

Synthesis, Structure, Strain Energy, and Excess Strain of a Phospha[3]triangulane

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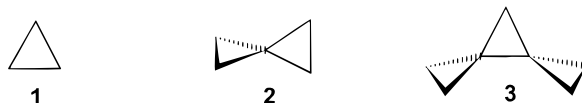
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Abstract: (7-Phenyl-7-phosphadispiro[2.0.2.1]heptane)pentacarbonyltungsten (**8**), a phospha[3]triangulane, was synthesized from bicyclopropylidene. Its single-crystal X-ray structure determination is reported. Comparison of the crystal structure data with those of the related phosphaspiropentane **7** and phosphirane **6** complexes suggests that the phosphirane ring tightens when the number of spiro atoms is increased. This is supported by the B3LYP and MP2/6-31G* computed geometries of the uncomplexed parent systems. Ab initio calculated heats of formation and strain energies (SE) are reported for the parent phosphirane **11**, phosphaspiropentane **12**, and phospha[3]triangulane **13** using both G2MP2 theory and ring separation reactions. Our best estimates for the ΔH_f of **11**, **12**, and **13** are 18.3, 48.4, and 78.2 kcal/mol, respectively, with corresponding SE values of 21.3, 54.7, and 87.9 kcal/mol. For comparison, the slightly modified G2MP2 method was also applied to cyclopropane **1**, spiro[2.1]pentane **2**, and [3]triangulane **3** to give respective ΔH_f values of 12.6, 44.3, and 75.3 kcal/mol, with corresponding SEs of 28.0, 64.6, and 100.5 kcal/mol, all of which are in excellent agreement with reported experimental data. These strain energies suggest that the excess strain per spiro atom is 5.3 kcal/mol for phospha[*n*]triangulanes, which is smaller than the 8.6 kcal/mol determined from the heat of combustion measurements for the [*n*]triangulanes.

Three-membered ring structures are of broad interest and have been subject to intense study.¹ Spiro compounds that connect such rings by joint carbons are even more intriguing, but much less is known about them. Several groups have excelled in the studies on hydrocarbons and have reported an array of exotic polyspiro condensed rings, such as the linear [*n*]triangulanes and the cyclic [*n*]rotanes, where *n* indicates the number of cyclopropane (**1**) rings.² Hetero[*n*]triangulanes have received only modest attention. Whereas spiro[2.1]pentane, the parent [2]-triangulane **2**,³ has been known for nearly a century, the

oxaspiropentanes,⁴ dioxaspiropentanes,⁵ and azaspiropentanes⁶ were reported some three decades ago. Also, dispirocyclohep-



tane, the parent [3]triangulane **3**,⁷ was synthesized in that period, while the substituted oxa-⁸ and sila[3]triangulanes⁹ are of more recent vintage. Building on the recently reported di- and tetraphosphaspiropentanes **4**¹⁰ and **5**¹¹ and our earlier work on

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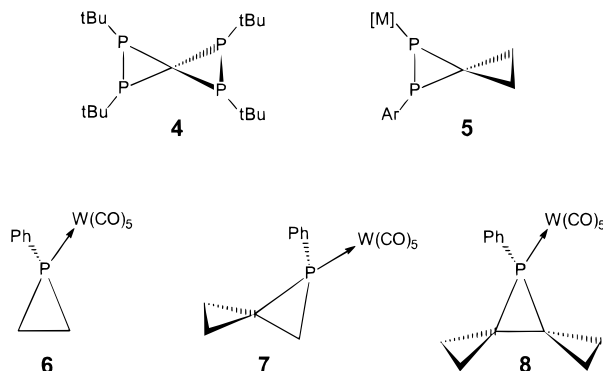
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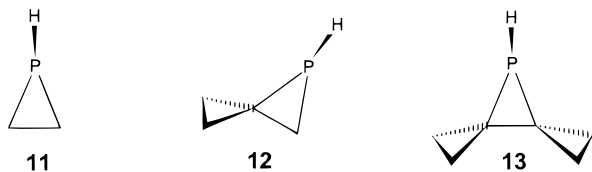
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the complexed phosphirane **6**¹² and phospha[2]triangulane **7**,¹² we here report the first synthesis of the remarkably stable phospha[3]triangulane complex **8** by employing the carbene-like reactivity of the in situ generated terminal phosphinidene complex $\text{PhPW}(\text{CO})_5$.¹³ As olefin we chose the well-character-

