Vinylphosphirane−Phospholene Rearrangements: Pericyclic [1,3]-Sigmatropic Shifts or Not?

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Abstract: The conversion of "free" and $Cr(CO)_5$-complexed 2-vinylphosphiranes into 3-phospholenes via [1,3]-sigmatropic shifts was studied with density functional theory and compared with the corresponding hydrocarbon system, that is, the vinylcyclopropane−cyclopentene rearrangement. All three systems behave similarly with subtle but important differences. No intermediate was found on any of the potential energy surfaces. 2-Vinylphosphiranes have smaller rearrangement barriers than vinylcyclopropane, and those carrying the $Cr(CO)_5$ group have still smaller ones. The rearrangement of both *anti-* and *syn*-2-vinylphosphiranes occurs in a concerted pericyclic manner with inversion of configuration at the migrating phosphorus, requiring, respectively, 29.3 and 36.7 kcal/mol, much in contrast to the 44.6 kcal/mol demanding diradical-like process for the hydrocarbon analogue. Epimerization at the phosphorus center (syn ⇌ anti) requires ∼32.0 kcal/mol and occurs in a single step, reflecting a diradical-like ring opening−ring closure process that can occur in both a clockwise and counterclockwise fashion. Complexation of the phosphorus center by $Cr(CO)_5$ results in the substantial stabilization of reagents and products and further reduces the barriers for rearrangement. The *anti* isomer has the lowest barrier for the [1,3]-shift ($\Delta E = 20.5$ kcal/mol), which is slightly less than that needed for P-epimerization and for conversion of the syn isomer, both of which are nonpericyclic processes. When a P-phenyl group is introduced, the diradical-like conversion of the *syn* isomer is favored over the *anti* isomer, in agreement with experimental reports. The influence of torquoselectivity is discussed for the rearrangements of these structures with their heavy substituents. The origin of the stabilization rendered by the $Cr(CO)_5$ group and its influence on the [1,3]-conversion are also analyzed. The DFT activation energies for the diradical-like [1,3]-sigmatropic shifts were verified with a multireference method.

Phosphorus and carbon are diagonally related in the Periodic Table because of their comparable electronegativities (C 2.2; P 2.5).[1] A manifestation of this relationship is found in the chemistry of low-valent organophosphorus compounds,[2] which often resembles that of the related hydrocarbons. Illustrative are the electrophilic phosphinidenes R−P,[3,4] which, when stabilized by $M(CO)_x$ complexes, react like electrophilic singlet carbenes.[5] They add to olefins to form three-membered phosphirane rings, just like carbenes add to olefins to give cyclopropanes. Addition to conjugated dienes results in vinylphosphiranes and phospholenes,[6,7] which are related by a simple [1,3]-sigmatropic shift. In this paper we explore, by computa-

tional methods, the very nature of this rearrangement and compare it with the same process of the corresponding hydrocarbons.

The rich literature on the vinylcyclopropane (**1**)−cyclopentene (**2**) rearrangement provides not only examples supporting both pericyclic and stepwise diradical pathways[8] but also cases in which this distinction is less evident.[9,10] For example, D-labeling
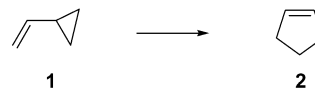
experiments for the parent system give a surprising ratio of 40:13:23:24 for the thermally allowed (*si, ar*) and forbidden (*sr, ai*) products, respectively, where *a* and *s* stand for antara- and suprafacial, *i* for inversion, and *r* for retention. This ratio is corrected for the competing stereoisomerization of the cyclo-

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(1) Pauling, L. *The nature of the chemical bond*; Cornell University: Ithaca, NY, 1960.
(2) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*, John Wiley & Sons Ltd., 1998.
(3) Vlaar, M. J. M.: Lammertsma, K. *Eur. J. Org. Chem.* **2002**, *7*, 1127.
(4) Mathey, F. *Helv. Chim. Acta* **2001**, *84* (10), 2938.
(5) Jones, M.; Moss, R. A. *Reactive intermediates,* Vol. 3; Wiley: New York, 1985; pp 45−108.
(6) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.
(7) Wit, J. B. M.; van Eijkel, G. T.; de Kanter, F. J. J.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 2596−2599.
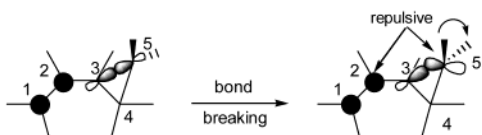
(8) For a recent review, see: Baldwin, J. E. *J. Comput. Chem.* **1998**, *19*, 222
(9) (a) Baldwin, J. E.; Villarica, K. A.; Freedberg, D. I.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994**, *116*, 10845. (b) Baldwin, J. E.; Bonacorsi, S., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 8258 and references therein.
(10) (a) Gajewski, J. J.; Olson, L. P.; Willcott, M. R., III. *J. Am. Chem. Soc.* **1996**, *118*, 229. (b) Gajewski, J. J.; Squicciarini, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6717.

Figure 1. Effect of torquoselectivity on the stereochemistry of the vinylcyclopropane rearrangement.

propane ring, which occurs in a diradical manner with a ~3 kcal/mol lower barrier than the 51.7 kcal/mol that is required for the [1,3]-sigmatropic shift. Detailed DFT and CASSCF ab initio studies give potential energy profiles that agree with the experimental observations, but they also reveal that the rearrangement involves singlet-state diradical-like transitions, without diradical (or zwitterionic) intermediates.[11,12] The diradical character of the transition structures indicates that orbital overlap between the migrating carbon and the allylic unit cannot be maintained throughout the reaction path. The transition structures lie on a broad, flat plateau of the potential energy surface where they interconvert without passing through minima, resulting in conformational scrambling. Repulsion between the π-orbital on carbon C(2) and the σ-orbital of the migrating carbon C(5) (Figure 1) has been argued to cause the latter to turn away from the vinyl group on cleaving the C−C bond of the cyclopropyl ring (torquoselectivity),[13] resulting in a suprafacial (s) rearrangement with inversion (i) of the migrating carbon, thereby mimicking the Woodward−Hoffmann allowed concerted process. Dynamics trajectory studies confirm the diradical-like transition structure to give indeed preferentially, though not exclusively, to the *si* product.[14]
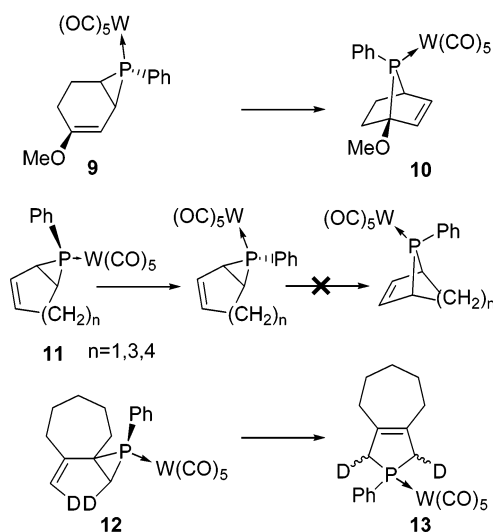
Heteroatom analogues of the vinylcyclopropane−cyclopentene rearrangement are known, but the mechanistic detail is more limited and even differs per heteroatom. For example, the thermal rearrangement of vinylaziridine **3** to dihydropyrrole **4** reportedly occurs by a diradical mechanism,[15,16] the conversion of vinylsilirane **5** to silolene **6** is considered to involve a free silylene,[17] while the rearrangement of *trans*-vinylphosphirane **7** into phospholene **8** is again believed to occur diradically.[18]

