

Synthesis, Structures, and Strain Energies of Dispirophosphiranes. Comparisons with Dispirocyclopropanes

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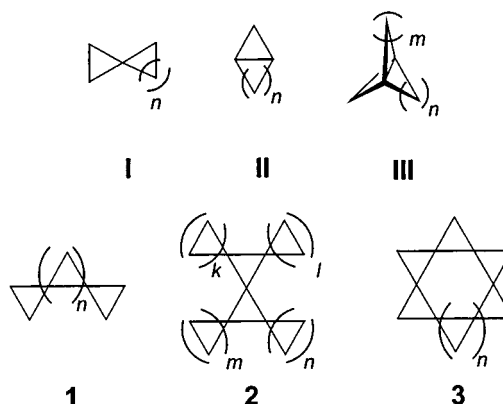
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Six novel dispirophosphirane complexes have been synthesized from the reaction of bicycloalkylidenes with the electrophilic phosphinidene complex PhPW(CO)₅. They contain a central phosphirane ring, which is spirofused on one side to a cyclopropane or cyclobutane ring and on the other side with a three-, four-, five-, or six-membered ring. Their crystal structures and MP2/6-31G* computed geometries for simplified parent systems suggest that spirofusion with small rings results in a tightening of the central three-membered phosphaheterocycle, while spirofusion with larger rings results in a relaxation of the phosphirane geometry. Similar theoretical predictions are made for the corresponding annulated hydrocarbons. Strain energies for both the hydrocarbon and phosphorus series of structures have been calculated at G3(MP2). Whereas the [3]triangulane hydrocarbon and phosphat[3]triangulane have a significant excess strain of 8.1 and 5.2 kcal/mol per spiroatom, respectively, the excess strain for systems spirofused with larger rings are negligible for the hydrocarbons and even negative for the phosphorus-containing species because of hyperconjugative stabilization.

Introduction

The inherently strained three-membered ring structure is unique among the monocyclic compounds because of its special electronic and chemical properties.¹ The hydrocarbon archetype cyclopropane, with its small valence angles, bend C–C bonds, and embedded ring strain of 27.5 kcal/mol,^{2,3} is a key structural unit in the numerous highly strained polycyclic structures that have been synthesized in the past century. Spirofused (I), bicyclic (II), and propellane (III) skeletons represent the annulated and condensed forms, while the linear (1) and branched [n]triangulanes (2) and the cyclic [n]rotanes (3) contain extended arrays of cyclopropanes.⁴ All these polycyclic compounds are surprisingly stable even though their strain energies (SE) are significantly higher than the sum of the separate rings.

Far fewer of the corresponding heteropolycycles are known. Whether they contain an aziridine, oxirane, thirine, or silirane ring, all the reported heterocyclic (poly)spiro condensed rings are chemically less stable



than their hydrocarbon analogues. Even fewer systems were known containing a phosphirane ring,⁵ until 1982 when Mathey showed their accessibility through cycloaddition of complexed phosphinidenes to olefins.^{6,7} Using the in-situ-generated carbene-like synthon PhPW(CO)₅, we have already reported on spirofused phosphiranes that are stabilized by the W(CO)₅ transition-metal group. These include the 1-phosphaspiro[2,n]alkanes **4a–d** ($n = 2–5$)⁸ and phosphat[3]triangulane **5a**.⁹

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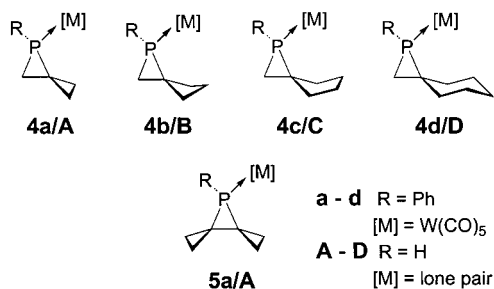
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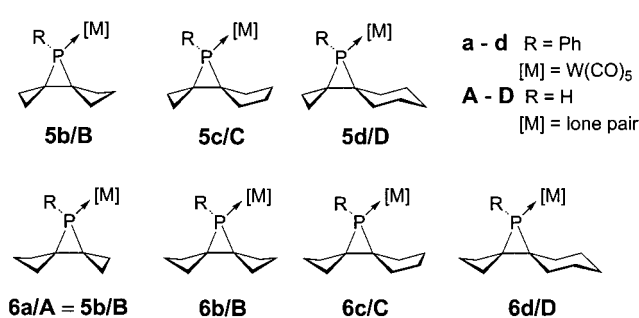
(7) (a) Mathey, F. *Angew. Chem.*, **1987**, *99*, 285–296; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275–286. (b) Dillon, K. B.; Mathey, F.; Nixon, J. F. In *Phosphorus: The Carbon Copy*; John Wiley: Chichester, 1998.

(8) (a) Hung, J.-T.; Yang, S.-W.; Gray, G. M.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 6786–6790. (b) Goumans, T. P. M.; Ehlers, A. W.; Vlaar, M. J. M.; Strand, S. J.; Lammertsma, K. *J. Organomet. Chem.*, in press.

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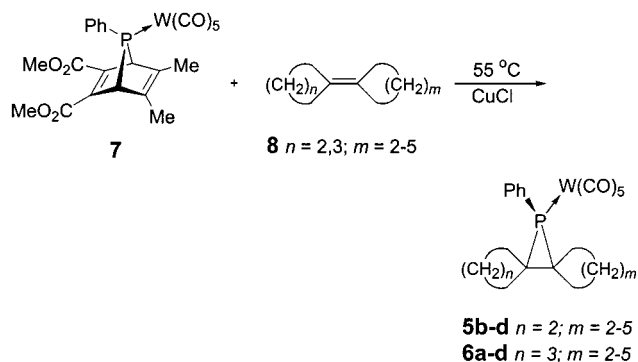
This series is now extended with six new stable phosphadispairoalkanes, i.e., **5b–d** and **6a–d**, in which the phosphirane is spirofused on one side with a cyclopropane (**5**) or cyclobutane (**6**) ring and on the other side with a three- (**a**), four- (**b**), five- (**c**), or six-membered (**d**) cycloalkane ring. The strain energy (SE) of such poly-cycles will depend on the size of the rings. Using G3-(MP2)-computed heats of formation, we establish the cumulative ring strain for each parent system (R = H, no M complex), including the monospiro compounds, in relationship to all the corresponding hydrocarbons. All these compounds can be envisioned to be more strained than the sum of the separate rings. For example, de Meijere showed earlier that the [*n*]triangulane hydrocarbons (**1**, $n \leq 5$) have an excess SE per cyclopropane increment of 8.6 kcal/mol.¹⁰ Phospha[3]triangulane **5A** has a smaller excess SE of 5.3 kcal/mol per spirocarbon, which may be related to the smaller ring strain of 21.4 kcal/mol for phosphirane^{11,12} as compared to the 28.4 kcal/mol for cyclopropane¹¹ (all G3(MP2)). The present study provides an analysis of the ring size effect on the strain energies of mono- and dispiroannulated phosphirane and cyclopropane.



Results and Discussion

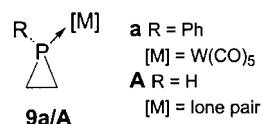
Synthesis. Reaction of bicycloalkylidenes **8** with the carbene-like phosphinidene complex PhPW(CO)₅, generated in situ by CuCl-catalyzed decomposition of 7-phosphanorbornadiene complex **7** at 55 °C, gives the W(CO)₅-complexed cyclopropanated and cyclobutanated dispiro-phosphiranes **5b–d** ($n = 2$; $m = 3–5$) and **6a–d** ($n = 3$; $m = 2–5$), respectively, in yields of over 70%.

Compounds **5b–d** and **6a–d** have characteristic ³¹P NMR resonances between $\delta = -126.7$ and -137.2 ppm with ¹J(W,P) coupling constants of 230–255 Hz. No correlation exists between the ³¹P NMR resonances and the size of the annulated rings. This is in contrast to the



¹³C NMR resonances of the spirocarbons. Namely, those of the cyclopropyl rings have their chemical shifts between $\delta = 28.4$ and 29.7 ppm and those of the cyclobutyl rings are between $\delta = 38.2$ and 41.7 ppm. Both deshield with increasing the size of the other spirofused ring.

