Epimerization of Cyclic Vinylphosphirane Complexes: The Intermediacy of Biradicals

Bing Wang, Charles H. Lake,† and Koop Lammertsma*

Contribution from the Department of Chemistry, University of Alabama at Birmingham, UAB Station, Birmingham, Alabama 35294

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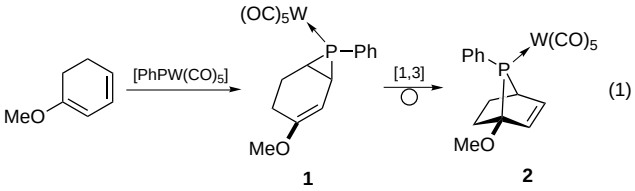
Abstract: The phosphinidene complex Ph−P−$W(CO)_5$ reacts with cyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, and 1,3-cyclooctadiene to give in each case isomeric mixtures of *syn*- and *anti*-vinylphosphiranes. With longer reaction times and/or higher reaction temperatures, the anti adducts isomerize to the syn adducts. These epimerizations are likely to proceed via biradical intermediates. Only the *syn*-vinylphosphirane of 1,3-cyclohexadiene undergoes a [1,3]-sigmatropic shift to yield a *syn*-phopholene. The dichotomy of biradical and concerted mechanisms is discussed in relationship with the analogous mechanism for the vinylcyclopropane → cyclopentene rearrangement.

Introduction

Recently, we reported on the syntheses of vinylphosphiranes and their subsequent rearrangements to phospholenes.[1,2] A remarkably high stereoselectivity was observed for both the Ph−P−$W(CO)_5$ phosphinidene addition to 1-methoxy-1,3-cyclohexadiene and the rearrangement of the resulting vinylphosphirane (eq 1).[1] Of particular interest is the formal [1,3]-sigmatropic shift which was shown to occur exclusively with inversion of the P-center. The observed high stereoselectivity suggests a concerted mechanism. This result is surprising because the steric crowding at the P-center is expected to hinder an inversion. A sterically less demanding process would involve a ring-opening and ring-closure sequence. However, such a process is expected to favor retention of the P-configuration, which contrasts with the observed data.



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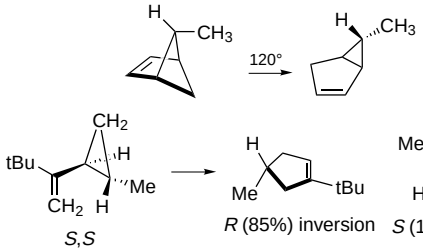
Insight may be obtained from the related hydrocarbon rearrangements for which the issue of concerted versus biradical mechanisms has been intensely studied. The rich literature on the [1,3]-sigmatropic shift of vinylcyclopropanes to cyclopentene and related cis−trans isomerizations, starting as early as 1959,[3] is particularly informative.[4] Numerous reactions were studied to validate the Woodward−Hoffmann rules for [1,3]-sigmatropic shifts. Examples have been reported that support either a concerted or a biradical pathway, while this distinction is not clear in some cases. Inversion of the apical cyclopropane carbon (*si*, suprafacial-inversion) is considered to be the mechanistic evidence for the one-step concerted process of which the reactions shown in eqs 2 and 3 are representative.[5]



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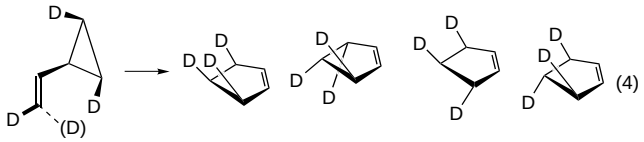
However, reactions have also been reported that show the [1,3]-shift of isotopically labeled vinylcyclopropanes to occur with *si*, *sr* (r = retention), *ar* (a = antarafacial), and *ai* stereochemistry.[6] An example is shown in eq 4. In these cases the mechanistic pathway is considered to involve a biradical intermediate. An elegant illustration of a biradical process is the thermally or photochemically induced "walk" or circumambulatory rearrangement of bicyclo[4.1.0]hepta-2,4-diene which occurs though mainly with inversion of the apical cyclopropane carbon (eq 5).[7] Using an optically active diazo precursor to



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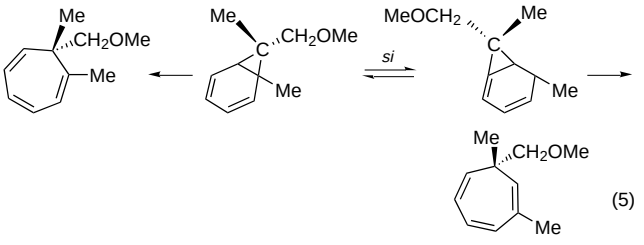

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† Author to whom correspondence regarding the X-ray crystallographic data should be addressed.