Tbt=2,4,6-tri[bis(trimethylsilyl)methyl]phenyl
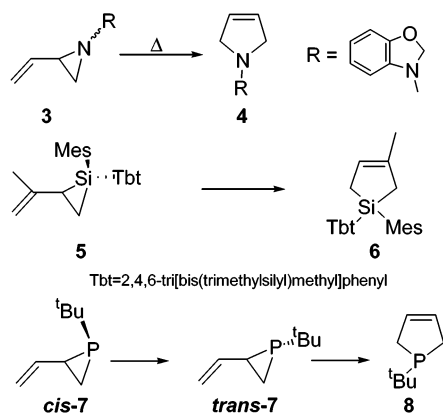
Similar to the case of the hydrocarbons, *cis*−*trans* stereoisomerism, also termed P-epimerization, occurs for vinylphosphirane **7**, of which the trans isomer undergoes a [1,3]-sigmatropic shift to give 3-phospholene (**8**).[18]

Of more recent vintage are studies on transition metal complexed vinylphosphiranes, which depict a more intricate picture. For example, *syn*-**9**, which is the major phosphinidene adduct of 1-methoxy-1,3-cyclohexadiene, converts to 7-phos-

phanorbornene **10** with inversion of the phosphorus center, thereby suggesting a concerted, pericyclic pathway.[19] In the absence of the methoxy ring substituent, P-epimerization (i.e., *syn* → *anti* isomerism) occurs as well, implying a diradical process. Bicyclic vinylphosphiranes **11**, with both smaller (5-) and larger (7-, 8-) olefinic rings, do not undergo a [1,3]-shift but, instead, only P-epimerize to the more stable anti form.[20] Conversion of D_2-labeled exocyclic 2-vinylphosphirane complex **12** into phospholene **13** suggests the simultaneous occurrence of P-epimerization and either pericyclic or diradical [1,3]-sigmatropic shifts.[21]

These experimental observations suggest that the very nature of the vinylcyclopropane−cyclopentene rearrangement is mimicked by the phosphorus analogues. In this paper, we use density functional theory (DFT) to investigate not only the mechanistic consequences of replacing CH_2 for PH but also to report on the influence of a transition metal group on the rearrangement. If the [1,3]-shift occurs in a one-step diradical-like fashion, the dynamics of this process could become more pronounced with a bulky group like $Cr(CO)_5$. Because of the sheer size of this group, DFT is the only viable theoretical method to explore the mechanistic intricacies of this process. The validity of DFT methods for such investigations has been demonstrated.[11]

(11) Houk, K. N.; Nendel, M.; Wiest, O.; Storer, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 10545−6.
(12) Davidson, E. R.; Gajevski, J. J. *J. Am. Chem. Soc.* **1997**, *119*, 10543.
(13) Dolbier, W. R., Jr.; Koroniak, H.; Houk, K. N.; Sheu, C. *Acc. Chem. Res.* **1996**, *29*, 471.
(14) Doubleday: C.; Nendel, M.; Houk, K. N.; Thweatt, D.; Page, M. *J. Am. Chem. Soc.* **1999**, *121*, 4720.
(15) Atkinson, R. S.; Rees, C. W. *Chem. Soc., Chem. Commun.* **1967**, 1232.
(16) (a) Hudlicky, T.; Frazier, J. O.; Seoane, G.; Tiedje, M.; Seoane, A.; Kwart, L. D.; Beal, C. *J. Am. Chem. Soc.* **1986**, *108*, 3755. (b) Pearson, W. H.; Celebuski, J. E.; Yam-Foo Poon; Dixon, B. R.; Glans, J. H. *Tetrahedron Lett.* **1986**, *27*, 6301. (c) Hudlicky, T.; Frazier, J. O.; Kwart, L. D. *Tetrahedron Lett.* **1985**, *26*, 3523.
(17) Takeda, N.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **2000**, 622.
(18) (a) Richter, W. J. *Chem. Ber.* **1983**, *116*, 3293. (b) Richter, W. J. *Chem. Ber.* **1985**, *118*, 1575.
(19) Lammertsma, K.; Hung, J. T.; Chand, P.; Gray, G. M. *J. Org. Chem.* **1992**, *57*, 6557−6560.
(20) Wang, B.; Lake, C, H.; Lammertsma, K. *J. Am. Chem. Soc.* **1996**, *118*, 1690−1695.
(21) van Eis, M. J.; Nijbacker, T.; de Kanter, F. J. J.; de Wolf, W. H.; Lammertsma, K.; Bickelhaupt, F. *J. Am. Chem. Soc.* **2000**, *122*, 3033−3036.

Computational Details

All geometry optimizations were performed with the ADF program[22] using a triple ζ basis set with polarization functions, the local density approximation (LDA) in the Vosko−Wilk−Nusair parametrization[23] with nonlocal corrections for exchange (Becke88),[24] correlation (Perdew86)[25] included in a self-consistent manner, and the analytical gradient method of Versluis and Ziegler.[26]

Noodleman's sum method for spin correction[27] (eq 1) is typically used to extract the open-shell singlet energies from the mixture of singlet and triplet states that are obtained on calculating open-shell singlet energies with spin unrestricted DFT. This method adds the converged open-shell singlet−triplet energy difference, using the same geometry, to the open-shell singlet energy.

$$E_{s,pure}^{(1)} = 2E_s - E_t \tag{1}$$

The disadvantage of this procedure is that it does not account for reduced spin contamination in species with diminished diradical character. To adjust for this, Houk and co-workers[28] included a correction based on spin projection (eq 2) even though the DFT orbitals are not eigenfunctions of any operator. The spin projected energy,[29] which we apply in the present study, has the following form:

$$E_{s,pure}^{(2)} = E_s + f_{SC}(E_s - E_t) \tag{2a}$$

$$f_{SC} = \frac{{}^1\langle s^2 \rangle}{{}^3\langle s^2 \rangle - {}^1\langle s^2 \rangle} \tag{2b}$$

Spin-related corrections to the energy are not needed with multi-reference methods, but the significant computational expense makes them often impractical to use. We used the efficient multireference DFT/MRCI method[30] for selected transition structures to calibrate the above-noted spin-related correction to the energy. These single-point calculations on DFT-optimized structures were performed with the TURBOMOLE[31,32] suite of programs, using Becke's hybrid exchange correlation functional (BHLYP),[33] with the TZVP basis set for all atoms. An orbital energy window of 1 Hartree was used for the selection of the most important configurations.