Crystal Structures. For all of the dispiro-phosphirane complexes we obtained single-crystal X-ray structures. These are depicted in Figure 1. Selected bond lengths and angles, including those of the earlier reported **5a**⁹ and **9a**,⁸ are given in Table 1; note that the structure with a three- and a four-membered ring is identified both as **5b** and as **6a**. Not surprisingly, structures **5d** and **6d** crystallized with their six-membered rings in chair-conformations. The five-membered ring of **6c** has a single envelope-conformation, while we found disorder for the cyclopentane ring in the crystal of **5c**, which was refined as two conformers in a ratio of 50(4):50(4). To facilitate the comparison of the effects of cyclopropane (**5a–d**, $n = 2$) and cyclobutane (**6a–d**, $n = 3$) spiroannulation, we will treat them as two separate series.



Is there a correlation between the size of either of the annulated rings, i.e., n and/or m , and the bond lengths and angles of the central phosphirane ring? The crystallographic data do suggest so. Cyclopropanated dispiro-phosphiranes **5a–d** ($n = 2$) have shorter C1–C2 (~ 0.01 Å) and C2–P (~ 0.04 Å) bonds than those of the cyclobutanated compounds **6a–d** ($n = 3$), while the P–C1 bonds are instead longer by 0.02–0.03 Å; cf., compare **5a** with **6a**, **5b** with **6b**, etc. (the P–C1 bond is distal to the smaller (n) ring). These differences in bond lengths are also reflected in the smaller P–C1–C2 ($\sim 2^\circ$) and larger P–C2–C1 ($\sim 2^\circ$) bond angles of the cyclopropanated systems ($n = 2$). While the size of the other, larger (m) ring hardly influences the C1–C2 and P–C2 bond lengths, the P–C1 bond lengthens with increasing m for both series of compounds. This bond is the shortest in the $m = 2$ series (**5a**: 1.820(8) Å; **6a**: 1.790(3) Å) and the longest in the $m = 5$ series (**5d**: 1.879(2) Å; **6d**: 1.860(4) Å) with the largest change (~ 0.04 Å) taking place in going from a three- to a four-membered ring (**5a** → **5b**, **6a** → **6b**). These findings suggest that smaller rings tighten the phosphirane ring most, but some of the differences are within the experimental error limits. Therefore, we must conclude that the crystal structures do not reflect adequately a systematic effect on the phosphirane ring by annulating it with differently sized rings, even though

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(12) Strain energy of phosphirane at HF/6-31G* = 20.1 kcal/mol: Bachrach, S. M. *J. Phys. Chem.* **1989**, *93*, 7780–7784.

Table 1. Selected Bond Lengths and Angles from the Crystal Structures of 5a–d and 6b–d

bond (Å)/ angle (deg)	5a ^a	5b ^b	5c	5d	6b	6c	6d	9a ^c
C1–C2	1.48(1)	1.500(4)	1.477(12)	1.506(3)	1.514(6)	1.512(5)	1.512(7)	1.50(2)
C1–P	1.820(8)	1.866(3)	1.871(8)	1.879(2)	1.836(4)	1.846(3)	1.860(4)	1.83(2)
C2–P	1.807(8)	1.790(3)	1.787(11)	1.794(2)	1.832(5)	1.848(3)	1.842(4)	1.80(2)
P–W	2.495(2)	2.5028(8)	2.485(3)	2.5004(6)	2.4928(10)	2.5035(8)	2.5156(10)	2.504(2)
C1–P–C2	48.1(4)	48.39(13)	47.6(4)	48.33(10)	48.77(19)	48.32(15)	48.2(2)	48.6(7)
P–C1–C2	66.4(5)	63.14(15)	63.2(5)	62.87(12)	65.5(2)	65.88(17)	65.3(2)	64.5
P–C2–C1	65.5(4)	68.48(16)	69.2(5)	68.79(12)	65.7(2)	65.79(18)	66.5(2)	67.2
W–P–Ph	122.3(3)	125.20(10)	120.3(3)	117.54(7)	120.68(14)	117.96(10)	116.03(14)	122.9(3)

^a Reference 9. ^b 5b is identical with 6a. ^c Reference 8a.

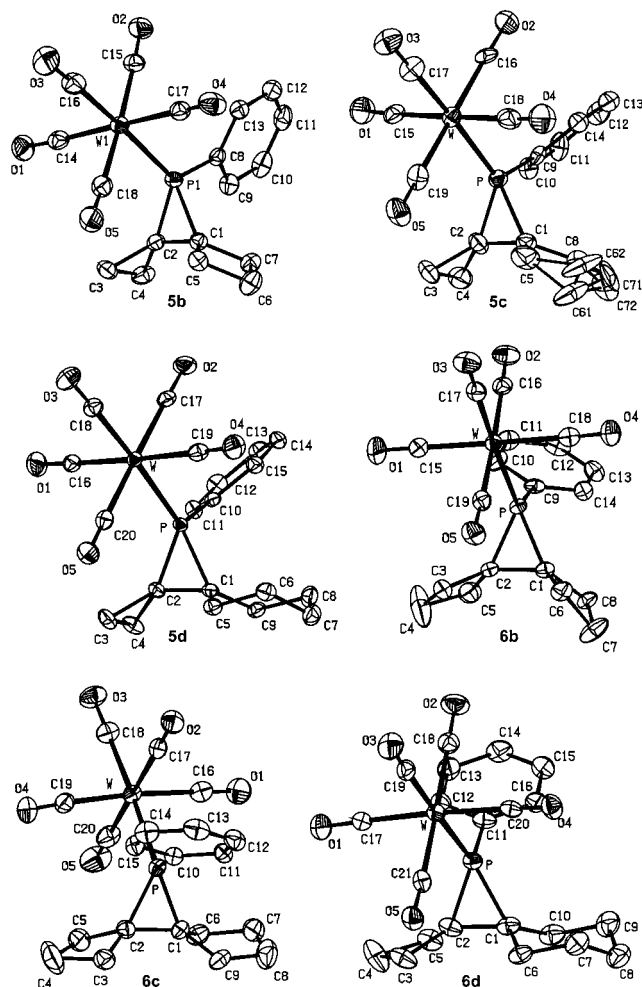


Figure 1. Displacement ellipsoid plot of structures 5b–d and 6b–d drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The cyclopentane ring of 5c is disordered.

differences between the C1–P and C2–P bond lengths of unsymmetrical dispirophosphiranes can be as large as 0.085 Å.

Ab Initio Structures. To obtain more insight into the influence of spirofusion on the geometry of the central phosphirane ring, we resorted to ab initio theory to compute their parent structures in which the W(CO)₅ group is eliminated and the phenyl group replaced for a hydrogen. They are designated in accordance with the experimental structures but with a capital letter instead. The C–C and C–P bond distances of the central ring of the MP2/6-31G*–optimized geometries are given in Table 2; the structures are shown in Figure 1S in the Supporting Information. Parent phosphirane 9A serves as anchor in this study. Its P–C bond length of 1.866 Å is in

excellent agreement with the 1.867 Å determined by microwave spectroscopy,¹³ and its C–C bond of 1.488 Å is only slightly shorter than the experimental value of 1.502 Å. The computed minimum energy conformations for 5A–D (*n* = 2) and 6B–D (*n* = 3) are also in good agreement with those of the experimental crystal structures when the absence of the stabilizing phenyl and W(CO)₅ substituents is taken into account.⁸ The conformation of the five-membered ring of structure 6C differs from the experimentally determined one (6c), but the energy difference between the two conformers of only 0.32 kcal/mol at MP2(Full)/6-31G* is very small. A similar effect is evident from the disorder in the crystal of 5c.