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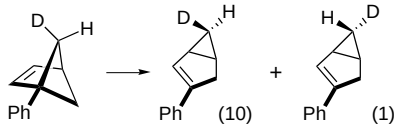
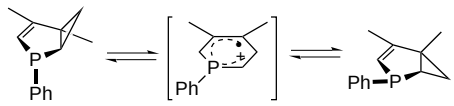
generate the biradical intermediate, Klärner showed that its ring closure occurs faster than the rotation of the single bond. Carpenter[8] has highlighted cases where the distinction between biradical and concerted processes is less clear, such as for the thermal isomerization of 1-phenylbicyclo[2.1.1]hex-2-ene-*endo*-5-*d*. Its temperature-independent 10:1 product ratio for the formation of the preferred (concerted) endo over the exo (biradical) epimer (eq 6) defies differences in activation enthalpies for product formation via the concerted as well as the biradical pathway.



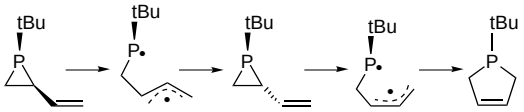
(6)

If biradical intermediates are prominent in cyclopentene ⇌ vinylcyclopropane rearrangements, they can also be expected in analogous heterocyclic isomerizations. In fact, this has been demonstrated for the 1,5-electrocyclization of homophospholes (eq 7), homopyrroles, homothiophenes, and homofurans.[9] Thermal isomerizations of vinylaziridines have been shown to yield 3-pyrrolines,[10] but no mechanistic detail was provided in these studies. The same applies to the Cope rearrangements of divinylaziridines[11] and the thermal isomerizations of vinylacetyloxiranes.[12]



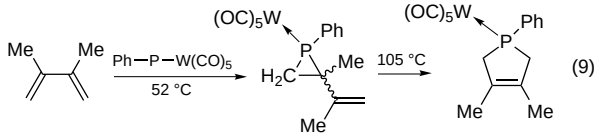
(7)

Even less information is available on the vinylphosphirane ⇌ phospholene rearrangement. In an elegant kinetic study, Richter postulated that the thermal isomerization of (*Z*)-1-*tert*-butyl-2-vinylphosphirane to the corresponding phospholene involves sequential first-order reactions via biradical intermediates (eq 8).[13] A key component in this process is the observed



(8)

initial P-epimerization of the phosphirane, which is best explained via a ring-opening−ring-closure sequence. Such cis−trans isomerizations, which obviously make mechanistic interpretations more difficult, are also well-known in the noted vinylcyclopropanes.[6,14] Marinetti and Mathey[15] reported in an exploratory study that Ph−P−W(CO)$_5$ reacts at 55 °C with conjugated dienes to give 1,2-adducts, which in the case of 2,3-dimethyl-1,3-butadiene was shown to rearrange to 3-phospholene at temperatures ≥95 °C (eq 9). No mechanistic details



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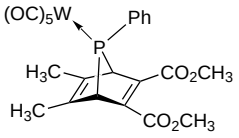
were provided. The same group[16] reported later on the similar addition of NEt$_2$−P−W(CO)$_5$ at 70 °C, in which case only the phospholene was isolated and not the vinylphosphirane. Our noted study on a cyclic W(CO)$_5$-complexed vinylphosphirane, summarized in eq 1, suggests a concerted isomerization pathway. While this system had the advantage of restricted syn ⇌ anti isomerization due to the bicyclic structure, it is clear that the nature of these [1,3]-sigmatropic shifts warrants closer scrutiny. We report here on the Ph−P−W(CO)$_5$ addition to other conjugated cyclodienes and their subsequent isomerizations. Because of their importance, the structural assignments are summarized in the Results section prior to discussing the isomerizations.

Results

In our approach, we first conducted 1,2-cycloadditions to 1,3-cycloalkadienes (**5**) with the terminal phosphinidene complex Ph−P−W(CO)$_5$, which is generated in situ from thermal degradation of the corresponding 7-phosphanorbornadiene precursor **4**. The resulting vinyl phosphiranes (obtained in ca



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60−80% isolated yields) were then subjected to thermal isomerizations. The product assignments are based on ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data, except for the anti isomer **5b** for which also a single-crystal X-ray structure was determined.

1,3-Cycloalkadienes. Reaction of **4** with cyclopentadiene in toluene at 55 °C with 10% of CuCl as catalyst gave a 4:1 isomeric mixture of the vinylphosphiranes **5a** and **5b**, respectively. The major product is syn isomer **5a**; syn is defined as having the P−W(CO)$_5$ group over the hydrocarbon ring. The structural assignment of the anti isomer **5b** was ascertained by a single-crystal X-ray structure determination, which is shown in Figure 1. The assignment of the syn and anti isomers are further supported by their ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data. For example, the chemical shift difference between the olefinic protons of **5b** (δ 5.17 and 5.73 ppm) and those of isomer **5a** (δ 5.80 and 6.45 ppm) is attributed to the shielding effect of the bridging *P*-phenyl; this group is located over the hydrocarbon ring in the anti isomer **5b**. A distinction between the syn and anti isomers is also found in the ^{31}P NMR chemical shifts and the ^1J(P−W) coupling constants of all the vinylphosphiranes of this and earlier studies. The ^1J(P−W) coupling constant of the syn isomer is in all cases significantly larger than that of the anti isomer (*vide infra*) with a difference of 17.5 Hz for the vinylphosphiranes **5a** and **5b**. The difference in ^{31}P NMR chemical shifts is less clear, although the anti isomer has in all cases the more shielded resonance. In the ^{13}C NMR spectrum the magnitude of the ^2J(C−P) coupling constant of the CH$_2$ group is characteristic for the identification of the syn vs anti form with the anti isomer having the larger coupling. In accord with our previous work and Mathey's earlier studies on the