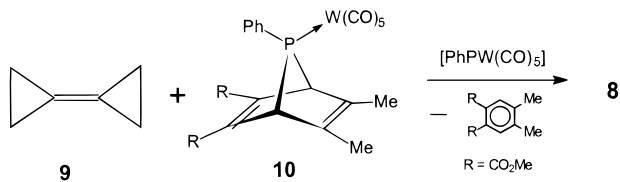


ized bicycpropylidene **9**,¹⁴ which has also been used for the synthesis of [3]triangulanes, their oxo derivatives, and Ti and Co complexes.¹⁵ Because of the importance of strain energies (SE) for small rings and catenated rings, we also report computed SE values for the parent phosphirane **11**, phospha[2]triangulane **12**, and phospha[3]triangulane **13**.



Results and Discussion

Catalyzed by CuCl , the addition reaction of the complexed phosphinidene precursor **10** with an excess of **9** in toluene at 55 °C for 2 h in a pressure chamber gives the desired product **8** in 70% yield as colorless, air-stable crystals after workup.



While we concentrate on the structural properties and strain energies, it is of interest to note that the ³¹P NMR resonance of **8** at $\delta -129.4$ ppm is at surprisingly low field as compared to the $\delta -154.8$ ppm for phospha[2]triangulane complex **7** and the $\delta -187.6$ ppm for phosphirane complex **6**.

X-ray and Ab Initio Structures. The results of the single-crystal X-ray structure analysis are shown in Figure 1, with selected bond lengths and angles summarized in Table 1. Table 2 compares the bond lengths and angles of the phosphirane ring of **8** with those of **6** and **7**. The P–C(1) and P–C(2) bonds of **8** are equal to each other within experimental error limits, which is in line with the orthogonality of the phosphirane ring with both cyclopropyl rings (angles of 89.5(6)° and 89.7(7)°) and with the WPC(7) plane. The intercept of 72.0(7)° between the

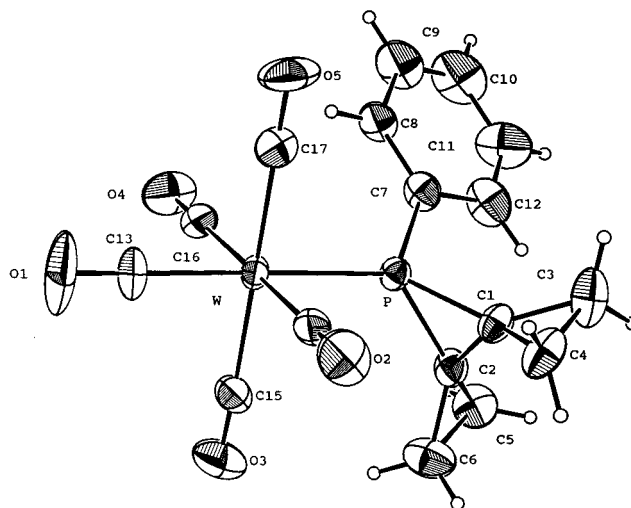


Figure 1. ORTEP presentation scaled to 50% probability ellipsoids of **8**.

planes containing the two cyclopropyl rings is normal and illustrates the absence of any distortion. The P-phenyl is orthogonal (86.4(5)°) to the phosphirane ring but slightly rotated (9.5°) from bisecting it. Likewise, the $\text{W}(\text{CO})_5$ group is rotated by 9.0° from eclipsing the P-phenyl group. The phosphirane ring of **8** is very similar to that of **6** and derivatives thereof. Only **7** shows P–C bonds of quite different lengths. This differentiation in bond lengths is common in hetero[2]triangulanes, which are also thermally more labile and sensitive to acidic rearrangements.^{8,9,15a,b} We note that **8** is stable in toluene for 48 h at 60°.