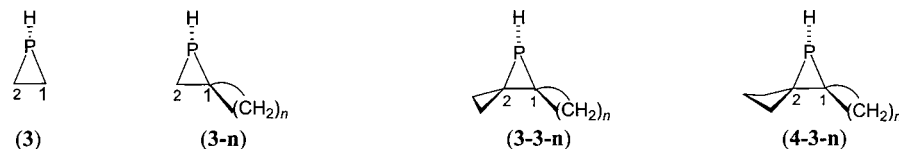
Dispirophosphiranes. The MP2/6-31G* structures of the *n* = 2 and 3 series of compounds show the geometrical changes due to spirofusion with differently sized rings much more clearly than the crystal structures. For example, the PC bonds of 5a and 6b are equally long within the experimental error limits, but they differ in the theoretical structures. Namely, in bicyclopropanated 5A they are shorter (by 0.016 Å) than in phosphirane 9A but in bicyclobutanated 6B they are longer by a similar amount; each has a shorter C1–C2 bond than 9A (i.e., 0.036 and 0.015 Å, respectively). Further, both PC bonds of all four cyclobutanated dispirophosphiranes 6A–D (*n* = 3) are elongated from that of 9A, whereas one of them, the P–C2 bond, is shorter in the cyclopropanated series 5A–D (*n* = 2). This same bond is much shorter (~0.04 Å) in the *n* = 2 series than in the *n* = 3 series, when structures with similarly sized “*m*” rings are compared.

The size of the annulated “*m*” ring correlates with the geometrical parameters of the central phosphirane ring. Enlarging from a three- to a six-membered ring (A → D) results in an elongation of the P–C1 bond in both series of dispirophosphiranes (5A–D and 6A–D) of up to 0.058 Å. The single largest difference (~0.04 Å) is observed on changing from a three- to a four-membered ring, i.e., 5A → B and 6A → B. In contrast, the P–C2 bonds shorten (up to 0.020 Å) on spirofusion with larger “*m*” rings with a concomitant lengthening of the C1–C2 bond (of up to 0.022 Å). As in the crystal structures, enlarging the annulated ring is reflected in a widened C1–C2–P angle and a tightened C2–C1–P angle. It is evident that spirofusion with smaller rings gives a more condensed phosphirane ring, whereas larger rings have a relaxing effect. The geometrical parameters of the annulated “*m*” ring itself are, however, not influenced by the size of the other “*n*” ring.

Monospirophosphiranes. Do the two annulated “*m*” and “*n*” rings have a cumulative effect on the geometry


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Table 2. Selected Bond Lengths (Å) from the MP2/6-31G*-Optimized Structures of 9A, 4A–D, 5A–D, and 6A–D

Rings																
	(3)	(3-n)	(3-3-n)	(4-3-n)	9A	4A	4B	4C	4D	5A	5B ^a	5C	5D	6B	6C	6D
Bond Length																
C1–C2	1.488	1.469	1.476	1.478	1.483	1.452	1.458	1.472	1.467	1.473	1.480	1.475				
C1–P	1.866	1.830	1.867	1.878	1.882	1.850	1.890	1.890	1.908	1.874	1.876	1.895				
C2–P	1.866	1.889	1.878	1.877	1.874	1.850	1.838	1.836	1.836	1.876	1.875	1.874				

^a Structure **5B** is identical to **6A**.

Table 3. Selected Bond Lengths (Å) from the MP2/6-31G*-Optimized Structures of 13, 10A–D, 11A–D, and 12B–D^a

Rings																
	(3)	(3-n)	(3-3-n)	(4-3-n)	13	10A	10B	10C	10D	11A	11B ^b	11C	11D	12B	12C	12D
Bond Length																
C2–C3	1.501	1.523	1.491	1.502	1.499	1.456	1.467	1.481	1.477	1.489	1.498	1.492				
C1–C2	1.501	1.477	1.496	1.502	1.505	1.497	1.517	1.522	1.527	1.499	1.507	1.514				
C1–C3	1.501	1.477	1.511	1.505	1.508	1.497	1.485	1.479	1.482	1.504	1.498	1.502				

^a The row entries are given in the same sequence as in Table 2. ^b Structure **11B** is identical to **12A**.

and strain of the central phosphirane ring? To evaluate this effect requires the related monospiro compounds. Whereas **4a–d** are already known,⁸ only the crystal structure of **4a** has been reported.⁹ Therefore, we resort to MP2/6-31G* geometries of the parent structures (**4A–D**), again without the W(CO)₅ group and with the phenyl replaced by a hydrogen (see Table 2 for selected bond distances; Figure 2S in the Supporting Information shows their geometries). They show that the C1–C2 bonds are shorter than that of **9A** and that the PC bonds are longer, except for the P–C1 bond of **4A**, which is 0.036 Å shorter. The trend in the geometrical changes of the phosphirane ring is similar to that observed for the bisannulated structures, i.e., enlarging the “*m*” ring elongates the P–C1 and C1–C2 bonds, and shortens the P–C2 bond. The phosphirane unit of **4A** appears to be tighter than **9A**, while those with larger rings are more relaxed.

What is then the additional influence of the second ring on the phosphirane unit? Of course, there is a direct impact on C2, which becomes a spirofused atom, but also the distal P–C1 bond is effected through hyperconjugation. Because the monospiro compounds have more relaxed phosphirane rings they are expected to have the longer P–C2 bonds. They are indeed longer than in the cyclopropanated dispiro compounds, but those of the cyclobutanated series are surprisingly of similar length. For example, the P–C2 bond of **4D** is 0.038 Å longer than in **5D**, but it has the exact same length (1.874 Å) in **6D**. The other P–C1 phosphirane bond is the longest in the cyclobutanated series and the shortest in the monospiro compounds, with a concomitant opposite trend for the C1–C2 bond length. These geometrical evaluations suggest that the phos-

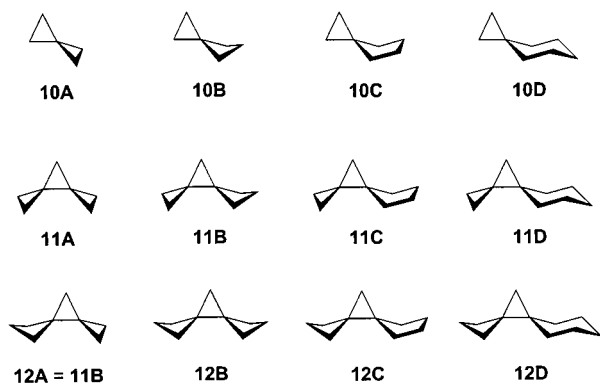
phirane rings of **4A–D** are less tight than those of the cyclopropanated series **5A–D** but similar to those in the cyclobutanated series **6A–D**.

(Di)spirocyclopropanes. To establish a broader context for the influence of spiroannulation on the phosphirane ring, we evaluate in this section the corresponding effect of mono- and dispirofusion on the isovalent cyclopropane ring. Such an extensive and detailed hydrocarbon study has not yet been performed.^{1,10} For direct comparison with the organophosphorus series, we report on the corresponding mono- and dispiro hydrocarbon compounds **10A–D**, **11A–D**, and **12A–D**. We use uppercase characters to identify the MP2/(Full)/6-31G*-optimized structures, which are shown in Figures S3 and S4 in the Supporting Information. Bond distances of the central cyclopropyl ring are listed in Table 3. Experimental structures are identified with lower case characters. We use the same nomenclature as discussed above to identify the dispiro compounds, i.e., *n* = 2 for the cyclopropanated series and *n* = 3 for the cyclobutanated series.

Many of the above hydrocarbons are known in the literature, but to the best of our knowledge, only the single-crystal X-ray structures have been reported for structures **10a**¹⁴ and **11a**,¹⁵ both of which are in excellent agreement with the computed geometries. We therefore assume that the MP2(Full)/6-31G* geometries for the other hydrocarbons are also adequate. Their C1–C2 and C2–C3 bonds of the “central” cyclopropane ring lengthen

(14) Boese, R.; Bläser, D.; Gomann, K.; Brinker, U. H. *J. Am. Chem. Soc.* **1989**, *111*, 1501–1503.