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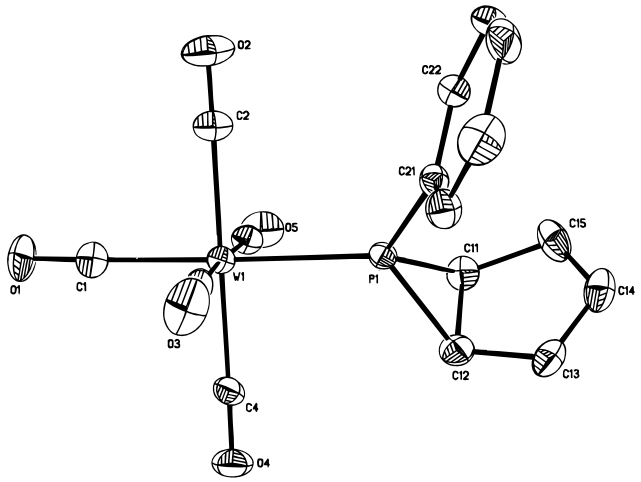
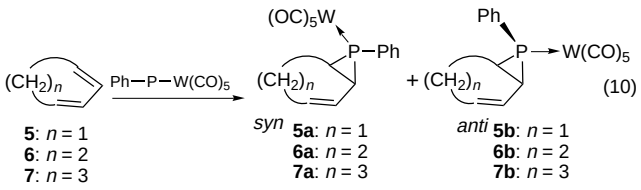


Figure 1. ORTEP representation of **5b**.

phosphiranes of 1,4-cyclohexadiene,[18] we find that the syn isomer shows no ^2J(C−P) coupling with the CH_2 group, while the coupling constant of the anti isomer is 8.4 Hz.[2,17] Finally, we note the unexpectedly large coupling constants of 36.9 and 30.8 Hz for the two olefinic hydrogens in **5a**. These are tentatively assigned to long-range P−H couplings. In earlier work on phenyl-substituted phosphiranes we have shown the presence of a W-type conjugation between the *P*-phenyl group and a *trans*-phenyl group of the 3-membered phosphirane ring. Such an electronic effect may underlie these large couplings.

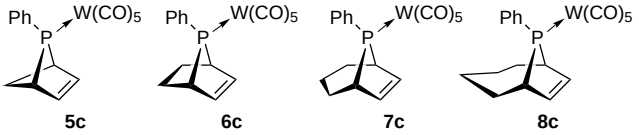
The same 1,2-addition reaction with 1,3-cycloheptadiene gave a ca. 7:1 mixture of the syn and anti vinylphosphiranes **7a** and **7b**, respectively (eq 10). Only for the syn isomer could all NMR



spectroscopic data be obtained. The small ^2J(C−P) coupling constant of 4.3 Hz for the CH_2 group substituted at the phosphirane ring and the larger ^1J(P−W) coupling constant of 265.5 Hz are assigned to isomer **7a**. The difference in the P−W coupling constants between **7a** and **7b** is 15.9 Hz.

A ca. 2:3 anti−syn isomeric mixture **8a,b** is obtained for the phosphinidene addition to 1,3-cyclooctadiene. The assignments are again based on the NMR characteristics, which are (1) the more shielded ^{1}H NMR chemical shifts for the olefinic hydrogens, (2) the absence of a ^2J(C−P) coupling constant for the α-CH_2 of the syn isomer (versus 12.3 Hz for **8b**), and (3) the 9.1 Hz larger ^1J(P−W) coupling constant of 261.5 Hz for the syn isomer.

P-Epimerizations. Heating of the isomeric mixtures of the vinylphosphiranes **5ab**, **7ab**, and **8ab**, obtained from the phosphinidene additions, for up to 4 h in toluene at 60 °C led in each case to a slow conversion of the anti isomer **b** into the syn isomer **a**. These P-epimerizations were also conducted for the isolated anti isomers **5b** and **8b** under the same reaction conditions. The isomerizations were monitored by ^{31}P NMR spectroscopy using reaction aliquots. They showed the disappearance of the ^{31}P chemical shift of the anti form (*i.e.*, −149 (**5b**), −157 (**7b**), and −168 ppm (**8b**)) with the concurrent appearance of the resonance of the corresponding syn form (*i.e.*, −146 (**5a**), −142 (**7a**), and −153 ppm (**8a**)) in addition to formation of some side products.[19] For example, the syn:anti ratio changed for **5ab** from 0.4 (1 h) to 0.8 (2 h), for **7ab** from 2 (1 h) to 7 (4 h), and for **8ab** from 0.1 (45 min) to 0.4 (1.5 h) to 1 (4 h). These anti → syn epimerizations occur faster at higher temperatures. After 4 h at 110 °C the conversions were nearly complete with syn:anti ratios of ca. 10. Under these conditions the ^{31}P NMR spectra did also show, among various decomposition products, indications of minute amounts (too small to integrate) of products attributable to [1,3]-sigmatropic shifts. Thus, resonances were observed at δ 51.1 and 95.8 ppm for 1,3-cyclopentadiene, at δ 58.7 and 93.8 ppm for 1,3-cyclooctadiene, and at δ 55.0 and 97.3 ppm for 1,3-cyclooctadiene. These high-field resonances at δ 50−60 ppm, which compare with the δ 65.7 ppm for **3**, could be from the *syn*-phospholenes **5c**, **7c**, and **8c**, respectively. It is noted that overnight heating of the *syn*-phosphiranes at 90 °C did not lead to increased formation of the 1,3-shift products but instead to increased decomposition.



