σ -1-(cis-fused bicyclo[n .3.0]alkanone)methylpalladium(II) complexes (**4e** and **4f**). Consideration with CPK molecular model suggests that the 1,2 shift of carbon bond $\text{C}_7\text{--C}_1$ to carbon bond $\text{C}_7\text{--C}_{11}$ in the oxidative cleavage of the palladium carbon bond of **4g** leading to the expected 1-chlorobicyclo[5.3.1]undecan-9-one (**9g**) is susceptible to severe steric hindrance owing to the bond $\text{C}_7\text{--H}$. A detailed understanding of the reaction mechanism^{19,20} must await further study.

Acknowledgment. We are indebted to Dr. T. Hiyama, Kyoto University, for ^{13}C NMR measurements. We are grateful to Shin-etsu Chemical Industry Co., Ltd., for providing the trimethylsilyl chloride.

References and Notes

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- 3d**: IR (KBr disk) 1655, 1565 cm^{-1} ; NMR (CD_3CN with Me_4Si) δ 1.8–2.8 (m, 6 H), 4.23 (br s, 1 H), 4.89 (s, 1 H), 6.8–7.5 (m, 5 H); mol wt (vapor pressure osmometry in CHCl_3) calcd for dimer 630, found 647. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{ClO}_2\text{Pd}$: C, 45.74; H, 4.16; Cl, 11.25. Found: C, 45.79; H, 4.41; Cl, 11.02. Hydrogenation of **3d** gave 5-phenyl-2-hexanone in a quantitative yield. **3e**: IR (KBr disk) 1655, 1512 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.25–3.00 (m, 11 H), 4.39 (br s, 1 H), 4.60 (br s, 1 H). **3f**: IR (KBr disk) 1656, 1563, 1517 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.34–3.10 (m, 13 H), 4.05 (s, 1 H), 4.48 (s, 1 H). **3g**: IR (KBr disk) 1655, 1555, 1518 cm^{-1} .
- Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{INO}_2\text{Pd}$ (**4d**): C, 47.21; H, 4.53; Cl, 9.96; N, 3.93. Found: C, 47.29; H, 4.76; Cl, 9.74; N, 3.83.
- 4e**: IR (KBr disk) 2320, 2260, 1725 cm^{-1} . **4f**: IR (KBr disk) 2308, 2290, 1725 cm^{-1} . **4g**: IR (KBr disk) 2307, 2280, 1735 cm^{-1} .
- 6e**: IR (neat) 1743, 1450, 1404 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.15 (s, 3 H), 1.38–2.45 (m, 11 H). **6f**: IR (neat) 1743, 1455, 1444 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.13 (s, 3 H), 1.18–2.45 (m, 13 H). **7**: 2,4-Dinitrophenylhydrazone of **6f**: mp 142–145 $^\circ\text{C}$.
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- 6g**: IR (neat) 1745, 1450, 1405 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 0.94 (s, 3 H), 1.15–2.75 (m, 15 H). Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.92. Found: C, 79.68; H, 11.03.
- NMR signals of methyl groups of *trans*-1-methylbicyclo[3.3.0]octan-3-one (**6e**)⁹ and *trans*-1-methylbicyclo[5.3.0]decan-10-one¹⁰ are more shielded than those of the respective *cis* isomers.
- Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 290.
- 6g**: IR (neat) 1743, 1455, 1403 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.11 (s, 3 H), 1.16–2.20 (m, 13 H), 2.35–2.89 (m, 2 H).
- Karliner, J.; Budzikiewicz, H.; Djerassi, C. *J. Am. Chem. Soc.* **1965**, *87*, 580. **7**: IR (neat) 3040, 1690, 1609, 1445 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.00–2.88 (m, 10 H), 1.18 (s, 3 H), 2.23 (s, 2 H), 5.69 (s, 1 H).
- For instance, σ -1-(*cis*-fused bicyclo[4.3.0]nonan-8-one)methylpalladium(II) chloride (acetonitrile) complex (**4f**, 1 mmol) was reacted with methyl vinyl ketone (3 mmol) in 10 mL of benzene at room temperature for 12 h to produce a mixture of *cis*-fused 1-(*trans*-4-oxo-1-pentenyl)bicyclo[4.3.0]nonan-8-one (**8f-I**, 21%) and *cis*-fused 1-(*trans*-4-oxo-2-pentenyl)bicyclo[4.3.0]nonan-8-one (**8f-II**, 32%). **8f-I**: IR (neat) 1740, 1710, 978 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.11–2.68 (m, 13 H), 2.13 (s, 3 H), 3.14 (m, 2 H), 5.58 (m, 2 H). **8f-II**: IR (neat) 1735, 1668, 1623, 980 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.11–2.75 (m, 15 H), 2.18 (s, 3 H), 5.58–6.21 (m, 1 H), 6.36–7.03 (m, 1 H).