(15) Boese, R.; Haumann, T.; Jemmis, E. D.; Kiran, B.; Kozhushkov, S.; de Meijere, A. *Liebigs Ann.* **1996**, 913–919.



with increasing the size of the annulated “*m*” ring, which mimics the trend for the corresponding P1–C1 and C1–C2 bonds of the discussed spirophosphiranes. As expected, this effect is less pronounced for the hydrocarbons. For example, replacing a three- for a six-membered ring (A → D) results in a lengthening of the C1–C2 bond by ~0.03 Å, compared to ~0.05 Å for the P–C1 bond of the corresponding organophosphorus compounds. It is then evident that the tightest annulated cyclopropanes have the smaller spirofused rings, just like the annulated phosphiranes.

There are other trends as well. The cyclopropanated series **11** have the longest C1–C2 bonds (cf. P–C1 in **5**) and the monospiranes **10** the shortest (cf. **4**). The opposite applies to the C2–C3 bonds. For all these spirofused cyclopropanes they are shorter than in cyclopropane itself (**13**), except for **10D**. This analysis suggests that the cyclopropane ring is the least strained in the monospiranes and the most strained in cyclopropanated series **11**.

Heats of Formation (ΔH_f). The geometrical changes of the central three-membered rings are clearly related to the size of their spiroannulated ring(s). However, the above discussion also illustrates that this relationship is difficult if not impossible to quantify. Because geometrical distortions are also related to changes in molecular strain, a comparison of strain energies may provide a more general quantification. An abundance of literature is available on small rings, but this is not the case for the systems of the present study, not for the organophosphorus compounds and neither for the hydrocarbons. Accurate heats of formations are needed to establish their strain energies. Because of the absence of experimental heats of formation for all of the organophosphorus compounds and for most of the hydrocarbons, we decided to obtain them by theoretical methods. Pople’s G3(MP2) method has been shown to accurately calculate ΔH_f values with an average absolute deviation from experiment of 1.18 kcal/mol⁻¹ for the G2/97 test set.¹⁶ Still, it is important to verify first the accuracy of the G3(MP2) method for the systems of our interest. For this purpose we computed heats of formation for the hydrocarbons for which experimental values are available. The G3(MP2) calculated ΔH_f values for cyclopropane (**13**) of 13.5 kcal/mol (exptl 12.7),³ for spiro[3.0]pentane (**10A**) of 44.8 kcal/mol (exptl 44.2),¹⁷ for spirohexane (**10B**) of 31.3 kcal/mol (exptl 29.9),¹⁰ for [3]triangulane (**11A**) of 75.5 kcal/

Table 4. G3(MP2) Energies (in –au), ΔH_f , SE, and ΔSE (in kcal/mol) for **4A–D**, **5A–D**, and **6A–D**

	4A	4B	4C	4D
<i>E</i>	497.18254	536.42775	575.69318	614.93907
ΔH_f	49.63	36.84	11.37	–1.84
SE	55.0	47.2	26.7	18.4
ΔSE	5.2	–1.0	–1.9	–3.5
ΔSE_c^a	4.6	–1.6	–2.5	–4.2
$\Delta SE/C^b$	5.2	–1.0	–1.9	–3.5
	5A	5B	5C	5D
<i>E</i>	574.41994	613.6646	652.94247	692.17762
ΔH_f	78.02	65.67	40.02	27.09
SE	88.2	79.5	58.8	50.9
ΔSE	10.0	3.1	2.0	0.6
ΔSE_c^a	9.3	2.3	1.3	–0.1
$\Delta SE/C^b$	5.0	1.6	1.0	0.3
	6A	6B	6C	6D
<i>E</i>	613.66646	652.91166	692.17758	731.42253
ΔH_f	65.67	52.89	27.11	14.49
SE	79.5	71.7	50.9	43.3
ΔSE	3.1	–3.1	–4.3	–5.4
ΔSE_c^a	2.3	–3.8	–5.0	–6.2
$\Delta SE/C^b$	1.6	–1.6	–2.2	–2.7

^a ΔSE_c is the excess strain energy obtained from G3(MP2) (0 K) without the zero-point energy corrections. ^b Excess strain per spirocarbon.

mol (exptl 72.3)¹⁸ and for dispiro[3.0.2.1]octane (**11B**) of 61.8 kcal/mol (exptl 58.4)¹⁹ are in good agreement with the corresponding experimental data. Whereas it is attractive to use the more economical B3LYP/6-31G* level of theory, the G3(MP2) method performs far superior in calculating accurate ΔH_f values, especially for the larger systems.²⁰ Because of this accuracy, we applied the G3(MP2) method throughout. The theoretically predicted ΔH_f values for the spiroannulated phosphiranes are listed in Table 4 and those of the corresponding cyclopropane analogues in Table 5. These show that for similar sized systems the organophosphorus compounds have a heat of formation that is about ~5 kcal/mol higher than their hydrocarbon counterparts.

Strain Energy (SE). Before commencing with the influence of the annulated rings on the strain of the central three-membered rings, it is relevant to briefly focus on the unsubstituted parent structures. The experimentally determined strain energy of 27.5 kcal/mol for cyclopropane^{2,3} is similar to that of the first-row heterocycles oxirane (**15**, 27.2 kcal/mol)²¹ and aziridine (**16**, 27.1 kcal/mol).²¹ Much smaller SE values are found for the second-row heterocycles phosphirane **9A** (21.3 kcal/mol at G2(MP2))⁹ and thiirane (19.8 kcal/mol).²² The larger value for silirane **17** (43.4²³ and 40.2²⁴ kcal/mol) has been attributed to the preference of Si for 90° bond

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(20) The calculated heats of formation at B3LYP/6-31G* are 13.9 kcal/mol for cyclopropane **13**, 46.2 kcal/mol for spiro[3.0]pentane **10A**, 34.6 kcal/mol for spirohexane **10B**, 78.5 kcal/mol for [3]triangulane **11A**, and 66.5 kcal/mol for dispiro[3.0.2.1]octane **11B**.

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Table 5. G3(MP2) Energies (in –au), ΔH_f , SE, and ΔSE (in kcal/mol) for 10A–D, 11A–D, and 12A–D

	10A	10B	10C	10D
E	–194.88777	–234.13411	–273.40075	–312.64549
ΔH_f	44.80	31.30	5.07	–7.42
SE	64.9	56.3	35.1	27.6
ΔSE	8.1	1.3	–0.4	–1.3
ΔSE_e^a	8.1	1.3	0.2	–1.4
$\Delta SE/C^b$	8.1	1.3	–0.4	–1.3
	11A	11B	11C	11D
E	–272.12345	–311.37063	–350.63728	–389.88198
ΔH_f	75.53	61.50	35.27	22.80
SE	100.8	91.7	70.4	62.9
ΔSE	15.6	8.3	6.6	5.7
ΔSE_e^a	15.5	8.1	6.5	5.5
$\Delta SE/C^b$	7.8	4.2	3.3	2.9
	12A	12B	12C	12D
E	–311.37063	–350.61746	–389.88379	–429.12796
ΔH_f	61.50	47.71	21.67	9.53
SE	91.7	82.9	61.8	54.6
ΔSE	8.3	1.1	–0.3	–0.9
ΔSE_e^a	8.1	1.0	–0.4	–1.2
$\Delta SE/C^b$	4.3	0.6	–0.2	–0.5

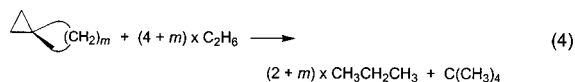
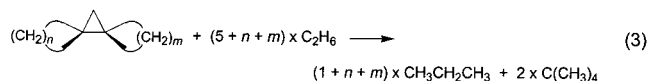
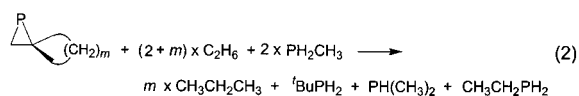
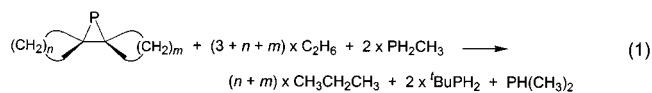
^a ΔSE_e is the excess strain energy obtained from G3(MP2) (0 K) without the zero-point energy corrections. ^b Excess strain per spirocarbon.