In earlier work on 1,3-cyclohexadiene, we reported on the isomerization of the *syn*-vinylphosphirane **6a** to the bicyclic phospholene **6c**. The anti isomer **6b** was thought to decompose; it diminished during reaction. In light of the results on the 5-, 7-, and 8-membered 1,3-cycloalkadienes, we repeated this earlier work, using both the isolated syn and anti isomers **6a** and **6b** in separate experiments. By monitoring the ^{31}P NMR spectra, these experiments showed unequivocally that the *anti*-vinylphosphirane **6b** (δ −139.9 ppm) epimerizes to the syn isomer **6a** (δ −137.1 ppm) and that this syn isomer rearranges to the *syn*-phospholene **6c** (δ 66.7 ppm) and possibly some of its anti form (δ 97.9 ppm). The *syn*-phosphirane **6a** does not epimerize to its anti form **6b**.

Structures. The conformational assignments in this study are of imminent importance. To make these unequivocal, a single-crystal X-ray structure was determined for the *anti*-phosphirane isomer **5b** (Figure 1) with subsequent verification of its ^{31}P NMR chemical shift (δ = −149.0 ppm) using the same crystal. Selected interatomic distances and angles are summarized in Table 1 (supporting information). Structural features are highlighted in relationship with those of syn **1**.[1] The anti conformation of **5b** is confirmed. The cyclopentene ring is planar with an average deviation from the plane of 0.007 Å. The plane formed by this ring intercepts the one formed by the syn *P*-phenyl group with an angle of 37.4°. This contrasts with the parallel orientation in syn **1**, in which these groups have an antiperiplanar arrangement. There is no apparent repulsion between the *P*-phenyl substituent and the 5-membered cyclopentene ring in **5b**. The angle of the intercept between the phosphirane and cyclopentene rings of 117.1° is normal and also the P-bonding angles are as expected, *i.e.*, the phosphirane CPC angle is 50.1(4)° and the WPC(phenyl) angle is 120.1-(3)°.[1,20]

Examination of the bond distances and angles in the crystal structure of **5b** shows that it exhibits static disorder. This is

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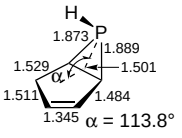
(18) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1985**, *107*, 4700.

(19) The epimerizations of **5**−**8** constitute 70−90% of the total isomerizations, as based on ^{31}P NMR data, with 60−80% isolated yields for the epimers.

(20) Hung, J.-T.; Yang, S.-W.; Gray, G. M.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 6786.

apparent from the identical bond lengths of 1.378(16) Å for C(13)−C(14) and 1.381(20) Å for C(14)−C(15), as they both represent an average value for a single and a double bond. The structure has also two equivalent C−C bonds connected to the CCP ring (*i.e.,* 1.479(14) Å for C(12)−C(13) and 1.503(13) Å for C(11)−C(15)), and the two phosphirane P−C bonds of equal length (*i.e.,* 1.836(9) Å for P−C(11) and 1.827(9) Å for P−C(12)). Apparently, there are two conformations of **5b** randomly distributed at equivalent sites in the crystal. This results in an averaging of the two structures and explains the large estimated standard deviations despite the small residual index of 2.85%. The static disorder is also apparent from a comparison with the crystallographic data of **1**. For example, the double bond of 1.319(9) Å in structure **1** is separated by a short C−C bond of 1.469(9) Å from the phosphirane ring, which has two different P−C ring bonds of 1.816(6) and 1.851(5) Å. This comparison between anti **5b** and syn **1** suggests that these vinylphosphiranes have indeed the same structural features.

To further examine the structural characteristics of **5b**, an ab initio molecular orbital geometry optimization at MP2/6-31G*, using the Gaussian 94 suite of programs,[21] was conducted on the parent system **9**. This structure differs from **5b** in that it



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(a) lacks the $W(CO)_5$ group and (b) has a P−H substituent instead of a P−Ph group. Its main geometrical features are given in the displayed structure. These show a relatively short C−C bond of 1.484 Å between the 1.345 Å double bond and the phosphirane ring, thereby underscoring the disorder in the crystal structure of **5b**. The geometrical parameters of unsubstituted **9** are similar to those of the crystal structure of the larger ring system, **1**.