Do cyclopropyl ring substituents increase the strain in the phosphirane ring? Comparison of the X-ray structure of **8** with those of **7** and **6** does not provide a clear answer. We therefore resorted to ab initio theory to compute their structures and strain energies. Parent structures **11**, **12**, and **13** were computed without the $\text{W}(\text{CO})_5$ group and without P substituents (i.e., only P–H) to maintain the calculations within manageable proportions. Their B3LYP and MP2(full)/6-31G* geometries are shown in Figure 2, which also contains the geometries of the hydrocarbons **1**, **2**, and **3**. B3LYP/6-31G* structural parameters of the phosphirane rings are summarized in Table 3, together with those determined by microwave spectroscopy for **11**. These data illustrate that the stabilizing $\text{Ph-P-W}(\text{CO})_5$ substituents (Table 1) shorten the C–P bonds by ~ 0.05 Å, lengthen the C–C bond by ~ 0.01 – 0.03 Å, and widen the CPC bond angle by $\sim 2^\circ$. Comparison between the B3LYP structures (Table 3) shows a decrease both in C–P and C–C bond lengths and in the CPC angle with each cyclopropyl increment (an average CP bond length is used for **12**). Thus, the cyclopropyl groups appear to

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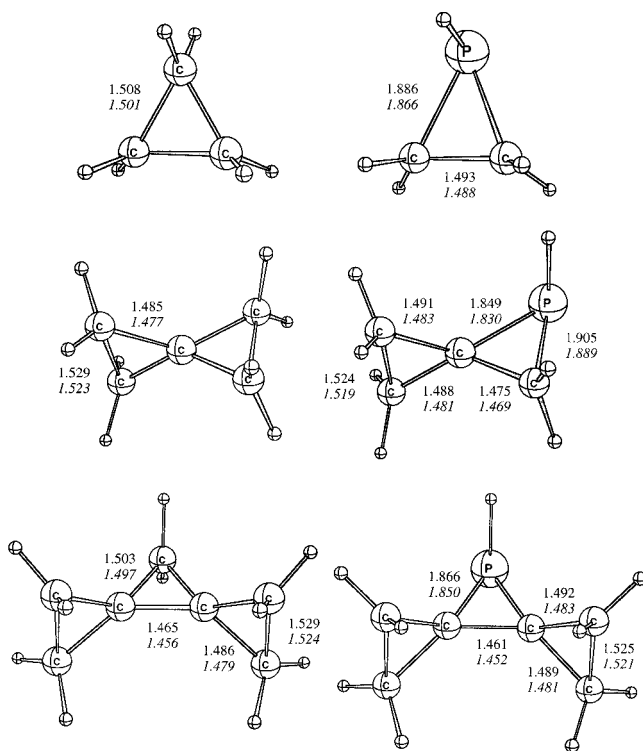
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Table 1. Selected Crystallographic Bond Distances (in Angstroms), Angles (in Degrees), and Dihedral Angles (in Degrees) with ESDs of **8**

atoms	distance/angle	atoms	distance/angle	atoms	distance/angle
W–P	2.495(2)	C(1)–C(2)	1.48(1)	C(2)–C(5)	1.50(1)
P–C(1)	1.807(8)	C(1)–C(3)	1.48(1)	C(2)–C(6)	1.51(1)
P–C(2)	1.820(8)	C(1)–C(4)	1.49(1)	C(5)–C(6)	1.53(1)
P–C(7)	1.833(8)	C(3)–C(4)	1.51(1)		
WPC(7)	122.3(3)	WPC(1)C(2)	107.9(4)	C(7)PC(2)C(1)	97.5(5)
C(1)PC(2)	48.1(4)	WPC(2)C(1)	–109.4(4)	C(3)C(1)C(2)C(5)	2.6(1.7)
C(3)C(1)C(4)	61.2(7)	C(7)PC(1)C(2)	–97.6(5)	C(4)C(1)C(2)C(6)	3.7(1.6)
C(5)C(2)C(6)	61.4(6)				

Table 2. Comparison of Selected Bond Lengths (in Angstroms) and Angles (in Degrees) for the X-ray Crystal Structures of **8**, **7**, and **6**

bond/angle	8	7 ^a	6 ^a
C(1)–C(2)	1.48(1)	1.508(9)	1.50(2)
C(1)–P	1.820(8)	1.855(7)	1.83(2)
C(2)–P	1.807(8)	1.794(6)	1.80(2)
P–W	2.495(2)	2.500(2)	2.504(2)
C(1)–P–C(2)	48.1(4)	48.6(3)	48.6(7)
W–P–Ph	122.3(3)	123.2(2)	122.9(3)

^a Reference 10.**Figure 2.** B3LYP and MP2/6-31G* optimized structures for **1–3** and **11–13**. Upper values are the B3LYP bond lengths (in angstroms) and angles (in degrees), while the lower italic values are those at MP2.

tighten the phosphirane ring. The X-ray structures suggest a similar effect, but those differences are well within experimental error limits.