angles; phosphasilirane **18** has an SE of 26.5 kcal/mol at G3(MP2).²⁵



The SEs for all the (di)spirophosphiranes (**4A–D**, **5A–D**, and **6A–D**) and their hydrocarbon analogues (**10A–D**, **11A–D**, and **12A–D**) were obtained from homodesmotic reactions (eqs 1–4) using G3(MP2) calculated ΔH_f values for all of the components.²⁶ The SE values are listed in Table 4 for the organophosphorus compounds and in Table 5 for the hydrocarbons. The SE values (in kcal/mol) for spiropentane **10A** (calcd 64.9, exptl¹⁷ 65.1), spirohexane **10B** (calcd 56.3, exptl¹⁰ 55.9), and [3]triangulane **11A** (calcd 100.8, exptl¹⁸ 98.5) show an excellent agreement with those that are based on experimental data.²⁷ The deviation of only 2.3 kcal/mol from the experimental value for **11A** is remarkably small considering that the homodesmotic equation contains 17 molecules. Thus, the G3(MP2) method appears to produce accurate SE values for the hydrocarbons.

The SE values of the organophosphorus compounds are on average 10 kcal/mol smaller than their hydrocarbons analogues, which must relate to the less strained nature of the phosphirane ring. Expectedly, the smaller SEs are obtained for the systems with the larger annulated rings. The monospiranes **4A–D** and **10A–D** are the least strained and the cyclopropanated dispiranes **5A–D** and



11A–D are the most strained in the respective organophosphorus and hydrocarbon series of compounds.

Excess Strain Energy (ΔSE). The total strain energy provides only limited insight into the effect of spirofusion on the central three-membered ring. More useful information is obtained from the excess strain energy (ΔSE , listed in Table 4 for the organophosphorus compounds and in Table 5 for the hydrocarbons), which is defined as the sum of the strain energies of the separate rings²⁸ minus the strain energy of the polycycle. For example, the 64.9 kcal/mol SE for spiropentane **10A** is a significant 8.1 kcal/mol more than twice the 28.4 kcal/mol for cyclopropane (all at G3(MP2)). For [3]triangulane **11A**, the difference in SE with three cyclopropane rings is 15.6 kcal/mol, which can also be expressed as 7.8 kcal/mol per spiro carbon ($\Delta SE/C$) and is in accord with the 8.6 kcal/mol that de Meijere¹⁰ reported for the average spiro increment for an extended set [n]triangulanes consisting of only three-membered rings. Whereas these $\Delta SE/C$ values are convenient for comparing bicyclic with tricyclic structures, they only represent averaged values for the spirocarbons of differently sized rings (see also Tables 4 and 5).

(Di)spirocyclopropanes. Comparing the excess strain between the various monospiranes already leads to an unexpected observation. For example, whereas spiropentane **10A** has a ΔSE of 8.1 kcal/mol that of spirohexane **10B** is negligible (1.3 and 0.8 (exptl) kcal/mol). This is surprising in light of the virtually equal strain energies for cyclobutane and cyclopropane. It appears that annihilation of strain energy occurs in the polycycles that contain four-membered rings. This effect has been recognized before.¹⁰ For example, the hydrocarbons **19** and **20** have hardly any excess strain and even [4]rotane **21** is remarkably small ΔSE of 2.4 kcal/mol. Even slightly negative values have been reported by molecular mechanics (MM2) for spiranes with cyclopentyl (**10C**, –0.5 kcal/mol) and cyclohexyl (**10D**, –1.3 kcal/mol) rings.²⁹ Those at G3(MP2) are very similar.

The same trend is found for the dispiranes. For example, **12A** has a ΔSE of 8.5 kcal/mol, whereas that

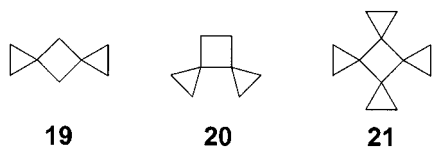
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(26) The G3(MP2) ΔH_f values for the components of eqs 1–4 are as follows (kcal/mol): $C_2H_6 = -20.10$; $PH_2CH_3 = -3.80$; $CH_3CH_2CH_3 = -25.07$; $tBuPH_2 = -22.09$; $PH(CH_3)_2 = -12.71$; $C(CH_3)_4 = -40.38$.

(27) The experimental ΔH_f values for the components of eqs 1–4 are as follows (kcal/mol): $C_2H_6 = -20.1$; $PH_2CH_3 = -4.0$; $CH_3CH_2CH_3 = -25.0$; $tBuPH_2 =$ not known; $PH(CH_3)_2 = -14.0$; $C(CH_3)_4 = -40.0$.

(28) The G3(MP2) SEs for the separate rings are computed from the following homodesmotic reactions: $C_3H_6 + 3 C_2H_6 \rightarrow 3 C_3H_8$ (SE cyclopropane = 28.37 kcal/mol; $\Delta H_f = 13.46$ kcal/mol); $C_4H_8 + 4 C_2H_6 \rightarrow 4 C_3H_8$ (SE cyclobutane = 26.69 kcal/mol; $\Delta H_f = 6.80$ kcal/mol); $C_5H_{10} + 5 C_2H_6 \rightarrow 5 C_3H_8$ (SE cyclopentane = 7.08 kcal/mol; $\Delta H_f = -17.78$ kcal/mol); $C_6H_{12} + 6 C_2H_6 \rightarrow 6 C_3H_8$ (SE cyclohexane = 0.52 kcal/mol; $\Delta H_f = -29.31$ kcal/mol); $C_2H_5P + 3 C_2H_6 \rightarrow 2 C_3H_8 + PH(CH_3)$ (SE phosphirane = 21.42 kcal/mol).

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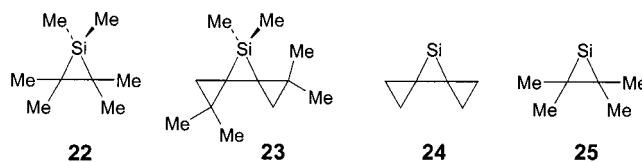
of **12B** is only 1.1 kcal/mol, and the cyclohexyl containing **12D** has a negative excess strain of -0.9 kcal/mol. The similarity in Δ SEs for this series and the monospiranes illustrates that the additional cyclobutyl ring does, in fact, not increase the excess strain energy. This is different for the cyclopropanated series **11** of which each member has about a 7 kcal/mol higher Δ SE value than the comparable members of the **10** and **12** series. Thus, Δ SE is 15.6 kcal/mol for [3]triangulane **11A**, 8.1 kcal/mol for **11B**, and still 5.7 kcal/mol for **11D**. Also this series illustrates that replacing one of the cyclopropyl rings for a cyclobutyl ring (**A** \rightarrow **B**) gives the largest reduction in Δ SE, which mimics the noted geometrical differences between these systems. Further enlarging the spiroannulated "m" ring (**B** \rightarrow **D**) reduces the incremental strain energy more, but the effect is only modest. The calculations do suggest that the Δ SE values can become negative, but they are so small that this may well be within the error limits of the G3(MP2) method. Thermodynamic corrections are not a contributor, however, because the Δ SE values do not change on their exclusion (see Δ SE_c in Table 5).

(Di)spiroposphiranes. The incremental strain energies for the organophosphorus compounds, listed in Table 4, are expectedly much smaller than those of the corresponding hydrocarbons (with Δ SE/C differences of 2–3 kcal/mol), but the patterns are very much the same if not more pronounced. They are also in accord with the findings of the geometrical analysis given in an earlier section. For example, the Δ SE values of the monospiranes **4** are larger than those of the cyclobutanated series **6**, but they are of course smaller than those of the cyclopropanated series **5**. Thus, spirofusion of any of the spiroposphalkanes (**4A–D**) with an additional cyclopropyl ring results in an *increase* in excess strain (i.e., a destabilization of about 4.2 kcal/mol), while an additional cyclobutyl ring results in a remarkable *decrease* in excess strain (i.e., a stabilization of about 2.1 kcal/mol).