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- Attempts to prepare an analytically pure sample of **9f** failed, because it partially decomposed during column chromatography and thin layer chromatography on silica gel and alumina. **9f**: IR (neat) 1710 cm^{-1} ; ^1H NMR (CDCl_3 with Me_4Si) δ 1.05–2.75 (m, 13 H), 2.86 (s, 2 H); mass M^+ 188 and 186 (1:3).
- 11**: mp 53–55 $^\circ\text{C}$; IR (Nujol) 1705 cm^{-1} ; ^{13}C NMR (CDCl_3 with Me_4Si) δ 26.03, 31.30, 34.74, 35.19, 48.49, 207.08.
- 12**: IR (neat) 3030, 1745 cm^{-1} ; ^1H NMR (CDCl_3 with Me_4Si) δ 0.31 (d, 1 H), 0.85 (m, 1 H), 1.08–2.83 (m, 14 H); ^{13}C NMR (CDCl_3 with Me_4Si) δ 25.28, 26.56, 28.43, 32.05, 33.29, 46.75, 216.80. Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.83. Found: C, 80.68; H, 10.10.
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- On treatment of **4f** with cupric chloride in the presence of furan, 1-(2-furyl)bicyclo[4.3.1]decan-8-one (**13**) was produced in a 30% isolated yield based on **3f**. **13**: IR (neat) 3100, 1710 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ



- 1.31–2.89 (m, 15 H), 5.96 (m, 1 H), 6.25 (m, 1 H), 7.31 (m, 1 H). This finding may be taken to suggest that carbonium-ion intermediate is generated in the present oxidative cleavage of palladium–carbon bond of palladium(II) complexes (**4**).
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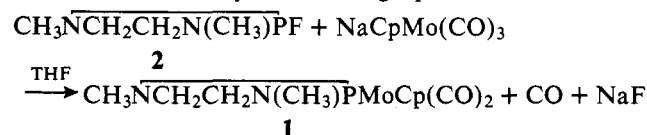
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Structure and Bonding in a Phosphenium Ion–Metal Complex, $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PMo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$. An Example of a Molybdenum–Phosphorus Multiple Bond

Sir:

Heterolytic cleavage of the phosphorus–halogen bond in aminohalophosphines, induced by halide ion acceptors, has been shown to result in the formation of novel dicoordinate aminophosphenium ions, $(\text{R}_2\text{N})_2\text{P}^+$.^{1–6} The molecular structure of only one aminophosphenium ion has been determined,⁶ and the bonding and coordination chemistry displayed by these cations have not been extensively explored.⁷ We have previously reported the synthesis of several neutral metallophosphenium ion coordination complexes;¹⁰ however, the molecular structures of these complexes have not been unambiguously determined, and the nature of the metal atom–phosphorus cation interaction is open to question.^{9,11–13} We report here the determination of the exact composition and molecular structure of a neutral metallophosphenium ion complex (**1**), isolated from the reaction of $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PF}$ (**2**) with $\text{Na}(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3$. An informative description of the bonding in **1** is also provided by quantitative molecular orbital calculations.

Compound **1** was prepared as described previously^{11,14} except that the addition of the ligand **2** to the THF solution of $\text{NaCpMo}(\text{CO})_3$ was accomplished in vacuo. Carbon monoxide was evolved and quantitatively recovered with a Toepler pump system. The amount of CO produced is consistent with a reaction summarized by the following equation:



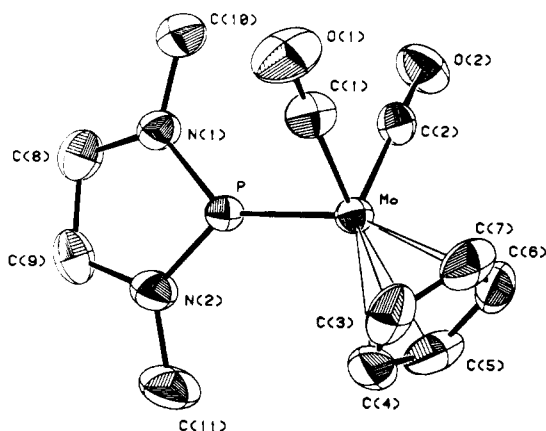


Figure 1. Molecular structure for $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PMo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ (50% probability ellipsoids).