Zero point energies (ZPEs), and intrinsic reaction coordinate (IRC) driving calculations (in mass-weighted coordinates (bohr.amu$^{1/2}$)), were performed with the *Gaussian98* program package,[34] using geometries optimized with the (U)BP86 exchange-correlation potentials and the LANL2DZ basis set for chromium and 6-31G* for all other elements. Minima were confirmed to have only positive force constants, and transition structures (**TS**), to have only one imaginary value; those associated with epimerization are identified with the character E.

Throughout the text, ADF optimized geometries and energies are used, whereas Figures 2, 3, 5, and 7 also contain relative enthalpies $\Delta\Delta H$.[298]

The bonds in the organophosphorus complexes between the transition metal and the phosphorus atom are analyzed with ADF's established energy decomposition[35] into an orbital interaction (ΔE_{oi}), a steric interaction (ΔE_{steric}), and a preperation energy (ΔE_{prep}), where the latter term results from preparation of the fragments for interaction by deforming them from their equilibrium structure to the geometry and electronic state they acquire in the complex:

$$\Delta E_{bond} = \Delta E_{oi} + \Delta E_{steric} + \Delta E_{prep}$$

Note that ΔE_{bond} is defined as the negative of the bond dissociation energy (BDE), that is, $\Delta E_{bond} = E(\text{molecule}) - \sum E(\text{fragments})$, thereby giving negative values for stable bonds. ΔE_{steric} represents the interaction between the prepared fragments when they are put, with unchanged electron densities, at the positions they occupy in the complex. ΔE_{oi} accounts for HOMO−LUMO interactions between occupied orbitals on one moiety with unoccupied orbitals on the other and polarization (empty/occupied orbital mixing on the same fragment). The charge-transfer component is the result of both electron donation from ligand to metal (σ-bonding) and donation from the metal back into the unoccupied orbitals of the ligand (π-back-bonding). An estimate of these contributions can be obtained by computing the orbital interaction energies with removal of the unoccupied orbitals on either one of the fragments, thereby obtaining ΔE_σ in one case and ΔE_π in the other.

Results and Discussion

The DFT methodology used in this study is briefly validated against reported high-level ab initio results for the [1,3]-shift of the hydrocarbons **1**−**2** before it is applied to analyze the same process for the phosphorus analogues **14**−**15** and **16**−**17**. Next, we address the influence of the Cr(CO)$_5$ group on this rearrangement. All optimized geometries and energies are provided in the Supporting Information. Selected geometrical parameters for transition structures are tabulated in the following sections.

Vinylcyclopropane−Cyclopentene Rearrangement. The lowest energy barrier of 44.6 kcal/mol for the exothermic [1,3]-sigmatropic rearrangement of vinylcyclopropane **1** to cyclopentene **2** (22.7 kcal/mol) is in excellent agreement with the 45.4 kcal/mol reported at 4,4-CAS/6-31G*.[12] A similar barrier of 43.2 kcal/mol is obtained at DFT/MRCI, illustrating that the applied spin-correction method performs adequately. The diradical-like character of transition structure **TS1** for this process is evident from its long C1−C5 and C3−C5 distances (Table 1). This is confirmed by the DFT/MRCI contributions, 0.717 for the ground state and 0.237 for the doubly excited state. Also the stereoisomerization of **1** has a diradical transition structure (**TSE1**). The 45.1 kcal/mol required for this process is slightly more than that reported at 4,4-CASSCF/6-31G* (42.5 kcal/

(22) (a) Fonseca-Guerra, C.; Visser, O.; Snijders, J. G.; Baerends, E. J. In METECC-95; Clementi, E., Corongiu, C., Eds.; STEFF: Cagliari, Italy, 1995; p 307. (b) Baerends, E. J.; Ellis, D. J.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.
(23) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1992**, *99*, 84.
(24) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(25) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(26) (a) Fan, L.; Versluis, L.; Ziegler, T.; Baerends, E. J.; Ravenek, W. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1988**, *S22*, 173. (b) Versluis, L.; Ziegler, T. J. *J. Chem. Phys.* **1988**, *322*, 88.
(27) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737.
(28) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036.
(29) For calculating the $\langle S^2 \rangle$ values, the following formula was implemented in the ADF algorithm: $\langle S^2 \rangle_{uhf} = \langle S^2 \rangle_{exact} + N^\beta - \sum_i^N \sum_j^N |S_{ij}^{\alpha\beta}|$ and $\langle S^2 \rangle_{exact} = [(N^\alpha - N^\beta)/2][(N^\alpha - N^\beta)/2 + 1)]$. S_{ij} is the overlap integral of α-orbital i with β-orbital j, and N is the number of electrons where $N^\alpha \geq N^\beta$. See: Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry,* 1st ed. revised; McGraw-Hill, 1989; p 107.
(30) Grimme, S.; Waletzke, M. *J. Chem. Phys.* **1999**, *111*, 5645.
(31) Ahlrichs, R.; Bähr, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.
(32) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346.
(33) $E_{xc}(\text{BHLYP}) = 0.5(E_x(\text{HF}) + E_x(\text{LDA}) + E_x(\text{B88}) + E_c(\text{LYP})$. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian98, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
(35) (a) Morokuma, K. *J. Chem. Phys.* **1971**, 1236. (b) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755. (c) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