Discussion

Addition of the phosphinidene Ph-P-$W(CO)_5$ to 1,3-cycloalkadienes readily provides isomeric mixtures of *anti*- and *syn*-vinylphosphiranes of varying ratios. The exciting result of the present study is the isomerization of the anti isomer to the syn isomer. This process represents an epimerization at the phosphorus center. These results are consistent for the 5-, 6-, 7-, and 8-membered ring systems with the exception that the *syn*-vinylphosphirane of 1,3-cyclohexadiene undergoes a subsequent [1,3]-sigmatropic shift to a phospholene.

The epimerizations are indicative of a biradical process.[22] That is, the phosphirane undergoes a ring opening to a biradical intermediate which closes again to return to the phosphirane ring. In this process, the syn and anti isomers interconvert by C−P bond rotation in the biradical species. Because the isomerizations yield in all cases the *syn*-vinylphosphiranes, these appear to be the thermodynamically preferred products except for 1,3-cyclohexadiene in which case the final product is phospholene **6c**. A similar biradical process was previously proposed by Richter to explain the syn → anti epimerization of the uncomplexed (*Z*)-1-*tert*-butyl-2-vinylphosphirane; anti is here defined as having the ring hydrocarbon substituents in a trans configuration (eq 8).

Surprising in these results is that seemingly both biradical and concerted pathways are available for the rearrangement of vinylphosphiranes. Thus, in the case of the 5-, 7-, and 8-membered 1,3-cyclodienes the anti → syn epimerization is evidence for the exclusive biradical reaction channel, while for the 1,3-cyclohexadiene the formation of a *syn*-phospholene suggests a concerted [1,3]-sigmatropic shift. The latter reaction does obscure the concurrent anti → syn epimerization of the vinylphosphiranes. Analogous to the Ph-P-$W(CO)_5$ addition to 1-methoxy-1,3-cyclohexadiene, which gives in ≥95% the syn adduct (within 45 min at 55 °C), the same addition with the nonactivated, unsubstituted system (**6**) affords a mixture of the *anti*- and *syn*-phosphiranes of which the syn isomer becomes the dominant product with longer reaction times and higher temperatures. In fact, the anti isomer **6b** is no longer present in the reaction mixture after 5 h at 90 °C while the conversion of the syn isomer **6a** to the phospholene **6c** is still incomplete, *i.e.,* the **6a**:**6c** ratio is 4. It is then evident that the vinylphosphiranes of all 1,3-cycloalkadienes **5**−**8** undergo anti → syn epimerizations which must proceed via biradical intermediates.

The syn isomers are the thermodynamically preferred products in these epimerizations. Their configuration enables a W-type conjugation between the vinyl group and the anti *P*-phenyl group. The presence of such a stabilizing effect has been demonstrated for phosphiranes with two trans phenyl substituents.[25] Apparently, this electronic stabilization overcomes any steric interaction that may be attributed to the bulky transition metal group that is located in the endo position. In fact, it may be argued that since the P−W bond is much longer than the P−C(phenyl) bond, the $W(CO)_5$ group in **5a** might interact less with the cyclopentene ring than the *P*-phenyl substituent in **5b**.

If biradicals are prevalent in the epimerizations, then shouldn't they also be present in the conversion of the vinylphosphiranes to the phospholenes? As noted, biradicals have been implicated in vinylcyclopropane → cyclopentene rearrangements. However, the [1,3]-sigmatropic shifts that take place in **1** → **2** and **6a** → **6c** seem to be best explained as pericyclic reactions. Firstly, these transformations occur with apparent inversions of the P-center in accord with such a *si* process. Secondly, a biradical process would be expected to give significant amounts of the anti isomers of **2** and **6c** assuming that the P−C bond breaking/making process is faster than the P−C bond rotation. The question can be raised, however, whether such anti isomers are in fact the primary rearrangement products, which rapidly undergo an anti → syn epimerization under the reaction conditions to give the thermodynamically more stable syn products. Whereas this would explain the observed products, such a multistep process is an unlikely event. Firstly, the anti → syn epimerization of the phospholenes and that of the

(21) Gaussian 94 (Revision B), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1995.

(22) A concerted epimerization is unlikely. The inversion barrier for the parent uncomplexed phosphirane (C_2PH_5) is estimated to be 68 kcal/mol at MP2/6-31G*.[23] With an additional $W(CO)_5$ group such a C_{2v} symmetrical transition is not possible and a "C_s symmetrical" transition is required, which is a much higher energy process. Such an edge inversion for the parent phosphirane is estimated at 127 kcal/mol (MP2/6-311G**). A biradical process is much less energy demanding. The average P−C bond strength is estimated to be only 63 kcal/mol.[24] Moreover, homolytic P−C bond cleavage is aided by the relief of ca. 20 kcal/mol in strain energy from the phosphirane[23] and by the additional allylic stabilization in the resulting diradical.