The crude yellow product was purified by extraction into benzene and single crystals of **1** were grown at 0 °C from a THF-pentane solution.¹⁵ The compound crystallizes in a monoclinic cell, $P2_1/n$, with four molecules per unit cell. Crystal data are as follows:¹⁶ $a = 8.239(2)$, $b = 12.447(4)$, $c = 13.236(5)$ Å; $\beta = 98.59(3)^\circ$; $V = 1342.1(7)$ Å³; $\rho_{\text{calcd}} = 1.64$ g cm⁻³; Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å); $\mu(\text{Mo } K\alpha) = 10.7$ cm⁻¹; $F(000) = 672$. The monomeric molecular structure of **1** is shown in Figure 1, and the significant interatomic bond distances and angles are summarized in Table I.

The molecular structure determination unequivocally defines the composition of **1** as $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PMo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$. The structure is clearly related to the structure of the anion in the isoelectronic complex $[(\eta\text{-C}_4\text{H}_9)_4\text{N}^+][\text{CpMo}(\text{CO})_3]^-$ (**3**).¹⁸ The molybdenum atom has a pseudooctahedral, C_s - m , coordination geometry made up by a pentahapto cyclopentadienyl ligand, two carbonyl ligands, and the coordinated phosphonium ion. The average molybdenum-carbonyl distance, 1.945 Å, is similar or slightly shorter than this distance in several $\text{CpMo}(\text{CO})_3\text{X}$ complexes (1.95–2.00 Å);²⁰ however, the Mo–CO distance in **1** is longer than the corresponding distances in the isolated anion of **3** (1.91 Å)¹⁸ or in $[\text{Cp}_2\text{Mo}(\text{H})\text{-CO}^+][\text{CpMo}(\text{CO})_3]^-$ (1.93 Å).¹⁹ The average C–O bond distance in **1**, 1.152 Å, is slightly shorter than this distance in **3**.¹⁸ Although force constants have not been evaluated for **1** and **3**, the CO infrared stretching frequencies correlate qualitatively with the C–O bond distance variations. The average Mo–C (ring) distance, 2.35 Å, also is comparable with this distance in several related compounds.²⁰

The more important stereochemical and bonding features involve the molybdenum atom and the phosphonium ion ligand. The molybdenum atom and all of the nonhydrogen atoms of the phosphonium ion lie in a plane which is nearly perpendicular (89.5°) to the $\text{Mo}(\text{CO})_2$ plane. Hence, the geometry about the phosphorus atom and each nitrogen atom is trigonal planar. The Mo–P bond distance, 2.213 Å, is quite short compared with the usual range of $\text{Mo} \leftarrow \text{P}$ dative bond distances, 2.40–2.57 Å,²¹ which suggests that there is a significant degree of multiple $\text{Mo}=\text{P}$ bond character in **1**. The bond angles and distances within the phosphonium ion ring are similar to those found by Parry and co-workers in the neutral ligand coordination complex $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{P}(\text{F})(\text{CO})_4$.^{22,23} In both compounds the mean P–N bond distance is shorter than the commonly accepted P–N single bond distance, 1.78(3) Å,²⁴ yet longer than the P–N distance in $(\text{CH}_3)_2\text{NPF}_2$, 1.628 Å,²⁵ and $(i\text{-Pr}_2\text{N})_2\text{P}^+$, 1.613 Å.⁶

Based upon the structural and existing spectroscopic data,¹¹ it is now possible to understand the nature of the metal

Table I. Selected Interatomic Distances (Ångstroms) and Angles (Degrees)

Distances			
Mo–C(1)	1.944 (6)	C(1)–O(1)	1.150 (7)
Mo–C(2)	1.946 (7)	C(2)–O(2)	1.155 (9)
Mo–C(3)	2.342 (8)	P–N(1)	1.641 (5)
Mo–C(4)	2.346 (7)	P–N(2)	1.650 (5)
Mo–C(5)	2.356 (8)	N(1)–C(10)	1.454 (9)
Mo–C(6)	2.358 (9)	N(2)–C(11)	1.444 (10)
Mo–C(7)	2.353 (7)	N(1)–C(8)	1.420 (9)
Mo–P	2.213 (1)	N(2)–C(9)	1.438 (8)
		C(8)–C(9)	1.498 (11)
Angles			
C(1)–Mo–C(2)	85.3 (3)	C(8)–C(9)–N(2)	106.8 (6)
C(1)–Mo–P	87.3 (2)	C(9)–C(8)–N(1)	108.7 (6)
C(2)–Mo–P	88.5 (2)	P–N(1)–C(10)	124.7 (5)
N(1)–P–Mo	132.4 (2)	P–N(2)–C(11)	124.5 (5)
N(2)–P–Mo	135.5 (2)	C(8)–N(1)–C(10)	118.8 (6)
N(1)–P–N(2)	92.1 (3)	C(9)–N(2)–C(11)	119.2 (6)
P–N(1)–C(8)	116.1 (5)		
P–N(2)–C(9)	116.3 (4)		