Table 1. Selected Distances (Å) and Angles (deg) for **TSE1** and **TS1**

	C1–C2	C2–C3	C1–C5	C3–C5	C2–C3–C4C5
TSE1	1.386	1.396	3.734	2.505	89.6
TS1	1.408	1.376	2.756	2.498	42.6
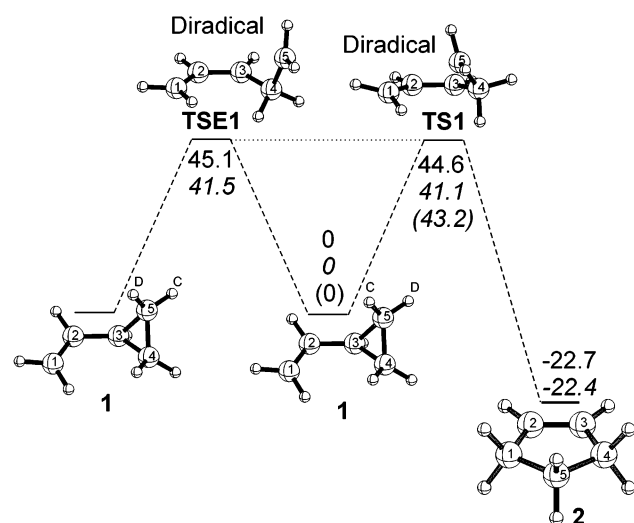
Figure 2. Relative B86-P88(*TZP*) energies (in kcal/mol) for the vinyl-cyclopropane−cyclopentene rearrangement. Temperature-corrected relative enthalpies are given in italics, and relative DFT/MRCI energies are given in parentheses.

mol).[36] The diradical character of **TSE1** is evident from its long C1−C5 and C3−C5 distances, reflecting an apparent absence of bonding to C5. Both transition structures lie on a very flat potential energy surface, enabling their interconversion (Figure 2).

While only a limited section of the energy surface of the vinylcyclopropane rearrangement was explored, it is evident that the applied DFT theory performs similar to 4,4-CASSCF.

2-Vinylphosphirane−3-Phospholene Rearrangement. Like its hydrocarbon analogue, 2-vinylphosphirane **14** rearranges to 3-phospholene **15**, but the potential energy surfaces of the two systems reveal important differences besides intriguing similarities. The P-containing system prefers concerted [1,3]-rearrangements, while its P-epimerization occurs in a diradical fashion, again without intermediates.

Two nearly isoenergetic vinylphosphirane isomers exist with the PH group in either an *anti* (**14a**) or a 0.1 kcal/mol more stable *syn* (**14b**) form. These interconvert (stereoisomerism) in a seemingly diradical fashion by cleaving and reforming the P−C3 bond without passing through intermediates. Two transition structures of nearly equal energies ($\Delta E = 0.5$ kcal/mol) were identified for this epimerization at the phosphorus center, reflecting a clockwise (**TSE14a**) and counterclockwise (**TSE14b**) rotation around the P−C4 bond of the *syn* isomer. The lowest energy barrier of 32.1 kcal/mol is associated with a *syn* → *anti*
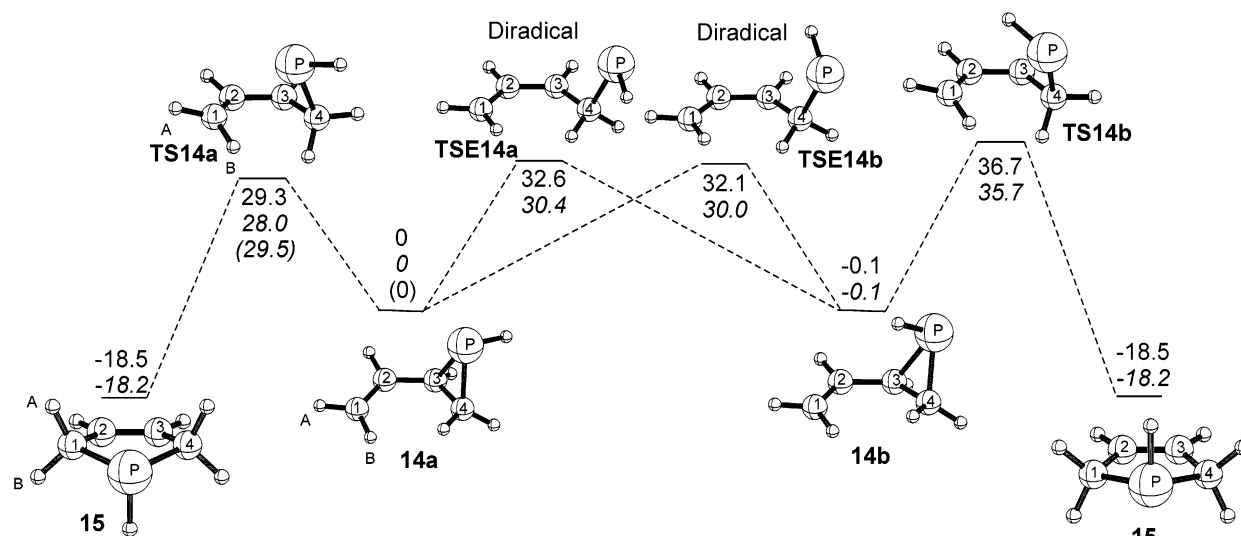
(36) We note that, in contrast to the experimental and 4,4-CASSCF data, the DFT barrier for stereoisomerization is slightly higher (0.5 kcal/mol) than that for the [1,3]-shift. This discrepancy can be attributed to the self-interaction error in density functional theory, which destabilizes localized electron distributions (such as diradical systems) with respect to delocalized ones,[37,38] as **TSE1** possesses more diradical character than **TS1**, which is reflected, for example, in the lengths of the C1−C5 and C3−C5 distances.

(37) Fois, E. S.; Penman, J. I.; Madden, P. A. *J. Chem. Phys.* **1993**, *98*(8), 6352.

(38) Johnson, B. G.; Gonzales, C. A.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1994**, *221*, 100.

conversion (Figure 3). An IRC confirms **TSE14b** to be connected to both vinylphosphirane isomers (Figure 4). Both transition structures display diradical character. The 103° (99°) large dihedral P−C4−C3−C2 angle and the more than 4.0 Å long P−C1 distance of **TSE14a** (**TSE14b**) do not enable the inverting phosphorus atom to interact with the terminal carbon of the allylic unit (Table 2).

Both 2-vinylphosphiranes rearrange into 3-phospholene **15** in a similar fashion. The concerted (closed-shell) 1,3-rearrangement of *anti* isomer **14a** requires 29.3 kcal/mol and is exothermic by 18.5 kcal/mol (Figure 3); expectedly, a similar barrier of 29.5 kcal/mol is obtained at DFT/MRCI. The associated transition structure **TS14a** has P−C1 and P−C3 distances of 2.670 and 2.416 Å, respectively, which are in the expected bonding range for a Woodward−Hoffmann "allowed" concerted suprafacial [1,3]-sigmatropic shift. Apparently, mixing with higher excited states is negligible, and this is confirmed by the DFT/MRCI contribution 0.922 for the ground state with only 0.047 for the doubly excited state. The inversion of the phosphorus center that occurs during the migration is evident and was confirmed by an IRC calculation. The concerted reaction path that was found for the rearrangement of *syn* isomer **14b** into **15** has a 7.5 kcal/mol higher barrier. This much higher energy pathway is reflected in the longer P−C1 and P−C3 distances of transition structure **TS14b** (Table 2).