Boese and de Meijere showed by low-temperature X-ray structure determinations the distal C–C bonds (the bonds away from the spiro carbon) of $[n]$ triangulanes to be slightly longer than their proximal bonds (the bonds connected to the spiro carbon).¹⁷ For example, for [3]triangulane **3** these are 1.531(1) and 1.485(1) Å, respectively, and the ab initio bond lengths show the same effect. The calculated phosphirane geometry of **13** (but also of **12**) displays the same behavior for the

Table 3. Selected B3LYP/6-31G* Bond Lengths (in Angstroms) and Angles (in Degrees) for **13**, **12**, and **11**

bond/angle	13	12	11 ^a
C(1)–C(2)	1.461	1.475	1.493 (1.502)
C(1)–P	1.866	1.905	1.886 (1.867)
C(2)–P	1.866	1.849	1.886 (1.867)
C(1)–P–C(2)	46.1	46.3	46.6 (47.48)
P–C(2)–C(1)	66.9	68.9/64.9	66.7 (66.26)

^a Experimental values from ref 16 are given in parentheses.

cyclopropyl rings. X-ray structure **8** only suggests this effect, with a distal C(3)–C(4) bond length of 1.51(1) Å and C(1)–C(3) and C(1)–C(4) proximal bonds of 1.48(1) and 1.49(1) Å, respectively, because the differences are within experimental uncertainties; the C(2)C(5)C(6) cyclopropyl ring has a distal bond of 1.53(1) Å, with proximal bonds of 1.50(1) and 1.51(1) Å.

Heats of Formation. With decreasing phosphirane bond lengths on cyclopropyl substitution, an increase in strain energy (SE) may be expected, i.e., tighter rings are more strained. For the parent phosphirane **11**, we report its heat of formation (ΔH_f) and SE at the G2MP2 level of theory. After validation of this methodology on the hydrocarbons **1**, **2**, and **3**, ΔH_f and SEs are given for the larger systems **12** and **13**. Throughout, we employ homodesmotic reactions (eqs 1, 2, 7–10) to calculate the SEs. Ring separation reactions (eqs 3–6) are also used as a simple means to estimate ΔH_f values for the spiro compounds.

(i) Phosphirane. It is informative to review first available SE values of various three-ring structures. The established (experimental) SE for cyclopropane of 27.5 kcal/mol is based on its heats of formation of 12.74 kcal/mol¹⁸—in the present work we use eq 1. Similar SEs have been reported for aziridine (27.1 kcal/mol) and oxirane (27.2 kcal/mol).¹⁹ Bachrach²⁰ reported earlier a SE for phosphirane of 20.1 kcal/mol computed at the HF/6-31G* level of theory (+ZPE at 3-21G*) using the homodesmotic reaction shown in eq 2. The reported SE of 19.8 kcal/mol for thiirane is of a similar magnitude,²¹ while the ab

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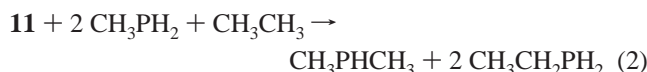
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initio estimate for silirane is much higher (43.4 kcal/mol).²²



In the absence of experimental data, such as its heat of formation, a more rigorous theoretical treatment seemed desirable to ascertain the SE of phosphirane. We estimate a ΔH_f value of 20.2 kcal/mol on the basis of the G2MP2 calculated heat of atomization. An SE of 21.3 kcal/mol is obtained using G2MP2 calculated ΔH_f values for all the fragments²³ of eq 2. Using experimental ΔH_f data instead gives a larger SE of 25.5 kcal/mol, but uncertainties in the experimental data render this a less reliable estimate. The accuracy of the G2MP2 method was verified for cyclopropane, giving calculated ΔH_f and SE values (eq 1) of 14.5 and 28.0 kcal/mol, respectively. These are in good agreement with the corresponding experimental values of 12.7 and 27.5 kcal/mol. The SE value of 21.3 kcal/mol for the low-coordinate phosphirane is similar in magnitude to that of thiirane and expectedly smaller than those of the three rings of the first row of the periodic table. Bachrach²⁰ explained this to result from the small CPC angle, which reduces the degree of C–C bending and thereby creates a stronger C–C bond. The rather large SE for silirane has been traced to the preference of silicon for angles near 90°.²²