(23) Bachrach, S. M. *J. Phys. Chem.* **1989**, *93*, 7780.
(24) Huheey, J. E. *Inorganic Chemistry*; Harper & Row: New York.
(25) Hung, J.-T.; Lammertsma, K. *J. Organomet. Chem.* **1995**, *489*, 1.

vinylphosphiranes would formally have one common biradical intermediate. In the absence of memory effects, the *anti*-phosphirane **6b** is then expected to directly yield *syn*-phospholene **6c**. This is not corroborated by the facts. Secondly, the epimerization of the thermodynamically preferred phospholenes is expected to be slower than that of the vinylphosphiranes.

These data on the isomerizations of phosphinidene-diene adducts show that biradicals are viable intermediates. This added dimension is currently being explored in our laboratories.

Conclusion. The important observation made in this study is that $W(CO)_5$-complexed vinylphosphiranes are subject to epimerization at the P-center. Anti isomers are converted to the syn forms, likely by way of a biradical intermediate. Only the syn adducts of 1,3-cyclohexadienes isomerize to phospholenes, and this process may proceed via a concerted pathway.

Experimental Section

NMR spectra were recorded on a GE NT-300, wide-bore FT-NMR spectrometer. Chemical shift are referenced in ppm to internal $(CH_3)_4$-Si for the ^1H and ^{13}C NMR spectra and external 85% H_3PO_4 for the ^{31}P NMR spectra. Downfield shifts are reported as positive. Product compositions were determined from integration of ^{31}P NMR spectra. IR spectra were recorded on a Nicolet IR44 spectrometer. Mass spectra were recorded on a HP 5985 at 70 eV. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. All materials were handled under an atmosphere of nitrogen. Reagents and solvents were used as purchased, except for THF, which was distilled from sodium benzophenone prior to use. Chromatographic separations were performed on silica gel columns (230−400 mesh, EM Science). The synthesis of [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten, **4**, is described in ref 26. The synthesis of *syn*- and *anti*-(6-phenyl-6-phosphabicyclo[4.1.0]hepta-3-ene)pentacarbonyltungsten **6a,b** has been described previously.[2,27]

(6-Phenyl-6-phosphabicyclo[3.1.0]hexa-3-ene)pentacarbonyltungsten (5a,b). Complex **4** (1.00 g, 1.53 mmol) and 1,3-cyclopentadiene (0.40 g, 6.12 mmol) were heated at 60 °C in toluene with CuCl (100 mg, 1.0 mmol) for 1.5−2 h. The reaction mixture was filtered, evaporated to dryness, and chromatographed on silica gel with hexanes to yield 0.46 g (60.4%) of a 4:1 mixture of *syn*-**5a** and *anti*-**5b**, based on integration of their ^{31}P NMR resonances. Fractional crystallization from hexanes gave **5a** as colorless crystals: mp 58−60 °C; ^{31}P NMR (C_6H_6) δ −146 ($^1J(^{31}P-^{183}W)$ = 268.5 Hz); ^{13}C NMR ($CDCl_3$) δ 135.1 (d, $^2J(C-P)$ = 10.1 Hz, C═CH), 130.5 (d, $^3J(C-P)$ = 2.0 Hz, C═CH), 36.4 (s, CH_2), 37.6 (d, $^1J(C-P)$ = 14.0 Hz, CHP), 27.6 (d, $^1J(C-P)$ = 13.7 Hz, CHP), 129.0−132.1 (m, phenyl), 195.9 (d, $^2J(C-P)$ = 8.0 Hz, cis CO), 197.9 (d, $^2J(C-P)$ = 31.4 Hz, trans CO); ^1H NMR ($CDCl_3$) δ 7.1−7.5 (m, 5H, phenyl), 6.45 (dd, $^3J(H-P)$ = 36.9 Hz, $^2J(H-H)$ = 4.5 Hz, 1H, CH═), 5.80 (d, $^4J(H-P)$ = 30.8 Hz, 1H, CH═), 3.07−2.83 (m, 2H, CH_2), 2.66 (t, $^2J(H-P)$ = 16 Hz, 1H, CHP), 2.45 (t, $^2J(H-P)$ = 7.5 Hz, 1H, CHP); MS (^{184}W) *m/e* (relative intensity) for **5a**,**b**: 498 (M^+, 20), 414 (M − 3CO, 5), 404 ($PhPW(CO)_4$, 47), 376 ($PhPW(CO)_3$, 18), 348 ($PhPW(CO)_2$, 100), 320 (PhPW(CO), 60), 292 (PhPW, 100). Anal. Calcd for $C_{16}H_{11}O_5PW$: C, 38.50; H, 2.21. Found: C, 38.61; H, 2.31. Minor isomer **5b**: colorless, mp 133−135 °C; ^{31}P NMR (C_6H_6) δ −149.0 ($^1J(^{31}P-^{183}W)$ = 251.0 Hz); ^{13}C NMR ($CDCl_3$) δ 133.9 (d, $^2J(C-P)$ = 10.5 Hz, C═CH), 130.3 (d, $^3J(C-P)$ = 1.80 Hz, C═CH), 35.9 (d, $^1J(C-P)$ = 8.4 Hz, CH_2), 39.2 (d, $^1J(C-P)$ = 14.7 Hz, CHP), 29.0 (d, $^1J(C-P)$ = 14.7 Hz, CHP), 129.0−132.1 (m, phenyl), 196.2 (d, $^2J(C-P)$ = 8.1 Hz, cis CO), 199.1 (d, $^2J(C-P)$ = 31.5 Hz, trans CO); ^1H NMR ($CDCl_3$) δ 7.1−7.3 (m, 5H, phenyl), 5.73 (s, 1H, CH═), 5.17 (d, $^3J(H-P)$ = 2.5 Hz, 1H, CH═), 2.95−2.76 (m, 2H, CH_2), 2.44 (dd, $^2J(H-H)$ = 7.5 Hz, $^2J(H-P)$ = 14.8 Hz, 1H, CHP), 2.19 (d, br, $^2J(H-P)$ = 16.4 Hz 1H, CHP).