Also an open-shell (diradical) transition structure **TS14a(ai)** was found for the [1,3]-sigmatropic shift (Figure 5). An IRC calculation showed it to be connected to phosphole **15**, but tracing in the opposite direction was not successful because of the near zero slope of the potential energy surface around **TS14a(ai)** (Figure 6).[39] The negative force constant for **TS14a(ai)** is associated with a rotation of the C1H$_{A/B}$ methylene group around the C1−C2 bond, which is indicative of an antarafacial conversion. This diradical-like rearrangement requires 4.3 kcal/mol more than the concerted suprafacial process. The long P−C1 and P−C3 distances (3.380 and 2.950 Å) and the nearly planar C1-methylene group ($\angle H_{A/B}$C1−C2−C3 $= +5°(H_B)/ -176°(H_A)$) of transition structure **TS14a(ai)** reflect the lack of orbital overlap of the phosphorus atom with the allylic unit and underscore its diradical character. We emphasize again that no intermediates were found.

Rearranging 2-vinylphosphirane into 3-phospholene via a retro [1,2]-addition, giving the free phosphinidene and butadiene, followed by a [1,4]-addition, as proposed for vinylsylirane, is an alternative but unlikely process. Already the first step is much
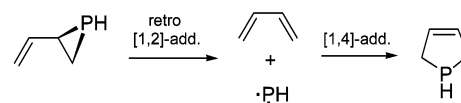
more demanding than any of the rearrangement barriers for 2-vinylphosphirane, namely 44.7 kcal/mol for liberating ³PH and even 24.7 kcal/mol more for the singlet species. Also, interconverting the *syn* and *anti* isomers of 2-vinylphosphirane by inverting the phosphorus center is unlikely, as such a process already requires 50.6 kcal/mol for the parent phosphirane.[40]

(39) A similar phenomenon has been reported for the [1,3]-sigmatropic rearrangement of bicyclo[3, 2, 0]-hept-2-ene to norbornene. See: Beno, B. R.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 4816.

(40) Goumans, T. P. M.; Ehlers, A. W.; Vlaar, M. J. M.; Strand, S. J.; Lammertsma, K. *J. Organomet. Chem.* **2002**, *643−644*, 369−375.

Figure 3. Relative B86-P88(*TZP*) energies (in kcal/mol) for the rearrangement pathways for uncomplexed 2-vinylphosphirane. Temperature-corrected relative enthalpies are given in italics, and relative DFT/MRCI energies are given in parentheses.
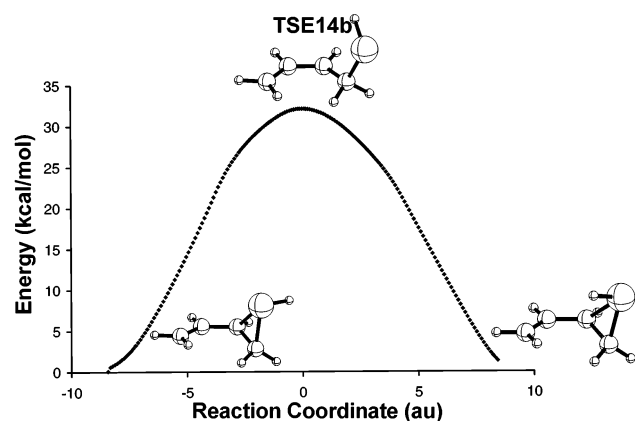

Figure 4. IRC interconverting **14a** and **b** via **TSE14b**.

Table 2. Selected Distances (Å) and Angles (deg) for **TSE14a**, **TSE14b**, **TS14a**, **TS14b**, and **TS14A(ai)**

	C1–C2	C2–C3	C1–P	C3–P	C2–C3–C4–P
TSE14a	1.384	1.399	4.231	2.799	−103.3
TSE14b	1.385	1.398	4.215	2.872	−99.0
TS14a	1.399	1.395	2.670	2.416	−64.3
TS14b	1.400	1.386	3.012	2.693	−68.3
TS14a(ai)	1.384	1.398	3.380	2.950	−41.3

On the basis of these data, it appears that the rearrangement of 2-vinylphosphirane into 3-phospholene proceeds primarily in a concerted manner via the *anti* isomer. P-epimerization between the *anti* and *syn* isomers has a slightly higher barrier ($\Delta\Delta E = 2.8-3.3$ kcal/mol), while rearrangement of the syn isomer into 3-phospholene is the most demanding process ($\Delta\Delta E = 7.4$ kcal/mol). These theoretical data are in remarkably good agreement with the elegant kinetic study of Richter, who showed that the *syn* isomer of the 1-*tert*-butyl derivative of **7** rearranges via the *anti* isomer to the corresponding 3-phospholene. Evidently, the concerted mechanistic pathway for the [1,3]-shift of vinylphosphiranes differs from that of the corresponding hydrocarbons, which favor a diradical-like pathway.