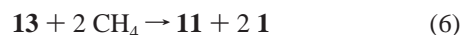
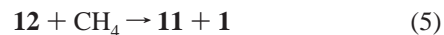
(ii) **Phospha[*n*]triangulanes.** The total ring strain of [*n*]triangulanes is not a simple addition of the SEs of the number of cyclopropane rings. For example, based on experimental heats of formation, the SEs are estimated to be 65 kcal/mol for [2]-triangulane **2** and 99 kcal/mol for [3]triangulane **3**,²⁵ which are more than twice and three times, respectively, that of cyclopropane **1**. De Meijere showed for a series of [*n*]triangulanes (*n* ≤ 5) that the excess SE per cyclopropane increment is 8.6 kcal/mol.²⁵ Whether the same effect applies to phospha[*n*]triangulanes is not easily established due to the noted lack of experimental heats of formation. We therefore resort to two computational approaches, i.e., ring separation reactions and G2MP2 theory, to obtain estimated ΔH_f values. The methods are also applied to the related hydrocarbons for reference.

(a) **Ring Separation Reactions.** This approach to obtain ΔH_f values for saturated spiro hydrocarbons, including **2** and **3**, was successfully employed earlier by Radom²⁶ and by Rüdchard and de Meijere.²⁵ Thus, using eqs 3 and 4 and the experimental heats

of formation for cyclopropane (12.74 kcal/mol) and methane (−17.89 kcal/mol) results in estimated ΔH_f values of 43.37 kcal/mol for **2** and 74.00 kcal/mol for **3**, which are in excellent agreement with the corresponding experimental values of 44.23 and 72.27 kcal/mol.²⁷



Applying the same approach to the phospha[*n*]triangulanes, by using eqs 5 and 6 and the G2MP2 calculated ΔH_f value of 20.2 kcal/mol for phosphirane **11**, gives estimated ΔH_f values of 50.7 kcal/mol for **12** and of 81.2 kcal/mol for **13**.



(b) **G2MP2 Heats of Formation.** To alleviate concerns about the accuracy of the heats of formation of the organophosphorus compounds, we computed them from atomization energies using the G2MP2 method. At this level of theory, the ΔH_f values are 51.2 kcal/mol for **12** and 82.0 kcal/mol for **13**, both of which compare remarkably well with those resulting from the above-discussed ring separation method.

To verify proper performance of the G2MP2 method, we also computed the heats of formation for spiro pentane **2** and [3]-triangulane **3**. Sizable deviations from experimental data were found, much to our surprise. For example, the G2MP2 calculated value of 47.08 kcal/mol for **2** is already larger than the experimentally determined value by a noticeable 2.85 kcal/mol. However, for **3** the difference amounts to a very significant 6.8 kcal/mol, well outside the range of <2 kcal/mol established for small systems. This suggests that the G2MP2 estimated ΔH_f (**3**) of 79.06 kcal/mol is too large, since the differences for the smaller alicyclic hydrocarbons, used in the homodesmotic reaction, are modest and within the expected range.²³ It appears that the G2MP2 method works well for small molecules but that its performance is less satisfactory for the larger ones, and in particular for [3]triangulane, the system of interest. The origin of this deviation lies mainly in the empirical higher level correction (HLC) that the G2MP2 method uses. This HLC correction becomes substantial for large systems because it is related to the number of valence electron pairs, $E(\text{HLC}) = (-0.19n\alpha - 4.81n\beta) \times 10^{-3}$. Arbitrarily increasing $E(\text{HLC})$ by 10%, which we denote as G2MP2',²⁸ results in the more reasonable ΔH_f values of 44.26 kcal/mol for **2** and 75.30 kcal/mol for **3**, while those for the smaller hydrocarbons are less affected. We note that the similarly computed ΔH_f of 12.57 kcal/mol for cyclopropane also agrees better with the experimental value.

If the ΔH_f values of **1**, **2**, and **3** require an HLC adjustment in the G2MP2 approach, we must assume that the same applies for the organophosphorus compounds. Indeed, the resulting G2MP2' calculated ΔH_f values are likewise smaller, although the effect is less than that for **1–3**, i.e., 18.3 kcal/mol for phosphirane **11**, 48.4 kcal/mol for **12**, and 78.2 kcal/mol for **13** (see Table 4).