(8-Phenyl-8-phosphabicyclo[5.1.0]octa-3-ene)pentacarbonyltungsten (7a,b). The same reaction of **4** with 1,3-cycloheptadiene, as described for **5**, gave a mixture of *syn*-**7a** and *anti*-**7b** in a 7:1 ratio (68% yield), based on integration of their ^{31}P NMR resonances. Fractional crystallization from hexanes gave **7a** as a colorless solid: mp 82−84 °C; ^{31}P NMR (C_6H_6) δ −142 ($^1J(^{31}P-^{183}W)$ = 265.5 Hz); ^{13}C NMR ($CDCl_3$) δ 197.1 (d, $^2J(C-P)$ = 21.9 Hz, trans CO), 194.5 (d, $^2J(C-P)$ = 7.5 Hz, cis CO), 127.3−130.5 (m, phenyl), 131.7 (d, $^2J(C-P)$ = 12.0 Hz, C═CH), 122.4 (d, $^3J(C-P)$ = 2.0 Hz, HC═C), 30.0 (d, $^4J(C-P)$ = 3.0 Hz, CH_2), 29.0 (d, $^1J(C-P)$ = 14.3 Hz, CHP), 28.5 (d, $^3J(C-P)$ = 15.1 Hz, CH_2), 26.7 (d, $^2J(C-P)$ = 4.3 Hz, CH_2), 23.5 (d, $^1J(C-P)$ = 13.5 Hz, CHP); ^1H NMR (C_6D_6) δ 6.9−7.1 (m, 5H, phenyl), 5.72 (m, 1H, CH═CH), 5.45 (m, 1H, CH═CH), 2.0−2.1 (m, 2H, CH_2), 1.71 (dd, $^2J(H-P)$ = 6.6 Hz, $^3J(H-H)$ = 1.5 Hz, 1H, CHP), 1.8−1.9 (m, 2H, CH_2), 1.2−1.5 (m, 2H, CH_2), 1.39 (d, $^2J(H-P)$ = 4.8 Hz, 1H, CHP); MS (^{184}W) *m/e* (relative intensity) for **7a,b**: 526 (M^+, 10), 442 (M − 3CO, 18), 404 ($PhPW(CO)_4$, 45), 376 ($PhPW(CO)_3$, 22), 348 ($PhPW(CO)_2$, 95), 320 (PhPW(CO), 60), 292 (PhPW, 100). Anal. Calcd for $C_{18}H_{15}O_5PW$: C, 41.06; H, 2.85. Found: C, 40.99; H, 2.86. Minor isomer **7b**: colorless, mp 68−70 °C; ^{31}P NMR (C_6H_6) δ −157 ($^1J(^{31}P-^{183}W)$ = 249.6 Hz); ^1H NMR (C_6D_6) δ 6.8−7.3 (m, 5H, phenyl), 5.55 (s, 1H, CH═CH), 5.42 (m, 1H, CH═CH), 2.5−2.8 (m, 4H, CH_2), 2.38 (d, $^2J(H-P)$ = 16 Hz, 1H, CHP), 2.12 (br, 2H, CH_2), 1.48 (m, 1H, CH_2).