Cr(CO)₅-Complexed 2-Vinylphosphirane−3-Phospholene Rearrangement. Introducing the Cr(CO)₅ transition metal group not only stabilizes the organophosphorus compounds but also
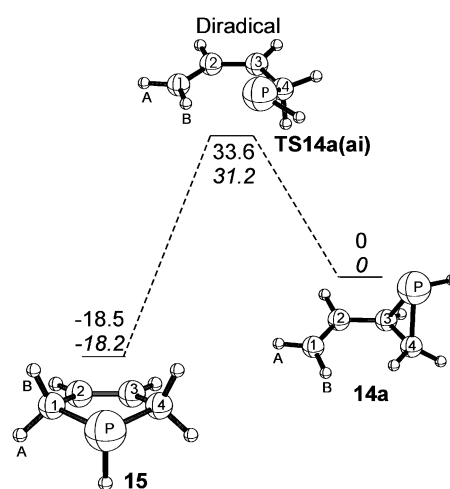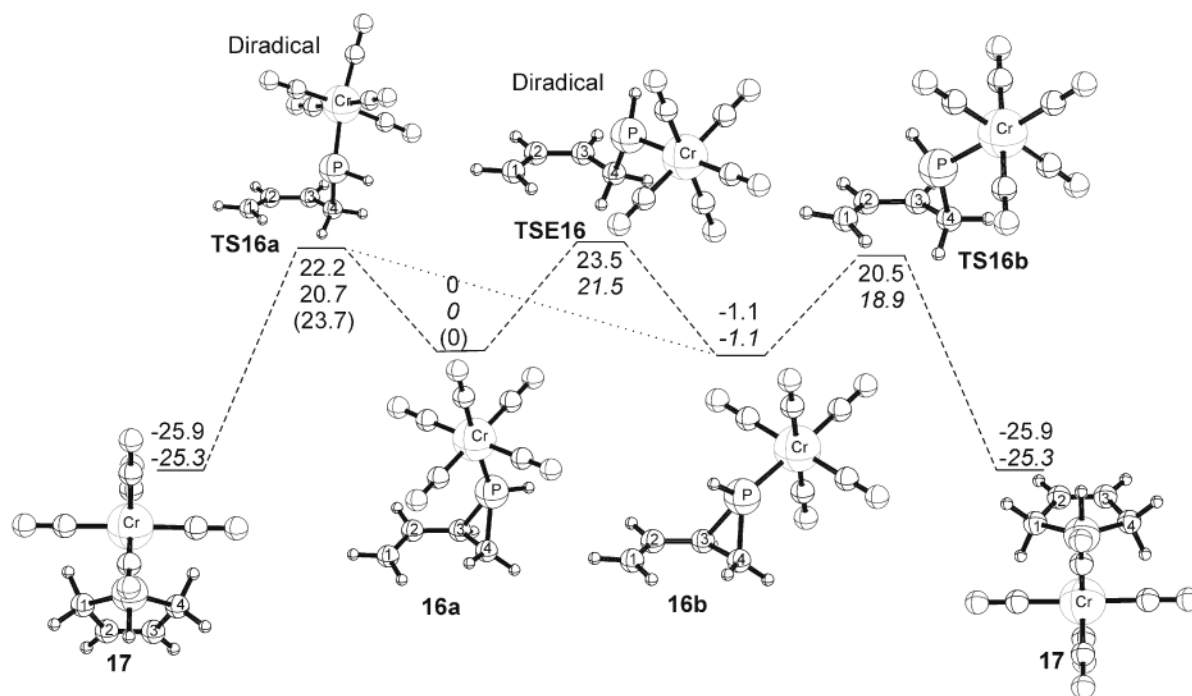

Figure 5. Relative B86-P88(*TZP*) energies (in kcal/mol) for the antarafacial rearrangement of 2-vinylphosphirane **14a** into 3-phospholene **15**. Temperature-corrected relative enthalpies are given in italics.
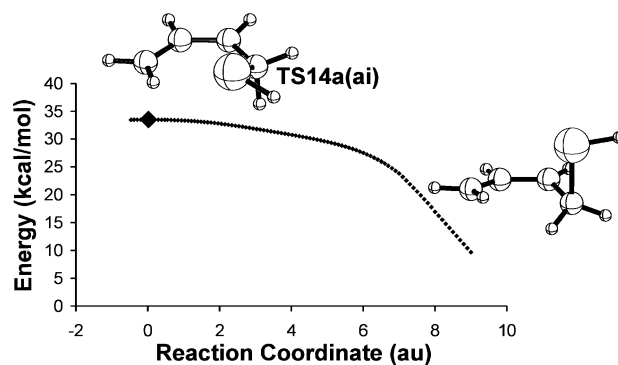
Figure 6. IRC starting from **TS14a** in the direction of **14a**.

changes the characteristics of the vinylphosphirane−phospholene rearrangement. Open-shell pathways without the presence of intermediates are again readily accessible, but a pericyclic mechanism still prevails albeit marginally. However, this concerted process is no longer competitive on additional phenyl substitution.

Figure 7. Relative B86-P88(*TZP*) energies (in kcal/mol) for the rearrangement pathways for Cr(CO)5-complexed 2-vinylphosphirane. Temperature-corrected relative enthalpies are given in italics, and relative DFT/MRCI energies are given in parentheses.

Table 3. Selected Distances (Å) and Angles (deg) for **TSE16**, **TS16a**, **TS16b**, and **TS18b**

	C1–C2	C2–C3	C1–P	C3–P	C2–C3–C4–P
TSE16a	1.381	1.401	3.781	2.866	−82.8
TS16a	1.376	1.406	3.583	2.790	−78.6
TS16b	1.381	1.404	3.084	2.652	−68.0
TS18b	1.377	1.404	3.787	2.863	−83.0

We start by inspecting in detail the effect of Cr(CO)5 complexation on the rearrangement. This is followed by a brief section that evaluates the influence of an additional phenyl substituent on the phosphorus to mimic more closely experimental systems.

A. Cr(CO)5 Group. The presence of this group slightly increases the energy difference between the *syn* and *anti* isomers of 2-vinylphosphirane to favor **16b** over **a** by 1.1 kcal/mol; anti-**16b** is the Cr(CO)5-complexed form of *syn*-**14b** because its Cr(CO)5 and vinyl groups are in an *anti* orientation (Figure 7). The two isomers interconvert by rotation of the HPCr(CO)5 unit around the P−C4 bond. Starting a clockwise motion from the most stable isomer (**16b**) leads to the open-shell transition structure **TSE16**. The diradical nature of this structure is reflected in its long P−C1 and P−C3 distances (3.781 Å, 2.866 Å) and large P−C4−C3−C2 dihedral angle (−82.8°) (Table 3). This P-epimerization requires 23.5 kcal/mol, which is much less than that needed for the uncomplexed vinylphosphirane. P-epimerization can also be accomplished by rotating the HPCr(CO)5 group of **16b** in a counterclockwise manner, but its energy profile is more complex. Even though the 1.3 kcal/mol more stable diradical-like transition structure (**TS16a**) has all the geometrical features associated with P-epimerization, such as long P−C1 and P−C2 distances (3.583 Å, 2.790 Å) and a large P−C4−C3−C2 dihedral angle (−78.6°), tracing its IRC leads instead to complexed 3-phospholene **17**, which is the thermodynamically favored product (ΔE = 25.9 kcal/mol). This identifies **TS16a** as a transition structure for the 2-vinylphos-
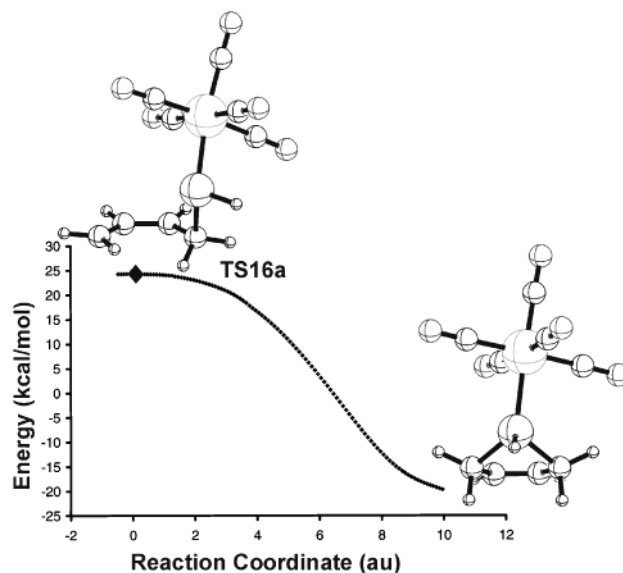
Figure 8. IRC for diradical transition state **TS16a**.