G2MP2 Strain Energies. First we evaluate the performance of G2MP2 theory by determining the strain energies for **2** and **3** using only calculated G2MP2 heats of formations for all the molecules of eqs 7 and 8.



(23) The G2MP2' ΔH_f ²⁹⁸ enthalpies (in kcal/mol), with G2MP2 (first) and reported experimental values²⁴ (second) in parentheses, are as follows: −18.94 (−17.99, −17.80) for methane, −21.29 (−19.72, −20.1) for ethane, −26.45 (−24.25, −25.0) for propane, −42.31 (−38.86, −40.0) for neopentane, −5.37 (−3.80, −4) for methylphosphine, −14.51, (−12.31, −14) for dimethylphosphine, −10.25 (−8.05, −9.7 (est.)) for ethylphosphine, and −24.57 (−21.11, −24) for *tert*-butylphosphine. The experimental ΔH_f of 9.7 for EtPH₂ is an estimate based on the G2MP2 calculated difference of 4.3 kcal/mol with the isomeric Me₂PH.

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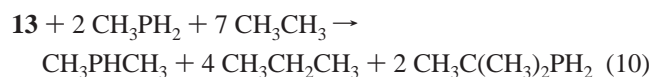
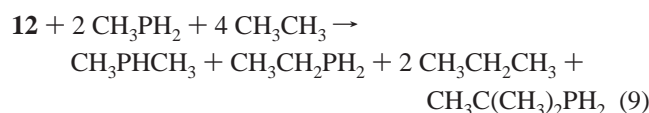
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We note that the SE values are not influenced by the discussed HLC correction because of the balance of valence electron pairs in the homodesmotic equations. The resulting SEs are 64.6 kcal/mol for **2** and 100.5 kcal/mol for **3**, which are 1.0 and 4.2 kcal/mol larger than those based on experimental data. This is a remarkably good comparison considering that eq 4 (for **3**) contains 17 molecules. The 4.2 kcal/mol difference in SE values for **3** results largely from the 3.8 kcal/mol difference between its G2MP2' and experimental ΔH_f values. It then appears that G2MP2 theory performs very satisfactorily in determining strain energies for the hydrocarbons.

For the organophosphorus compounds, using calculated ΔH_f values only for all the molecules of eqs 9 and 10 results in SE values of 54.7 kcal/mol for **12** and 87.9 kcal/mol for **13**. These are, as expected, considerably lower than those of the hydrocarbons **2** and **3**.



Excess Strain. From the computed SE (and ΔH_f) data, excess strain per cyclopropyl increment on the cyclopropane and phosphirane rings can be determined. Based on experimental heats of formation only, de Meijere showed, as already noted, that the excess SE per cyclopropyl is 8.6 kcal/mol for the hydrocarbon $[n]$ triangulanes ($n \leq 5$).²⁵ Using SE values based on G2MP2 calculated heats of formations for the more limited set **1**, **2**, and **3** ($n \leq 2$), we obtain, gratifyingly, a similar excess SE per cyclopropyl group of 8.4 kcal/mol.

Substitution of the phosphirane ring results in a smaller excess SE per cyclopropyl increment of 5.3 kcal/mol, which is based on the similarly determined SE values for **1**, **11**, **12**, and **13**. This ca. 40% reduction in excess SE reflects the lesser degree of rehybridization needed for the spiro atoms of the organophosphorus compounds, which is in line with phosphirane's 6.7 kcal/mol smaller SE than that of cyclopropane.

Conclusions

The first phosphat[3]triangulane has been synthesized as a $\text{W}(\text{CO})_5$ complex. This remarkably stable compound **8**, carrying only a Ph-P substituent, has been fully characterized by its X-ray crystallographic structure. Comparison with the X-ray structures of the similarly Ph-P substituted phosphaspiropentane (**7**) and phosphirane (**6**) complexes suggests a denser structure, but the geometrical differences are within experimental uncertainties.

Comparison of the B3LYP/6-31G* and MP2/6-31G* geometrical parameters of the parent compounds phosphirane (**11**), phosphaspiropentane (**12**), and phosphat[3]triangulane (**13**) shows, indeed, a tightening of the [3]triangulane structure.

