Ring Rearrangements

The Circumambulation of a Phosphirane: Taking 9-Phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene for a "Walk"**

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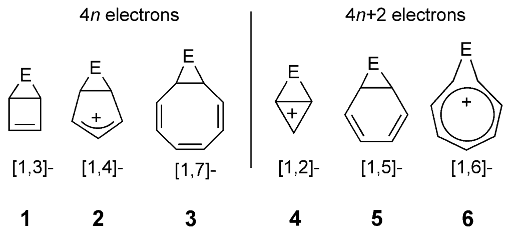
Degenerate rearrangements are among the most captivating features of bicyclic hydrocarbons with three-membered rings.[1] These bishapto circumambulations are referred to as "walks", with the cyclopropane ring moving around the perimeter of the other ring in a series of [1,n]-sigmatropic shifts. When $4n$ electrons participate (Scheme 1, **1**–**3**), the Woodward–Hoffmann (WH) rules for concerted pericyclic processes predict the migrating group to invert,[2] causing the structure to remain unaltered (Figure 1 a). With $4n+2$ electrons involved, (Scheme 1, **4**–**6**) the migrating group should retain its configuration, causing rearrangements between two isomeric structures that reflect a non-least motion pathway (Figure 1 b), but such systems often follow a symmetry-forbidden stereochemical path with diradical character.[3]



Scheme 1. Circumambulating $4n$ and $4n+2$ systems.

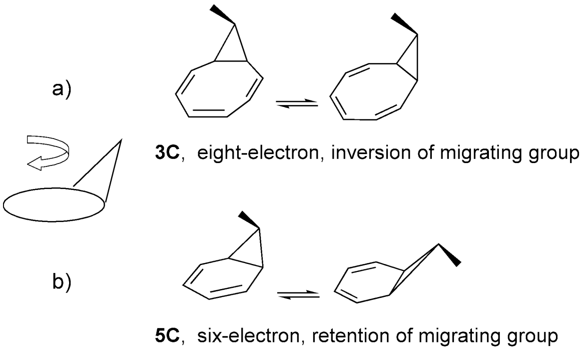


Figure 1. "Walk" rearrangement for a) six-electrons and b) eight-electron hydrocarbons.

"Walk" rearrangements are also known for **1**, **2**, and **5**, with sulfur, nitrogen, or oxygen as the migrating atom,[1] but not with phosphorus, though a degenerate rearrangement along part of a ring has been reported for a triphospha analogue of **1**, with a weak phosphorus–phosphorus bond.[4] Whereas thio,[5] oxa,[6] amino,[7] and phospha analogues[8] of **3** are known, the potential for "walk" activity has not been recognized for any. Herein we present the first such bishapto eight-electron phosphirane circumambulation for **3P** (E = PPh).

The reaction of the cyclooctatriene dianion with dichlorophenylphosphane affords exclusively *exo*-**3P**, the crystal structure of which is shown in Figure 2. The ^{1}H NMR spectrum of **3P** does not display noticeable line broadening at 300 K, but on selective inversion (by a DPFGE (double-pulsed field-gradient spin echo) sequence)[9] of one of the ring

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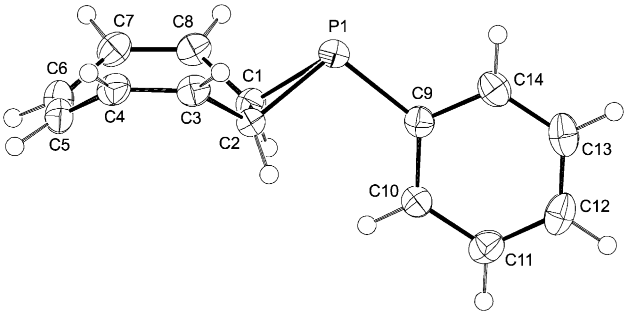


Figure 2. Displacement ellipsoid plot (50% probability level) of **3P**. Selected bond lengths [Å], angles [°], and torsion angles [°]: C1-C2 1.4954(18), P1-C2 1.8731(13), C2-C3 1.4819(18), C3-C4 1.332(2), C4-C5 1.454(2), C5-C6 1.334(2), P1-C9 1.8313(13), C1-P1-C2 47.18(6), C1-C2-P1 66.09(7), C8-C3-C4-C5 36.53(17). The angle between the phenyl ring and the C1-C2 bond is 81.10(8)°.