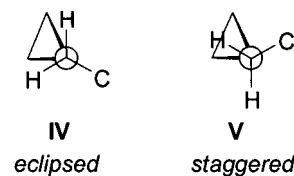
Enlarging the "m" ring reduces Δ SE for the spiroannulated phosphiranes in much the same way as for the hydrocarbons. For example, in going from a cyclopropyl to a cyclohexyl ring (**A** \rightarrow **D**) similar reductions result for **4**, **5**, and **6** of 8.7, 9.4, and 8.5 kcal/mol, respectively. The average value for the three series of hydrocarbons is 9.6 kcal/mol. However, the main distinction from the hydrocarbons is that all the noncyclopropanated phosphiranes have negative Δ SE values that can be as large as -5.4 kcal/mol for **6D**. Again, since thermodynamic corrections hardly influence the negative values (see Δ SE_c), these *stabilization* energies are likely to have an electronic origin.

Negative Excess Strain Energies. How can a spirofused structure be less strained than the sum of its separate rings? Before proceeding, it is relevant to note that the presented (di)spiroposphiranes are not isolated cases. In addition to the noted hydrocarbons **19–20** also heterocycles have been reported that are, in fact, stabilized through spiroannulation with four-membered rings.

For example, Bachrach³⁰ showed that tetraphosphacubane is 13.6 kcal/mol less strained at HF/6-31G* than its separate phosphetane rings. He contributed this to the ability of phosphorus to accommodate small angles and to the high ionic character of the P–C bonds leading to a more stable electrostatic environment. However, even cubane itself has a negligible experimental Δ SE of -0.3 kcal/mol.³⁰ A stabilizing effect has also been claimed for cyclopropanated siliranes. For example, Seyferth reported that 7-siladispiro[2.0.2.1]heptane **23** is much more stable than hexamethylsilirane **22**.³¹ Based on extended Hückel calculations on **24**, **25**, and the parent silirane **17**, Hoffmann attributed this stabilization to d- σ hyperconjugation.³² The stabilization resulting from methyl substitution on cyclopropane,³³ but also on phosphirane **9A**,³⁴ has likewise been attributed to hyperconjugation.



In more general terms, the (de)stabilization of a cyclopropane ring is described in terms of the σ -donor and π -acceptor abilities of the substituent. Several groups have shown that both types of substituents result in lengthening of the vicinal C–C bonds and a shortening of the distal bond due to increased electron density in the corresponding antibonding and bonding Walsh orbitals.³⁵ The lengthening of the P1–C1 bond and the shortening of the P1–C2 bond in **4**, **5**, and **6**, on increasing the size of the "m" ring, with analogous behavior of the C1–C2 and C1–C3 bonds in the hydrocarbons **10**, **11**, and **12**, suggests a similar hyperconjugative effect of the spiroconnected methylene groups. For methylcyclopropane, this effect is the largest when the methyl group is in a staggered conformation, with one of its hydrogens bisecting the cyclopropyl ring.



Similar hyperconjugative effects are present in the most strained and the least strained structures of this study. For example, the cyclopropanated phosphiranes (**4–5A**) and cyclopropanes (**10–12A**), which have the highest Δ SE values, have their spiroconnected CH₂ groups in an unfavorable eclipsed conformation **IV**.

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Instead, the cyclohexyl spirofused systems (**4–5D** and **10–12D**), which have the smallest Δ SE values, have these methylene groups in a stabilizing staggered conformation **V**. In particular, the negative Δ SE values of the organophosphorus structures **4D** and **6D** illustrate that this hyperconjugation effect has a significant stabilizing effect, although contributions resulting from steric repulsion can a priori not be entirely dismissed.

Conclusions

Six new dispirophosphirane complexes have been synthesized in high yields by 1,2-additions of a complexed phosphinidene to bicycloalkylidenes. Their single-crystal X-ray structures and the MP2/6-31G*-optimized geometries of simplified parent structures suggest that spirofusion with smaller rings tightens the central phosphirane ring, while it relaxes on annulation with larger rings. Spirofusion of cyclopropane results in very similar geometrical changes.

Heats of formation, strain energies, and excess strain energies have been calculated at the G3(MP2) level of theory for the mono- and dispirofused phosphiranes and for their hydrocarbon analogues. As expected, the strain energy for the organophosphorus structures is generally ~ 10 kcal/mol lower than that of their hydrocarbon counterparts. The excess strain of the spirofused phosphiranes and cyclopropanes decreases with increasing size of the annulated rings and becomes even negative for the larger organophosphorus structures. The excess strain energy of the cyclobutanated dispirophosphiranes **6A–D** is expectedly smaller than that of the cyclopropanated series **5A–D**, but is, surprisingly, also lower than that of the monospirophosphiranes **4A–D**. As to the hydrocarbons analogous, the cyclopropanated dispiro series **11A–D** have the largest Δ SE values, while those of the monospiro- (**10A–D**) and cyclobutanated dispiro-cyclopropanes (**12A–D**) are nearly equal. The lengthening of the vicinal bonds that occurs with the larger spirofused rings together with their reduced or even negative Δ SE values indicates an increased hyperconjugative stabilization of the spiroconnected methylene groups. The stabilization is attributed to a staggered conformation of these methylene units.

Computational Section

All electronic structure calculations were carried out using the GAUSSIAN 98 suite of programs.³⁶ Geometries were optimized at the HF and MP2(fc) levels of theory using the 6-31G* basis set. The Hessian index, which is the number of negative eigenvalues of the force constant matrix, was determined for all species to be zero. G3(MP2) theory was used to obtain more accurate absolute energies for the optimized structures.¹⁶ Heats of formation (ΔH_f^{298}) for the systems in eqs

1–4 were estimated from their heats of atomization calculated at G3(MP2).

Experimental Section

All experiments were performed under an atmosphere of dry nitrogen. Solids were dried in vacuo and liquids were distilled (under N_2) prior to use. Solvents were used as purchased except for toluene, which was distilled over sodium. NMR spectra were recorded on Bruker AC 200 (1H , ^{13}C) and WM 250 spectrometers (^{31}P) using $SiMe_4$ (1H , ^{13}C) and 85% H_3PO_4 (^{31}P) as external standards, IR spectra on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HR-MS) on a Finnigan Mat 90 spectrometer. Bicycloalkylidenes **8** were prepared according to literature procedures.³⁷

(8-Phenyl-8-phosphadispiro[3.0.2.1]octane)penta-carbonylungsten (5b). A mixture of 17 mg (0.18 mmol) cyclopropylcyclobutylidene, 300 mg (0.46 mmol) of complex **7**, 5 mg (0.05 mmol) of $CuCl$, and 3 mL of toluene was heated at 55 °C for 1.5 h. After evaporation of the solvent, the residue was chromatographed over silica with toluene/pentane 1:4 to yield 70 mg (73%) **5b** as a pale green oil. Crystallization from hexane afforded colorless crystals: ^{31}P NMR ($CDCl_3$) δ (ppm) = -129.8 ($^1J(W,P) = 252.3$ Hz); 1H NMR ($CDCl_3$) δ (ppm) = 0.5 – 2.5 (m, 10H, CH_2), 6.9 – 7.3 (m, 5H, Ph); ^{13}C NMR (C_6D_6) δ (ppm) = 8.9 (d, $^2J(P,C) = 3.4$ Hz, CH_2 c-prop), 9.0 (s, CH_2 c-prop), 16.8 (d, $^3J(P,C) = 6.2$ Hz, CH_2 c-bu), 27.4 (d, $^2J(P,C) = 4.4$ Hz, CH_2 c-bu), 28.8 (d, $^1J(P,C) = 4.5$ Hz, spiro-C c-prop), 29.1 (s, CH_2 c-bu), 38.2 (d, $^1J(P,C) = 12.9$ Hz, spiro-C c-bu), 128.7 – 134.8 (m, Ar), 196.0 (d, $^2J(P,C) = 8.5$ Hz, *cis*-CO), 198.2 (d, $^2J(P,C) = 28.8$ Hz, *trans*-CO); HRMS calcd for $C_{18}H_{15}O_5$ -PW 526.016702, found 526.017344 ($\delta = 2.1 \times 10^{-3}$).