Heats of formation were computed by ring separation reactions and by G2MP2 theory for the parent organophosphorus compounds and their hydrocarbon analogues. A small modification in the HLC correction used in the G2MP2 method was needed to obtain agreement between the G2MP2 calculated ΔH_f values and the experimental values reported in the literature for cyclopropane (**1**), spiroentane (**2**), and [3]triangulane (**3**). The resulting G2MP2' calculated ΔH_f values are 12.57 kcal/mol for **1**, 44.26 kcal/mol for **2**, and 75.30 kcal/mol for **3**. For

Table 4. Summary of ΔH_f and SE (in kcal/mol) from Ring Separation (RS) Reactions and G2MP2 Estimates

ΔH_f /SE	method	11	12	13	1	2	3
ΔH_f	RS		50.69	81.19		43.37	74.00
	G2MP2	20.19	51.24	81.99	14.46	47.08	79.06
	G2MP2'	18.31	48.41	78.22	12.57	44.26	75.30
SE	exp(g)				12.74 ^a	44.23 ^b	72.27 ^c
	G2MP2	21.3	54.7	87.9	28.0	64.6	100.5
	exp				27.5 ^a	63.6 ^{d,e}	96.4 ^{d,e}
excess SE	G2MP2		5.4	10.6		8.6	16.5

^a Reference 18. ^b Fraser, F. M.; Prosen, E. J. *J. Res. Nat. Bur. Stand.* **1955**, *54*, 143. ^c Reference 27. ^d Determined from eq 7 using experimental ΔH_f values. ^e Reference 29.

the organophosphorus analogues, for which no experimental data are available, the G2MP2' calculated ΔH_f values are 18.3 kcal/mol for **11**, 48.4 kcal/mol for **12**, and 78.2 kcal/mol for **13**.

Strain energies for the parent organophosphorus and hydrocarbon compounds were obtained from G2MP2 calculated ΔH_f values. These theoretical values are 21.3 kcal/mol for **11**, 54.7 kcal/mol for **12**, and 87.9 kcal/mol for **13**.

The excess strain in the phosphat[n]triangulanes ($n \leq 2$), which is the strain for spiro carbons in excess of that of the three-membered rings, amounts to 5.3 kcal/mol per spiro carbon. This is ca. 40% less than the excess strain in linear $[n]$ triangulane hydrocarbons.

Computational Section

All electronic structure calculations were carried out using the GAUSSIAN 94 suite of programs.³⁰ For the density functional theory (DFT) calculations, Becke's three-parameter hybrid exchange functional was used in combination with the Lee-Yang-Parr correlation functional,²¹⁻³³ denoted as B3LYP. The 6-31G* basis set was employed throughout for the geometry optimizations. The B3LYP and MP2(full) structures of **1-3** and **11-13** were characterized as minima by analysis of their Hessian matrices.

Heats of formation (ΔH_f^{298}) of methane, ethane, propane, neopentane, **1**, **2**, **3**, methylphosphine, dimethylphosphine, ethylphosphine, *tert*-butylphosphine, **11**, **12**, and **13** were estimated from their heats of atomization calculated at G2MP2.²³ This method³⁴ uses MP2/6-31G(d) geometries and obtains its energies from the QCISD(T) method,³⁵ using the 6-311G(d,p) basis set,³⁶ with basis set additivity corrections at the MP2 level of theory. The combination of basis set and correlation corrections and two empirical corrections yields where the empirical

$$\begin{aligned} E(\text{G2MP2}) = E(\text{QCISD(T)/6-311G(d,p)} + \\ E(\text{MP2/6-311G(d,p)} - E(\text{MP2/6-311G(d,p)} + \\ E(\text{HLC}) + E(\text{ZPE}) \end{aligned}$$

"higher level correction" is given by $E(\text{HLC}) = (-0.19n\alpha - 4.81n\beta)$

(29) Using the GI method gives SE values of 65.1 and 98.5 kcal/mol for **2** and **3**, respectively.²⁵