atom-phosphonium cation interaction. Qualitative electron counting for **1** provides an interesting picture. Normally a neutral phosphine ligand acts as a two electron donor toward an organometallic fragment, and it has been assumed that phosphonium ions also have available an electron pair for coordinate bond formation.^{5,8,9} Yet for a closed-shell complex belonging to the class $\text{CpMo}(\text{CO})_2\text{L}$, L should be a 3-electron donor. This dilemma is dismissed if **1** is conceptually formed by two electron donation from the dicoordinate cation $[\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{P}^+]$ (**4**) to the coordinatively unsaturated, 16-electron fragment $[\text{CpMo}(\text{CO})_2]^-$. A more thorough understanding of the bonding in **1** including the unexpectedly short Mo–P bond distance, is provided by approximate nonparameterized MO calculations.^{26,27} The results of the calculations are summarized in the MO energy level diagram (Figure 2). Three phosphonium ion ligand MO's are significant with regard to the Mo–4 interactions.²⁸ The $8a_1$ ligand MO is an in-plane sp^2 -type orbital which possesses predominately phosphorus lone-pair character. This MO forms a $\text{P} \rightarrow \text{Mo}$ dative σ bond in the complex through overlap with the molybdenum d_{z^2} orbital. The $3a_2$ ligand HOMO is a nonbonding out-of-plane orbital localized on the two nitrogen atoms, and it does not interact with any of the metal orbitals in the complex. The $4b_2$ ligand LUMO is an out-of-plane three-center antibonding orbital which is delocalized over the N–P–N unit of the free ligand ion. Overlap of the $4b_2$ MO of **4** with the molybdenum d_{xz} orbital results in a synergic interaction between the molybdenum atom and the N–P–N unit. This unique interaction simultaneously strengthens the Mo–P bond and weakens the two P–N bonds. This quantitative model is in accord with the short Mo–P bond distance in **1** and the trend in P–N bond distances outlined above.

A Mulliken population analysis reveals that 0.58 electron is transferred from the phosphonium cation to the metal atom via the phosphorus-metal σ donation ($2a'$ MO). The charge transfer is offset by the metal-phosphorus π interaction ($5a''$ MO) which transfers 0.77 electrons from the metal atom to the phosphorus atom thereby leaving a net +0.73 electronic charge on the phosphorus atom in the coordinated phosphonium ion complex **1**. The $4a'$ and $5a'$ MO's for the complex are predominately metallic orbitals which are involved in back-bonding to the carbonyl ligands.²⁹ The LUMO ($6a''$) is a π symmetry Mo–P antibonding MO. The relative energy of the latter orbital suggests that a reduced species (**1**[–]) may be available and electrochemical studies of **1** are in progress. The bonding model also indicates that the phosphorus atom in **1** would be strongly deshielded in relation to the phosphorus