(9-Phenyl-9-phosphadispiro[2.0.4.1]nonane)penta-carbonylungsten (5c). A mixture of 230 mg (2.2 mmol) of cyclopropylcyclopentylidene, 700 mg (1.1 mmol) of complex **7**, 29 mg (0.3 mmol) of $CuCl$, and 4 mL of toluene was heated at 55 °C for 6.5 h. After evaporation of the solvent, the residue was chromatographed over silica with toluene/pentane 1:1 to yield 470 mg (80%) of **5c** as a pale green oil. Crystallization from hexane afforded colorless crystals: mp 86–87 °C; ^{31}P NMR (toluene): δ (ppm) = -126.7 ($^1J(P,W) = 255.2$ Hz); 1H NMR ($CDCl_3$) δ (ppm) = 0.7 – 2.2 (m, 12H, c-pent), 7.2 – 7.4 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$) δ (ppm) = 8.8 (s, *anti*- CH_2 c-prop), 8.9 (d, $^2J(P,C) = 3.6$ Hz, *syn*- CH_2 c-prop), 26.1 (d, $^2J(P,C) = 3.0$ Hz, *syn*- CH_2 c-pent), 26.3 (d, $^2J(P,C) = 4.3$ Hz, *anti*- CH_2 c-pent), 28.4 (d, $^1J(P,C) = 5.7$ Hz, spiro-C c-prop), 32.5 (d, $^2J(P,C) = 2.5$ Hz, *syn*- CH_2 c-pent), 34.3 (d, $^2J(P,C) = 4.2$ Hz, *anti*- CH_2 c-pent), 40.2 (d, $^1J(P,C) = 9.4$ Hz, spiro-C c-pent), 128.3 – 132.0 (m, Ar), 132.9 (d, $^1J(P,C) = 24.3$ Hz, *ipso*-Ph), 195.6 (d, $^2J(P,C) = 8.3$ Hz, *cis*-CO), 198.1 (d, $^2J(P,C) = 28.8$ Hz, *trans*-CO); HRMS calcd for $C_{19}H_{17}O_5$ PW 540.3235, found 540.032449 ($\delta = 6.2 \times 10^{-4}$); IR (KBr) ν (CO) 1916 (s), 1987 (s), 2074 (s).

(10-Phenyl-10-phosphadispiro[2.0.5.1]decane)penta-carbonylungsten (5d). A mixture of 140 mg (1.17 mmol) of cyclopropylcyclohexylidene, 500 mg (0.78 mmol) of complex **7**, and 20 mg (0.2 mmol) of $CuCl$ in 4 mL of toluene was heated at 55 °C for 6.5 h. After evaporation of the solvent, the residue was chromatographed over silica with toluene/pentane 1:7 to yield 402 mg (93%) **5d** as a pale green oil. Crystallization from hexane afforded colorless crystals: mp 80–81 °C; ^{31}P NMR (toluene) δ (ppm) = -128.4 ($^1J(W,P) = 254.8$ Hz); 1H NMR (C_6D_6) δ (ppm) = 0.8 – 1.8 (m, 14H), 7.1 – 7.4 (m, 5H, Ph); ^{13}C NMR (C_6D_6) δ (ppm) = 7.0 (s, *anti*- CH_2 c-prop), 7.1 (s, *syn*- CH_2 c-prop), 25.5 (s, CH_2 c-hex), 25.6 (s, *syn*- CH_2 c-hex), 26.1 (d, $^2J(P,C) = 5.3$ Hz, *anti*- CH_2 c-hex), 29.7 (d, $^1J(P,C) = 6.5$ Hz, spiro-C c-prop), 31.3 (d, $^2J(P,C) = 2.9$ Hz, *syn*- CH_2 c-hex), 33.9 (d, $^2J(P,C) = 5.4$ Hz, *anti*- CH_2 c-hex), 36.2 (d, $^1J(P,C) =$

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11.0 Hz, spiro-C c-hex), 126.9–129.9 (m, Ar), 132.2 (d, $^1J(\text{P},\text{C}) = 10.9$ Hz, *ipso*-Ph), 196.3 (d, $^2J(\text{P},\text{C}) = 8.1$ Hz, *cis*-CO), 198.4 (d, $^2J(\text{P},\text{C}) = 28.5$ Hz, *trans*-CO); HRMS calcd for $\text{C}_{20}\text{H}_{19}\text{O}_5\text{PW}$ 554.04800, found 554.047891 ($\delta = 6.4 \times 10^{-4}$).

(9-Phenyl-9-phosphadispiro[3.0.3.1]nonane)pentacarbonyltungsten (6b). A mixture of 72 mg (0.66 mmol) of bicyclobutylidene, 592 mg (0.9 mmol) of complex 7, 27 mg (0.27 mmol) of CuCl, and 3 mL of toluene was heated at 55 °C for 6.5 h. After evaporation of the solvent, the residue was chromatographed over silica with toluene/pentane 1:4 to yield 354 mg (72%) **6b** as a pale green oil. Crystallization from hexane afforded colorless crystals: mp 83–84 °C; ^{31}P NMR (toluene) δ (ppm) = -137.2 ($^1J(\text{W},\text{P}) = 230.8$ Hz); ^1H NMR (CDCl_3) δ (ppm) = 2.0–2.5 (m, 12H, CH_2), 7.2–7.4 (m, 5H, Ph); ^{13}C NMR (CDCl_3) δ (ppm) = 17.3 (d, $^3J(\text{P},\text{C}) = 7.4$ Hz, CH_2), 26.4 (d, $^2J(\text{P},\text{C}) = 4.6$ Hz, *anti*- CH_2), 28.0 (d, $^2J(\text{P},\text{C}) = 2.7$ Hz, *syn*- CH_2), 40.5 (d, $^1J(\text{P},\text{C}) = 18.0$ Hz, spiro-C), 128.7–122.4 (m, Ar), 132.8 (d, $^1J(\text{P},\text{C}) = 17.0$ Hz, *ipso*-Ph), 195.4 (d, $^2J(\text{P},\text{C}) = 8.4$ Hz, *cis*-CO), 198.3 (d, $^2J(\text{P},\text{C}) = 28.5$ Hz, *trans*-CO); HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{O}_5\text{PW}$ 540.03235, found 540.032241 ($\delta = 6.4 \times 10^{-4}$); IR (KBr) ν (CO) 1914 (s), 1989 (w), 2074 (w).

(10-Phenyl-10-phosphadispiro[3.0.4.1]decane)pentacarbonyltungsten (6c). A mixture of 268 mg (2.2 mmol) of cyclobutylcyclopentylidene, 700 mg (1.1 mmol) of complex 7, 29 mg (0.3 mmol) of CuCl, and 4 mL of toluene was heated at 55 °C for 3 h. After evaporation of the solvent, the residue was chromatographed over silica with toluene/pentane 1:1 to yield 518 mg (85%) of **6c** as a pale green oil. Crystallization from hexane afforded colorless crystals: mp 92–93 °C; ^{31}P NMR (toluene) δ (ppm) = -130.4 ($^1J(\text{W},\text{P}) = 247.2$ Hz); ^1H NMR (CDCl_3) δ (ppm) = 1.6–2.0 (m, 8H, c-pent), 2.1–2.4 (m, 6H, c-bu), 7.2–7.4 (m, 5H, Ph); ^{13}C NMR (CDCl_3) δ (ppm) = 16.9 (d, $^3J(\text{P},\text{C}) = 4.5$ Hz, CH_2 c-bu), 25.7 (d, $^2J(\text{P},\text{C}) = 5.4$ Hz, *anti*- CH_2 c-pent), 26.0 (d, $^2J(\text{P},\text{C}) = 3.5$ Hz, *syn*- CH_2 c-pent), 26.6 (d, $^2J(\text{P},\text{C}) = 4.6$ Hz, *anti*- CH_2 c-bu), 28.7 (d, $^2J(\text{P},\text{C}) = 2.8$ Hz, *syn*- CH_2 c-bu), 31.7 (d, $^2J(\text{P},\text{C}) = 3.0$ Hz, *syn*- CH_2 c-pent), 32.7 (d, $^2J(\text{P},\text{C}) = 6.6$ Hz, *anti*- CH_2 c-pent), 40.9 (d, $^1J(\text{P},\text{C}) = 19.2$ Hz, spiro-C c-bu), 44.0 (d, $^1J(\text{P},\text{C}) = 14.0$ Hz, spiro-C c-pent), 128.7–132.5 (m, Ar), 132.9 (d, $^1J(\text{P},\text{C}) = 16.0$ Hz, *ipso*-Ph), 195.6 (d, $^2J(\text{P},\text{C}) = 8.6$ Hz, *cis*-CO), 197.0 (d, $^2J(\text{P},\text{C}) = 27.9$ Hz, *trans*-CO); HRMS calcd for $\text{C}_{20}\text{H}_{19}\text{O}_5\text{PW}$ 554.04800, found 554.048051 ($\delta = 3.7 \times 10^{-4}$); IR (KBr) ν (CO) 1925 (s), 1991 (m), 2070 (m).