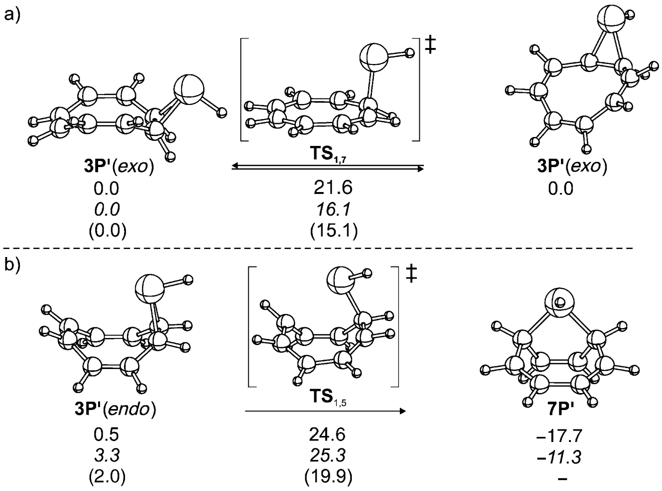


Figure 3. Relative SCS-MP2/cc-pVTZ, B3LYP6-31G* (in italics), and CASPT2(10,10)/6-31G* (in parenthesis) enthalpies at 298 K (in kcal/mol) for a) the "walk" rearrangement of **3P′** and b) its 1,5-sigmatropic shift.

protons (with a mixing time of 1 s) subsequent magnetization transfer occurs to all the other ring protons, the transfer rate to the nearest protons being strongest. This is indicative of interconversion of the ring hydrogen atoms and thus of circumambulation. Clearly, at room temperature in solution, the PPh group *walks* around the hydrocarbon ring. An activation enthalpy $\Delta H^{\neq}$ of 20 kcal mol^{-1} was deduced for this dynamic process by ^{31}C NMR spectroscopy line-shape analysis over a temperature range of 300–332 K (Table 1).

Table 2: Relative enthalpies[a] for the **7C** and **7P′** conformers, transition states, and products.

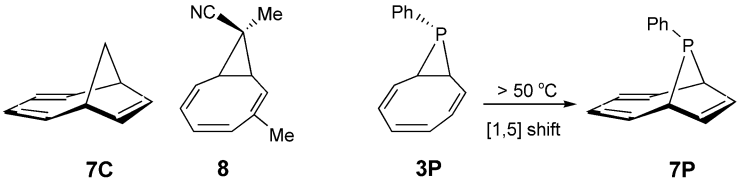
3	Method	*exo*	$TS_{1,7}$	TS_{inv}	*endo*	$TS_{1,5}$	7
3C	UB3LYP[b]	0.0	33.0	5.8	3.7	38.2/35.9	−18.1
3C	CASPT2(8,8)[b,c]	0.0	34.3	7.8	1.1	40.0/39.2	–
3P′	B3LYP[b]	0.0	16.1	3.6	3.3	25.3	−11.3
3P′	CASPT2(10,10)[b,d]	0.0	15.1	–	2.0	19.9	–
3P′	SCS-MP2[d–f]	0.0	21.6	3.5	0.5	24.6	−17.7

[a] B3LYP6-31G* zero-point energy and temperature corrections included. [b] The 6-31G* basis set was used. [c] Reference [13]. [d] The B3LYP geometry was used. [e] Basis set: cc-pVTZ. [f] Reference [11].