phirane−3-phospholene rearrangement. Very similar barrier heights are calculated for this process at DFT/MRCI and with the DFT spin projected method (Figure 7), both of which are much lower than the barrier for the concerted rearrangement of uncomplexed vinylphosphirane (29.3 kcal/mol). The diradical nature of the transition structure (and, thus, the long P−C1 and P−C3 distances) can be attributed to the steric bulk of Cr(CO)5, which prohibits the phosphorus atom from remaining close to the vinyl group. This diradical influence is reflected by the DFT/MRCI contributions, 0.7762 for the ground state and 0.0404 and 0.0718 for the singly and the doubly exited states, respectively. Surprisingly, tracing the IRC in the opposite direction was not successful because of the near zero slope of the potential energy surface around **TS16a** (Figure 8). For the

vinylcyclopropane–cyclopentene rearrangement, such a very flat potential energy surface seemingly results in the interconversion of diradical-like transition structures and/or in the bifurcation of reaction paths. A similar situation likely exists for **TS16a**, which, in fact, would connect it to both vinylphosphiranes **16a** and **b**. This behavior can also be surmised as follows: rotation of the heavy HPCr(CO)$_5$ group of **16a** in a clockwise manner around the P–C4 bond leads either to ring closure (**17**) if the P–C1 interaction dominates or to P-epimerization (**16b**) if the process is governed by the momentum of the outward rotating heavy transition metal group. Establishing the distribution over these two reaction channels requires dynamic trajectory studies, analogous to those reported for vinylcyclopropane but, unfortunately, these are currently well beyond our computational means.

The energetically most favorable process is the concerted [1,3]-rearrangement of *anti*-vinylphosphirane **16b**, which has a barrier of 20.5 kcal/mol. Transition structure **TS16b** differs most noticeably from the 1.7 kcal/mol higher lying diradical-like transition structure **TS16a** by its 0.499 Å shorter P–C1 distance (Table 3), reflecting better overlap between the orbitals on phosphorus and those on the vinyl unit.

In summarizing this section, the following observations are made: (1) P-epimerization between the *syn* and *anti* isomers of Cr(CO)$_5$-complexed 2-vinylphosphirane occurs in a diradical fashion without an intermediate, just like that for both the uncomplexed system and the C-epimerization of vinylcyclopropane. (2) *Anti* isomer **16b** has the lowest barrier for a [1,3]-sigmatropic rearrangement to 3-phospholene. The pathway is a pericyclic one. (3) *Syn* isomer **16b** has a modestly higher rearrangement barrier ($\Delta\Delta E$ < 1.5 kcal/mol) and a pathway that is instead nonpericyclic. (4) The transition structure for this process can bifurcate to give P-epimerization.

The dichotomy of pericyclic versus nonpericyclic pathways is in line with the observed rearrangements of W(CO)$_5$-complexed vinylphosphirane derivatives. However, reactions such as **9** → **10** and *anti*-**11** → *syn*-**11** illustrate a preference for the *syn* isomer and its [1,3]-sigmatropic shift, whereas the depicted energy profile suggests a slightly lower barrier for the anti isomer. The difference must be attributed to the presence of a P-phenyl substituent in the experimental systems.

B. P-phenyl Group. P-phenyl substitution is expected to hamper the concerted rearrangement of **16b** because of the added congestion in the transition structure. A limited evaluation of the potential energy surface (**18b** → **19**), excluding frequency calculations and the tracing of IRCs, validates this assumption. Phenyl substitution raises the barrier for rearranging the *anti* isomer by 3.7 kcal/mol and also changes its nature from a pericyclic to a diradical-like pathway (Figure 9), but its effect on the barrier height for the same process of the *syn* isomer is more modest ($\Delta\Delta E$ = 1.5 kcal/mol). **18b** is still slightly more stable than *syn* form **18a** $\Delta\Delta E$ = 0.2 kcal/mol).

Evidently, the [1,3]-sigmatropic rearrangement of Cr(CO)$_5$-complexed vinylphosphiranes to their phospholenes is dominated by single-step diradical-like processes displaying torquoselectivity.

Influence of the Cr(CO)$_5$ Group. When compared to its hydrocarbon analogues, the pericyclic nature of the uncomplexed 2-vinylphosphirane–3-phospholene rearrangement is attributable to its "softer" potential energy surface (the P–C bond is much
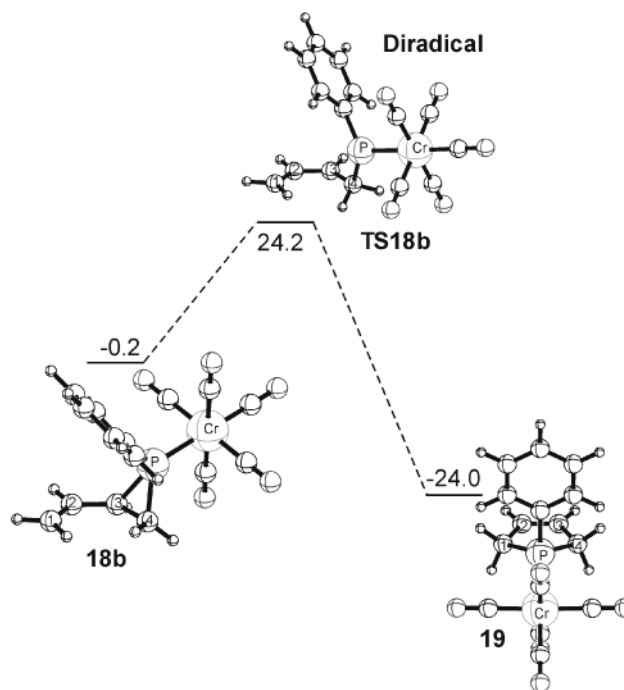
Figure 9. [1,3]-Rearrangement of Cr(CO)$_5$-complexed *anti*-1-phenyl-2-vinylphosphirane. Relative DFT energies are in kcal/mol.