(11-Phenyl-11-phosphadispiro[3.0.5.1]undecane)pentacarbonyltungsten (6d). A mixture of 300 mg (2.2 mmol) of cyclobutylcyclohexylidene, 700 mg (1.1 mmol) of complex 7, 29 mg (0.3 mmol) of CuCl, and 4 mL of toluene was heated at 55 °C for 3 h. After evaporation of the solvent, the residue was chromatographed over silica with toluene/pentane 1:4 to yield 620 mg (99%) **6d** as a pale green oil. Crystallization from hexane afforded colorless crystals: mp 101–102 °C; ^{31}P NMR (toluene) δ (ppm) = -128.6 ($^1J(\text{W},\text{P}) = 255.2$ Hz); ^1H NMR (C_6D_6) δ (ppm) = 1.4–1.8 (m, 10H, c-hex), 2.1–2.5 (m, 6H, c-bu), 7.2–7.4 (m, 5H, Ph); ^{13}C NMR (C_6D_6) δ (ppm) = 17.7 (d, $^3J(\text{P},\text{C}) = 5.5$ Hz, CH_2 c-bu), 25.3 (s, CH_2 c-hex), 25.5 (d, $^2J(\text{P},\text{C}) = 7.0$ Hz, *anti*- CH_2 c-hex), 25.8 (d, $^2J(\text{P},\text{C}) = 3.5$ Hz, *syn*- CH_2 c-hex), 26.2 (d, $^2J(\text{P},\text{C}) = 4.5$ Hz, *anti*- CH_2 c-bu), 28.1 (d, $^2J(\text{P},\text{C}) = 2.5$ Hz, *syn*- CH_2 c-bu), 30.6 (d, $^2J(\text{P},\text{C}) = 3.5$ Hz, *syn*- CH_2 c-hex), 32.3 (d, $^2J(\text{P},\text{C}) = 7.0$ Hz, *anti*- CH_2 c-hex), 38.6 (d, $^1J(\text{P},\text{C}) = 15.6$ Hz, spiro-C c-hex), 41.7 (d, $^1J(\text{P},\text{C}) = 20.6$ Hz, spiro-C c-bu), 128.6–132.7 (m, Ar), 133.9 (d, $^1J(\text{P},\text{C}) = 26.5$ Hz, *ipso*-Ph), 195.8 (d, $^2J(\text{P},\text{C}) = 8.0$ Hz, *cis*-CO), 198.1 (d, $^2J(\text{P},\text{C}) = 28.7$ Hz, *trans*-CO); HRMS calcd for $\text{C}_{21}\text{H}_{21}\text{O}_5\text{PW}$ 568.06365, found 568.063542 ($\delta = 5.8 \times 10^{-4}$); IR (KBr) ν (CO) 1966 (s), 1989 (m), 2070 (m).

Crystal Structure Determinations. X-ray intensities were measured on an Enraf-Nonius CAD4T (structure **5c**) or a Nonius KappaCCD diffractometer (structures **5b**, **5d**, **6b**, **6c**, and **6d**), both equipped with a rotating anode ($\lambda = 0.71073$ Å). The structures were solved with the automated Patterson program DIRDIF.³⁸ The structures were refined with SHELXL97³⁹ against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups (structures **5c**, **6b**, **6c**, and **6d**) or freely with isotropic displacement parameters (structures **5b** and **5d**). In structure **5c**, the cyclopentane ring was refined with a disorder model. Structure calculations, checking for higher symmetry and preparations of molecular plots were performed with the PLATON⁴⁰ package.

Compound **5b**: $\text{C}_{18}\text{H}_{15}\text{O}_5\text{PW}$, $M_r = 526.12$, $T = 150(2)$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 7.7780(4)$ Å, $b = 10.249(3)$ Å, $c = 20.5192(9)$ Å, $\beta = 109.1885(15)^\circ$, $V = 1822.27(15)$ Å³, $Z = 4$. $R_1 [I > 2\sigma(I)] = 0.0225$. wR_2 (all reflections) = 0.0573.

Compound **5c**: $\text{C}_{19}\text{H}_{17}\text{O}_5\text{PW}$, $M_r = 540.15$, $T = 150(2)$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.761(3)$ Å, $b = 10.249(3)$ Å, $c = 15.380(4)$ Å, $\beta = 118.223(16)^\circ$, $V = 1911.3(9)$ Å³, $Z = 4$. $R_1 [I > 2\sigma(I)] = 0.0576$. wR_2 (all reflections) = 0.1485.

Compound **5d**: $\text{C}_{20}\text{H}_{19}\text{O}_5\text{PW}$, $M_r = 554.17$, $T = 125(2)$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 14.3208(2)$ Å, $b = 10.3413(1)$ Å, $c = 16.1024(2)$ Å, $\beta = 121.9828(8)^\circ$, $V = 2022.72(4)$ Å³, $Z = 4$. $R_1 [I > 2\sigma(I)] = 0.0185$. wR_2 (all reflections) = 0.0479.

Compound **6b**: $\text{C}_{19}\text{H}_{17}\text{O}_5\text{PW}$, $M_r = 540.15$, $T = 150(2)$ K, orthorhombic, space group $Pbca$ (No. 61), $a = 10.4498(1)$ Å, $b = 15.1021(1)$ Å, $c = 24.4789(2)$ Å, $V = 3863.11(5)$ Å³, $Z = 8$. $R_1 [I > 2\sigma(I)] = 0.0323$. wR_2 (all reflections) = 0.1006.

Compound **6c**: $\text{C}_{20}\text{H}_{19}\text{O}_5\text{PW}$, $M_r = 554.17$, $T = 150(2)$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.9837(2)$ Å, $b = 16.4149(3)$ Å, $c = 14.5060(2)$ Å, $\beta = 122.2920(10)^\circ$, $V = 2009.59(6)$ Å³, $Z = 4$. $R_1 [I > 2\sigma(I)] = 0.0263$. wR_2 (all reflections) = 0.0687.

Compound **6d**: $\text{C}_{21}\text{H}_{21}\text{O}_5\text{PW}$, $M_r = 568.20$, $T = 150(2)$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.8042(1)$ Å, $b = 12.0630(2)$ Å, $c = 19.4565(3)$ Å, $\beta = 110.7840(8)^\circ$, $V = 2151.34(5)$ Å³, $Z = 4$. $R_1 [I > 2\sigma(I)] = 0.0324$. wR_2 (all reflections) = 0.0854.

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Supporting Information Available: Cartesian coordinates for the MP2/6-31G*-optimized geometries and their G3-(MP2) energies (in hartrees) for **4A–D**, **5A–D**, **6B–D**, **9A**, **10A–D**, **11A–D**, **12B–D**, and **9A** and all their components used in eqs 1–4. X-ray crystallographic data and details for the X-ray data acquisition for **5b–d**, and **6a,c,d**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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