(9-Phenyl-9-phosphabicyclo[6.1.0]nona-3-ene)pentacarbonyltungsten (8a,b). The same reaction of **4** with 1,3-cyclooctadiene, as described for **5**, gave a mixture of *syn*-**8a** and *anti*-**8b** in a 3:2 ratio (71% yield), based on integration of their ^{31}P NMR resonances. Fractional crystallization from hexane gave **8a** as a colorless crystals: mp 67−69 °C; ^{31}P NMR (C_6H_6) δ −153 ($^1J(^{31}P-^{183}W)$ = 261.5 Hz); ^{13}C NMR ($CDCl_3$) δ 196.7 (trans CO), 194.4 (d, $^2J(C-P)$ = 8.5 Hz, cis CO), 127.6−130.5 (m, phenyl), 137.1 (d, $^2J(C-P)$ = 13.3 Hz, C═CH), 120.0 (s, HC═C), 30.6 (d, $^1J(C-P)$ = 12.4 Hz, CHP), 29.9 (d, $^1J(C-P)$ = 14.7 Hz, CHP), 28.7 (s, CH_2), 27.7 (d, $^3J(C-P)$ = 13.0 Hz, CH_2), 24.7 (s, CH_2), 23.1 (s, CH_2); ^1H NMR ($CDCl_3$) δ 7.17−7.47 (m, 5H, phenyl), 5.54 (d, $^3J(H-P)$ = 12.6 Hz, 1H, CH═), 5.85 (m, 1H, CH═), 2.71 (t, $^3J(H-P)$ = 9.8 Hz, 2H, CH_2), 1.2−2.47 (m, 8H, $3CH_2$, 2CHP); MS (^{184}W) *m/e* (relative intensity) for **8a**,**b**: 540 (M^+, 20), 456 (M − 3CO, 10), 404 ($PhPW(CO)_4$, 70), 376 ($PhPW(CO)_3$, 25), 348 ($PhPW(CO)_2$, 100), 320 (PhPW(CO), 65), 292 (PhPW, 90); Isomer **8b**: colorless crystals, mp = 84−86 °C; ^{31}P NMR (C_6H_6) δ −168 ($^1J(^{31}P-^{183}W)$ = 252.4 Hz); ^{13}C NMR ($CDCl_3$) δ 195.9 (trans CO), 195.5 (d, $^2J(C-P)$ = 11.0 Hz, cis CO), 128.7−133.3 (m, phenyl), 137.2 (d, $J(C-P)$ = 12.1 Hz, C═CH), 119.5 (s, HC═C), 31.2 (d, $^1J(C-P)$ = 17.4 Hz, CHP), 30.1 (s, CH_2), 28.5 (d, $^1J(C-P)$ = 22.7 Hz, CHP), 25.9 (s, CH_2), 25.6 (d, $J(C-P)$ = 12.1 Hz, CH_2), 24.2 (d, $J(C-P)$ = 12.3 Hz, CH_2); ^1H NMR ($CDCl_3$) δ 7.17−7.47 (m, 5H, phenyl), 5.30 (d, $^3J(H-P)$ = 8.4 Hz, 1H, CH═), 5.25 (m, 1H, CH═), 2.31 (d, $^2J(H-P)$ = 9.0 Hz, 1H, CHP), 1.78−0.76 (m, 9H, $4CH_2$, CHP). Anal. Calcd for $C_{19}H_{12}O_5PW$: C, 42.22; H, 3.15. Found: C, 42.21; H, 3.22.

X-ray Structure Determination of 5b. Structure Solution and Refinement. A suitable crystal of **5b** was sealed into a thin-walled capillary and was mounted and aligned on an Enraf Nonius CAD4 diffractometer. The crystal belongs to the orthorhombic crystal system, with the space group uniquely defined as the most common noncentrosymmetric space group $P2_12_12_1$ (No. 19) by the systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$ and $00l$ for $l = 2n + 1$. All data were collected by a coupled $\omega-2\theta$ scan. A total of 3059 reflections were colllected with Mo Kα radiation. An empirical absorption correction was applied to all data. These were then merged to produce 2216 independent reflections.

All crystallographic calculations were carried out with the aid of the SHELXTL-PC program package. The analytical form of the scattering factors for neutral atoms was used with both of the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion included in the calculations. The positional and anisotropic thermal parameters were refined for all non-hydrogen atoms. All hydrogen atoms were included in calculated positions ($d(C-H)$ = 0.96 Å) with the appropriate staggered geometry. The isotropic thermal parameters of the hydrogen atoms were fixed equal to the U_{eq} of the carbon atoms to which they

(26) Marinetti, A.; Mathey, F *J. Am. Chem. Soc.* **1982**, *104*, 4484. Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488. Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Chem. Soc., Chem. Commun.* **1982**, 667.

(27) On the basis of the NMR spectroscopic arguments presented here, the assignment of **6a** and **6b** in the Experimental Section of ref 2 must be reversed.

are bonded. The absolute structure was determined by the η refinement procedure. The final value of $\eta = 1.06(4)$ confirms that the correct conformation of the molecule was chosen.

Crystal and Intensity Data. $C_{16}H_{11}O_5PW$, MW = 498.1 g/mol, orthorombic crystal system, $a = 6.6763(9)$ Å, $b = 13.5269(24)$ Å, $c = 18.8822(27)$ Å, $V = 1705.2(9)$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.940$ mg/m^3, crystal dimensions $0.20 \times 0.20 \times 0.10$ mm, absorption coefficient $\mu = 6.888$ mm^{-1}. A total of 3059 reflections were collected with index ranges of $0 \le h \le 7$, $0 \le k \le 14$, and $-20 \le l \le 20$, which were merged into a unique set of 2216 reflections ($R_{int} = 1.81\%$). Their refinement against 210 parameters converged (largest $\Delta/\sigma = 0.002$) with $R = 2.85\%$ and $R_w = 3.77\%$. $R = 2.47\%$ and $R_w = 2.83\%$ for those 1964 reflections with $|F| > 6.0\sigma(|F|)$. Largest features left on the difference Fourier map were a peak of 0.67 e Å^{-3} and a hole of -0.87 e Å^{-3}. Absolute structure was verified $\eta = 1.07(3)$.

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Supporting Information Available: Positional and thermal parameters, a complete listing of bond lengths and angles, and details of the X-ray structure determination (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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