Table 4. Decomposition of Complexation Energies in kcal/mol

	16a	17	TS16b
ΔE_{bond}	−30.2	−37.5	−46.4
1. ΔE_{oi}	−49.2	−52.3	−71.3
ΔE_{σ}	−30.7	−34.4	−41.8
ΔE_{π}	−20.9	−19.6	−26.6
2. ΔE_{steric}	17.4	13.2	20.3
3. ΔE_{prep}	1.6	1.6	4.5

weaker than the C–C bond) and diffuse orbitals on phosphorus (enabling better overlap over a longer distance). Adding a transition metal group to the phosphorus atom stabilizes all species, but transition structures most and some more than others (cf. Figures 3 and 7). The origin of this effect can be explained from the analysis of the M=P decomposition energies for the minima **16a** and **17** and transition structure **TS16b**, that are summarized in Table 4.

A. 2-Vinylphosphirane and 3-Phospholene. Complexating the Cr(CO)$_5$ group to the trivalent phosphorus of 2-vinylphosphirane (**14a** → **16a**) results in a stabilization of 30.2 kcal/mol, as determined by the complexation energy (Table 4). For phospholene, an even larger stabilization is found of 7.4 kcal/mol on comparing the relative energies of both **15** and **17** and of 7.3 kcal/mol as indicated by the complexation energy. Thus, transition metal complexation increases the exothermicity for rearrangement and, thereby, reduces the activation energy for this process.

Decomposition of the complexation energies shows **17** to have a 3.1 kcal/mol larger orbital interaction energy (ΔE_{oi}) than **16a**, mainly because of the difference in σ-donation (P(p)-Cr (d$_{z^2}$)) but also because the 4.2 kcal/mol smaller steric interaction component (ΔE_{steric}) contributes; the preparation energies (ΔE_{prep}) are similar for the two structures. Thus, both σ-electronic and steric factors underlie the larger stabilization of the five-membered ring system.
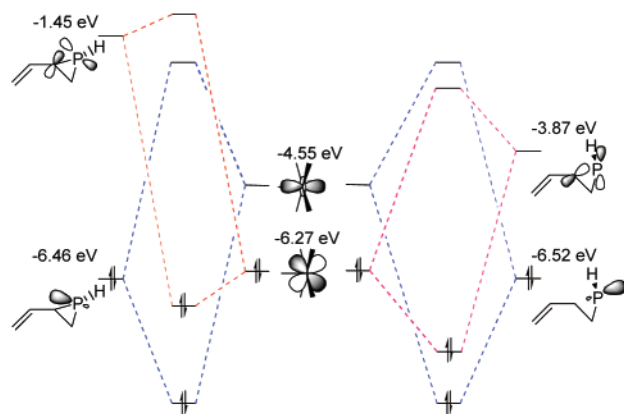
Figure 10. MO interaction diagram for the transition metal complexation of vinylphosphirane **16a** (left) and transition structure **TS16b** (right) with σ-donation shown in blue and π-back-donation in red.

B. Transition Structures. The $Cr(CO)_5$ group reduces the barrier for pericyclic rearrangement (involving **TS16b**) by 16.2 kcal/mol, which is much more than that expected from the increased exothermicity. This enhanced stabilization energy ($\Delta E_{bond} = 46.4$ kcal/mol) results largely from a 20−30% increase both in σ-bonding and in π-back-bonding as compared to the cases of **16a** and **17**, despite larger ΔE_{steric} and ΔE_{prep} components; elongation of the phosphirane P−C3 bond results in the stabilization of the LUMO and, thus, enhanced π-interaction. A comparison of the orbital interaction diagrams for **16a** and **TS16b**, given in Figure 10, highlights their different stabilization energies.

Conclusions

This density functional theory study shows that the established complexity of the [1,3]-sigmatropic rearrangement that converts vinylcyclopropane into cyclopentene is similarly operative in its phosphorus analogue, although the "free" and the $Cr(CO)_5$-complexed systems display subtle yet important mechanistic differences with the hydrocarbons. Just like the hydrocarbons, no intermediates could be located for either organophosphorus system, neither for the rearrangement nor for the epimerization at the phosphorus center. The distinguishing feature for all rearrangements is whether they occur in a pericyclic or non-pericyclic manner. Because the barriers for the [1,3]-sigmatropic rearrangements are of similar height when compared to those for P-epimerization, there is an appearance of bifurcation of reaction paths with torquoselectivity being a distinguishing factor.

The rearrangement barriers for vinylphosphiranes are smaller than those of the corresponding hydrocarbons, and still lower barriers are found on complexating the phosphorus atom with the $Cr(CO)_5$ group. The stabilizing effect of the transition metal group on the phosphorus center is very prominent in the transition structures through enhanced σ-bonding and π-back-bonding.

The phosphorus substituent(s) has (have) a distinguishing role on the mechanism of the rearrangement. Both *anti-* and *syn*-2-vinylphosphirane convert to 3-phospholene in a concerted pericyclic manner, with that of the *anti* isomer favored by 7.5 kcal/mol. Because this barrier of 29.3 kcal/mol is only slightly less than the 32.1 kcal/mol barrier for *syn* ⇌ *anti* isomerism, the *syn* form will preferentially convert via the *anti* isomer to the 18.5 kcal/mol more stable five-membered ring. Larger substituents on phosphorus are expected to enhance the discrimination between the *syn* and *anti* forms, which agrees with experimental data reported by Richter.

Adding the stabilizing $Cr(CO)_5$ group to the phosphorus atom not only reduces these barriers (to 20−23 kcal/mol) and increases the exothermicity (by 7−8 kcal/mol) for formation of the complexed 3-phospholene but also results in competing pericyclic and nonpericyclic reactions that are isoenergetic with epimerization at the phosphorus center. Steric congestion caused by the bulky transition metal group is a contributing factor. Thus, adding $Cr(CO)_5$ to *syn*-2-vinylphosphirane results in a diradical-like [1,3]-sigmatropic rearrangement that is slightly disfavored (by 0.6 kcal/mol) from that of its isomer which remains pericyclic. Additional substitution of the phosphorus atom by a phenyl group (instead of hydrogen) heightens these barriers and gives diradical character to the rearrangement of both the *anti* and *syn* forms. Structural analysis of the nonphenyl system and tracing of the intrinsic reaction coordinates for the diradical-like reaction paths indicate the importance of the torquoselectivity of the $Cr(CO)_5$-complexed phosphorus group.

We make the following summarizing observations. The last two decades have shown that low-valent organophosphorus reagents/compounds behave like their hydrocarbon analogues. The present study shows that also rearrangements of reaction products, such as the [1,3]-sigmatropic shift, are likewise remarkably similar.

Supporting Information Available: Cartesian coordinates, energies, and thermal corrections of all stationary points. $\langle S^2 \rangle$ values, number of reference determinants, and occupation numbers for selected points. This material is available free of charge via the Internet at http://pubs.acs.org.

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