The nature of the "walk", during which the migrating group inverts with each step ($3P' \rightarrow TS_{1,7} \rightarrow 3P'$ in Figure 3a), was also inspected theoretically[10] for the parent organophosphorus compound **3P′** (E = PH) and related to that for hydrocarbon **3C** (E = CH$_2$, Table 2). $\Delta H^{\neq}$ values of 16.1 and 15.0 kcal mol^{-1} were obtained at the B3LYP6–31G* and CASPT2(10,10)/6-31G* levels of theory,[11] respectively, and 21.5 kcal mol^{-1} with the improved second-order Møller–Plesset perturbation SCS-MP2/cc-pVTZ method of Grimme.[12] This method is a simple modification of MP2 theory and gives improved reaction energies, particularly when aromatic systems are involved. The [1,7] shift of **3P′** reflects such behavior, and, indeed, the agreement with the experimental value for **3P** (E = PPh) is excellent. A modestly lower barrier for **3P** should be expected, resulting from conjugation of the phenyl substituent with the p orbital on the phosphorus atom in the transition state ($TS_{1,7}$). Hydrocarbon **3C** has a much higher "walk" barrier, that is, 32.5, 31.5, and 34.2 kcal mol^{-1} at the SCS-MP2/cc-pVTZ, B3LYP6-31G*, CASPT2(8,8)//CASSCF(8,8)/6-31G*[13] levels of theory, respectively, but experimental verification is absent as ring opening to *cis,trans,cis,cis*-cyclonona-1,3,5,7-tetraene is favored instead. The closest comparison is between the calculated $\Delta H^{\neq}$ value of 27.3 kcal mol^{-1} (CASPT2(8,8)) for 9,9-(CN)$_2$-**3C** and the experimental $\Delta G^{\neq}$ value of 29 kcal mol^{-1} for **8** (Scheme 2).[14]

Table 1: Kinetic data for the circumambulation of **3P**.

T [K]	*k* [s^{-1}]	*T* [K]	*k* [s^{-1}]
300	1.0	308	1.8
313	4.0	318	7.5
323	11.5	328	19.0
332	23.0		



Scheme 2.

Heating **3P** above 50 °C yields only **7P**, which is the WH-allowed product for a [1,5] shift. An enthalpy barrier $\Delta H^{\neq}$ of 24 kcal/mol was obtained for this process from a kinetic ^{31}P NMR spectroscopic study (**3P**: $\delta = 179$ ppm; **7P**:[15] $\delta = -79$ ppm) over a temperature range of 323–363 K (Table 3). The barrier of 24.1 kcal/mol calculated at the SCS-MP2 level of theory for **3P′** ($3P' \rightarrow TS_{1,5} \rightarrow 7P'$ in Figure 3b) is in excellent agreement with the experimentally determined value; the small difference may reflect modest steric congestion by the phenyl substituent. B3LYP gives a slightly

Table 3: Kinetic data for the 1,5-phosphorus rearrangement of **3P**.

T [K]	$k\,10^7$ [s^{-1}]	T [K]	$k\,10^7$ [s^{-1}]
323	72	333	226
343	667	353	1940
358	3425	363	4683

smaller barrier (22.0 kcal mol^{-1}), and CASPT2(10,10) a much lower value (17.9 kcal mol^{-1}). The [1,5]-rearrangement is pericyclic without diradical character for transition state **TS**$_{1,5}$. In sharp contrast, the more-demanding conversion of hydrocarbon **3C** into **7C** occurs in a diradical manner, as inferred from the ^{15}N/N scrambling during the [1,5] shift of singly ^{15}N-labeled 9,9-(CN)$_2$-**3C**.[13] The reaction path for **3C** was reported to have two similar high-lying transition states (**TS**$_{1,5}$(a) 40.0 and **TS**$_{1,5}$(b) 39.2 kcal mol^{-1} at the CASPT2(8,8)[13] level of theory) without an intermediate (Figure 4), enabling both retention and inversion of configuration of the migrating carbon atom. Similar barriers of 37.8 (**TS**$_{1,5}$(a)) and 35.9 kcal mol^{-1} (**TS**$_{1,5}$(b)) are predicted at the UB3LYP level of theory using a spin-projection method to obtain proper open-shell singlet energies.[16,17] The origin of the diradical [1,5] shift for the hydrocarbons has been attributed to the too long distance between the migrating methylene carbon and the opposite ring carbon to allow for a pericyclic process.[13] Evidently, the longer C–P bonds and the more diffuse character of phosphorus underlie the *pericyclic* nature of the [1,5]-rearrangement of **3P** into **7P**.