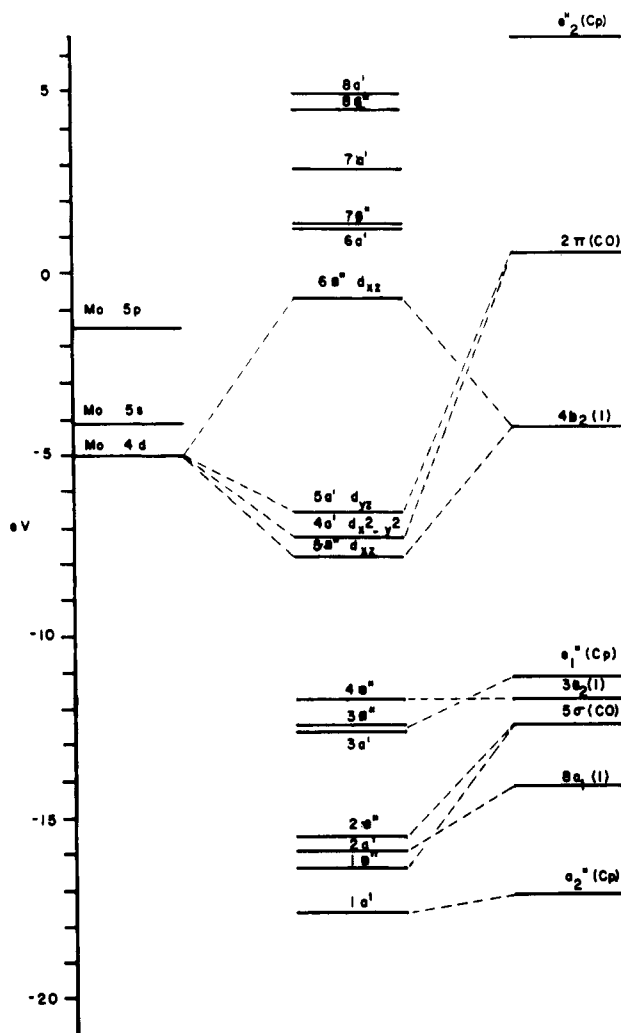


Figure 2. Molecular orbital diagram for $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{P}-\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$. The outside columns represent the orbital eigenvalues of the ligand fragments and metal. The center column represents the orbital energies of the complex.

atom in **2**, which is in part responsible for the large downfield ^{31}P NMR shift.¹¹ The combined results of the structural and theoretical studies of **1** show that the novel ligation properties of phosphonium ions warrant additional intensive study.

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- (14) The previously reported synthesis of **1** was performed under dry nitrogen on a small scale, and CO evolution was not detected.¹¹ The original chemical analysis data for the air-sensitive complex were most consistent with the presence of three carbon monoxide molecules on the metal atom; however, the highest mass ion observed in the mass spectrum of **1** suggested the presence of only two carbon monoxide molecules.
- (15) The spectroscopic properties of **1** prepared here are identical with those reported in our earlier work.¹¹ The ^{13}C NMR parameters have been redetermined: δ 87.66, 51.87 ($J_{\text{CNP}} = 3.7$ Hz), 33.85 ($J_{\text{CNP}} = 16.1$ Hz).
- (16) X-ray intensity data were collected at 298 K by the θ - 2θ technique with Mo K α radiation on a Syntex P3/F automated diffractometer equipped with a graphite-crystal monochromator, scintillation counter, and pulse height analyzer. Of a total of 3102 independent reflections examined with $3^\circ \leq 2\theta \leq 55^\circ$, 2219 (72%) had $I \geq 2\sigma(I)$, and these were used in the structure determination and refinement. The structure was solved by Patterson methods and refined by anisotropic least-squares techniques¹⁷ to yield $R_1(F) = 4.9\%$ and $R_2(F) = 6.2\%$ at the present stage of refinement.
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- (28) Other contributing ligand molecular orbitals listed in Figure 2 have the following free ligand characters: cyclopentadienyl anion, $a_2''(\text{Cp})$ (occupied), $e_1''(\text{Cp})$ (occupied), and $e_2''(\text{Cp})$ (unoccupied); carbonyl, $5\sigma(\text{CO})$ (occupied) and $2\pi(\text{CO})$ (unoccupied).
- (29) The calculations for **1** also reveal synergic interactions which lead to a net -0.096 charge on each CO ligand and a net -0.072 charge on the Cp ring.

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Hydroxyphosphorane Intermediates in Substitution Reactions at Phosphorus in Acyclic Phosphonofluoridates: Evidence from Nuclear Magnetic Resonance

Sir:

It is widely accepted that trigonal bipyramidal (TBP) hydroxyphosphoranes (such as **3**) or their conjugate bases, phosphoranoxides anions (such as **2**), are intermediates in nucleophilic displacements at tetracoordinate phosphorus in cyclic $\text{P}=\text{O}$ bond containing compounds.¹ Thermally² and hydrolytically³ stable cyclic hydroxyphosphoranes and phosphoranoxides anions have recently been prepared. Spectroscopic evidence for equilibrium between a cyclic hydroxyphosphate⁴ or hydroxyphosphinate³ and five-membered-ring hydroxyphosphoranes in solution has been reported. However, with acyclic phosphorus substrates⁵ it has been more difficult to find compelling evidence for existence of such conformationally mobile pentacoordinate species as intermediates in substitution at phosphorus. It has been suggested that the stability of such intermediates is determined by the relative apicophilicity⁶ of the nucleophile⁷ and the leaving group,⁸ in addition to the structural features known³ to stabilize hypervalent species.