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Table 5. Crystal Data and Data Collection Procedures for **8**

formula	C ₁₉ H ₁₃ O ₅ PW
molecular weight	512
crystal system	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	6.7571(5)
<i>b</i> (Å)	15.6324(44)
<i>c</i> (Å)	16.8693(36)
<i>V</i> (Å ³)	1781.9(6)
<i>Z</i>	4
ρ_{calc} (g/cm ³)	1.909
crystal dimensions (mm)	0.14 × 0.18 × 0.08
abs coeff (cm ⁻¹)	132.329
radiation (Å)	Cu K α (1.5418)
extinction coeff	5.4130 × 10 ⁻⁶
2 θ limits (deg)	0.1 < θ < 148
scan type	$\omega/2\theta$
scan width (Å)	1.64
no. of unique data	2088
no. of data with <i>I</i> > 3 σ	2040
no. of parameters	257
largest parameter shift/error	0.01
<i>R</i> (%)	3.43
<i>R_w</i> (%)	4.72
GOF	1.507
max peak in diff Fourier (e/Å ³)	0.719
min peak in diff Fourier (e/Å ³)	-0.538
decay	0%
max abs corn	1.513
min abs corn	0.707

× 10⁻³ au. *E*(ZPE) is obtained by scaling the SCF/6-31G(d) harmonic frequencies by 0.8929.

Experimental Section

NMR spectra were recorded on a Bruker NT-300, wide-bore FT-NMR spectrometer. Chemical shift are referenced in ppm to internal (CH₃)₄Si for the ¹H and ¹³C NMR spectra and external 85% H₃PO₄ for the ³¹P NMR spectra. Downfield shifts are reported as positive. The elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA.

(7-Phenyl-7-phosphadispiro[2.0.2.1]heptane)pentacarbonyl-tungsten (8). Reaction of complex **10**¹³ (0.33 g, 0.5 mmol) with 10 equiv of bicyclopropylidene **9**¹⁴ (0.45 g, 5 mmol) and ca. 10% CuCl (50 mg, 0.05 mmol) was carried out in toluene in a pressure chamber at 55 °C for 0.5–1 h until complex **10** was fully converted, as

determined by ³¹P NMR. The reaction mixture was filtered, evaporated to dryness, and chromatographed on silica gel with hexanes to yield 0.18 g (70%) of **8**, which after fractional crystallization from hexanes gave colorless crystals: mp 80–81 °C; ³¹P NMR (C₆D₆) δ -129.4 (¹*J*(³¹P–¹⁸³W) = 170.6 Hz); ¹³C NMR (C₆D₆) δ 7.96 (s, *syn*-CH₂), 9.67 (s, *anti*-CH₂), 26.0 (d, ¹*J*(P–C) = 27.7 Hz), 128.6–133.5 (Ph), 195.7 (cis CO); ¹H NMR (C₆D₆) δ = 0.97 (q, ³*J*(P–H) = 4.5 Hz, *syn*-CH₂), 1.18 (q, ³*J*(P–H) = 4.5 Hz, *syn*-CH₂), 1.33 (dt, ³*J*(P–H) = 7.5 Hz, *anti*-CH₂), 1.45 (dt, ³*J*(P–H) = 7.5 Hz, *anti*-CH₂), 7.56 (m, Ph); MS (¹⁸⁴W) *m/e* (relative intensity) 512 (M⁺, 20), 428 (M⁺ – 3CO, 30), 404 (Ph–P(W(CO)₄), 20), 376 (Ph–P(W(CO)₃), 100), 348 (Ph–P(W(CO)₂), 40). Anal. Calcd for C₁₇H₁₃O₅PW: C, 39.84; H, 2.54. Found: C, 39.59; H, 2.57.

X-ray Structure Determination of 8. Diffraction data of a single crystal, mounted on a glass fiber with epoxy cement, were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using Ni-filtered Cu K α radiation. Standard peak search and automatic indexing routines, followed by least-squares fits of 25 centered reflections, yielded the lattice constants for the crystal. Three reflections were measured periodically to monitor decay, and linear decay corrections were applied. Intensities were corrected for Lorentz and polarization effects; linear decay and numerical absorption corrections were applied. Variances were assigned on the basis of standard counting statistics, with the addition of an instrumental uncertainty term, 0.04 F_o^2 . Lorentz, polarization, and absorption corrections (using the DIFABS program) were made to the *I_s* and σ^2 terms. The structure was solved by standard Patterson and difference Fourier techniques and refined by weighted full-matrix least squares. The final difference Fourier map contained no interpretable peaks near the W atom as extra atoms. All computations used the MoLEN software. Details of the crystal data and structure solution procedures are summarized in Table 5.

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Supporting Information Available: Tables of bond distances, angles, positional parameters, and displacement parameters for **8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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