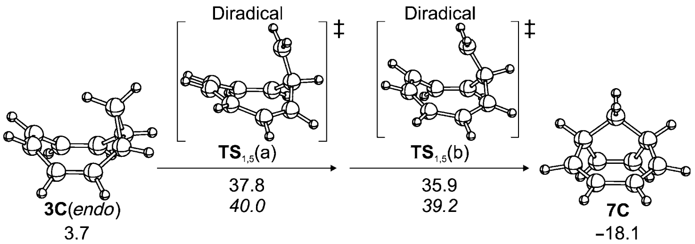


Figure 4. Relative (U)B3LYP6-31G* and CASPT2(8,8)[13] (in italics) enthalpies at 298 K (in kcal mol^{-1}) for the [1,5] shift of hydrocarbon **3C**.

The *exo* conformer of **3P′**, which shows excellent agreement with the X-ray structure of **3P**, readily inverts to the less-stable (0.5 kcal mol^{-1}) *endo* form (**3P′**(*exo*)→**TS**$_{inv}$→**3P′**(*endo*) SCS-MP2, Figure 3b) via a low-energy (3.5 kcal mol^{-1}), planar, eight-membered ring form (as does **3C**), indicating conformational fluxional behavior of the hydrocarbon frame.

In conclusion, we have demonstrated that 9-phenyl-9-phospha-bicyclo[6.1.0]nona-2,4,6-triene (**3P**) is a dynamic molecule that undergoes a perpetual degenerate [1,7] sigmatropic shift in solution and a pericyclic [1,5]-rearrangement at temperatures above 50 °C.

Experimental Section

3P: The cyclooctatrienyl dianion was treated with dichlorophenylphosphane.[18] Recrystallization from methanol at −78 °C gave light-yellow crystals (2.07 g, 34 %); m.p. 42–43 °C. ^{31}P NMR (250 MHz, CDCl$_3$): $\delta = 179$ ppm; ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 3.65$ (d, ^2J(H,P) = 2.7 Hz; H1), 5.95 (s; H4), 6.05 (d, ^3J(H,H) = 11.6 Hz; H 3), 6.40 (dd, ^3J(H,P) = 8.2 Hz, ^3J(H,H) = 11.6 Hz; H2), 7.25–7.35 (m; m-H$_{Ar}$ and p-H$_{Ar}$), 7.39–7.50 ppm (m, p-H$_{Ar}$); IR (KBr): $\tilde{\nu} = 696.4$, 665.5 cm^{-1} (w, P-C).

Crystal data for **3P**: $C_{14}H_{13}P$, $F_w = 212.21$, colorless cubic crystal, $0.36 \times 0.30 \times 0.15$ mm^3, orthorhombic, $P2_12_12_1$ (no. 19), $a = 8.9692(1)$, $b = 10.6590(1)$, $c = 11.8322(2)$ Å, $V = 1131.19(3)$ Å^3, $Z = 4$, $D_x = 1.246$ g cm^{-3}, $\mu = 0.205$ mm^{-1}; 15794 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1}; 2593 reflections were unique ($R_{int} = 0.036$); an absorption correction was not considered necessary. The structure was solved with direct methods (SHELXS-97)[19] and refined with SHELXL-97[20] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. H atoms of the phenyl ring were refined as rigid groups; all other H atoms were refined freely with isotropic displacement parameters; 168 refined parameters, no restraints. Flack x parameter[21]: −0.06(7); R values [$I > 2\sigma(I)$]: $R1 = 0.0255$, $wR2 = 0.0618$. R values [all reflections]: $R1 = 0.0292$, $wR2 = 0.0634$. GoF = 1.062. Residual electron density between −0.17 and 0.19 e Å^{-3}. Molecular illustration, structure checking, and calculations were performed with the PLATON package.[22] CCDC 205388 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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