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# Linear and Branched Phospha[*n*]triangulanes

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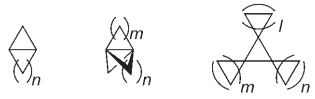
*Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 75th birthday*

**Abstract:** Novel, highly stable, linear and branched mono- and diphospha[*n*]-triangulanes were synthesized in high yields by the CuCl-catalyzed phosphinidene addition to spirocyclopropanated methylenecyclopropanes and bicyclopropylidenes. The effect of spirofusion on the electronic properties of these esthetically attractive phosphacycles is apparent from X-ray single crystal structure analyses, which reveals a tightening of the phosphirane ring on additional spirocyclopropanation, and from the NMR features that show deshielded chemical shifts for the ring-phosphorus and -carbon atoms. Steric factors play a role in the addition reaction when the substrate alkene carries a second sphere of spirocyclopropane rings and causes the formation of 2-phosphabicyclo[3.2.0]heptenes in small amounts. These by-products most probably result from addition of the [PhP(Cl)W(CO)$_5$]-Cu-L (L = alkene or solvent) reagent to the spirocyclopropanated bicyclopropylidene to give an intermediate σ-complex, which subsequently, facilitated by steric factors, undergoes a cyclopropylcarbinyl to cyclobutyl ring expansion followed by a [1,3]-sigmatropic shift.

**Keywords:** copper · cycloaddition · heterocycles · phosphorus · triangulanes

## Introduction

The inherently strained cyclopropane derivatives have unique electronic and chemical properties due to their small valence angles and bent C–C bonds.[1] Embedding the three-membered ring into oligocycles by annelation or spirofusion with additional small rings augments the total strain to exceed that of the sum of the separate rings. This is well established not only for the ring-annelated bicyclic (**1**) and tricyclic propellane skeletons (**2**), but also for the spirofused linear and branched so-called [*n*]triangulanes (**3**).[2] The current record of a branched [15]triangulane[3] and linear [9]triangulane[3] exemplifies the accessibility of such extended arrays of spirofused cyclopropanes that are surprisingly stable in spite of their high overall strain.

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By contrast to the large number of purely carbon-based triangulanes, far fewer spirocyclic compounds are known that contain a heteroatom, because of the higher reactivity of three-membered heterocycles.[2] Compounds such as 1-phosphaspiro[2,*n*]alkanes **4a–e**,[4] the 1-phosphadispiroalkanes **5a–d**,[5,6] and 1,4-diphosphaspiropentane **6**[7] with a phosphorus atom, that is, a phosphirane ring,[8] became accessible by the [1+2] cycloaddition of the in situ generated carbene-like electrophilic phosphinidene complexes R-P=W(CO)$_5$ to the respective alkenes.[9,10]

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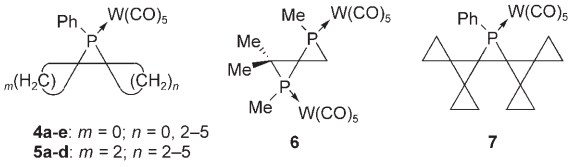
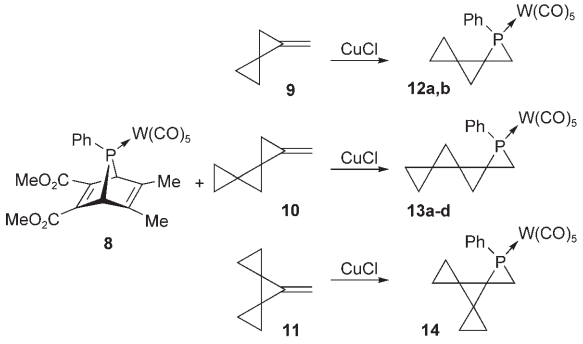



Recently, we described the synthesis of the first hetero[7]-triangulane **7** and showed that even the demetallated compound is stable at 150 °C.[11] In the present report we expand on these earlier studies and describe a series of novel stable phospha[*n*]triangulanes containing one or two phosphorus atoms.

## Results and Discussion

The syntheses of phospha[*n*]triangulanes ($n = 3$–5) was achieved by adding Ph-P=W(CO)$_5$ to terminal and non-terminal double bonds of spirocyclopropanated methylenecyclopropanes and bicyclopropylidenes, respectively. The influence of the CuCl catalyst on the addition reaction will also be addressed.

**Spirocyclopropanated methylenecyclopropanes, that is, terminal alkenes**: Reaction of Ph-P=W(CO)$_5$, generated in situ by the CuCl-catalyzed cycloreversion[12] of 7-phosphanorbornadiene complex **8**,[9,13] with methylenespiropentane (**9**) in toluene at 55 °C (1 h) gave in 78 % yield only the crystalline terminal phospha[3]triangulane complex **12** (Scheme 1) in a




Scheme 1.

5:4 ratio of the *anti* (**a**) and *syn* isomer (**b**). Figure 1 shows the X-ray crystal structure for the less congested *anti* isomer **12a** that has the P-W(CO)$_5$ group *anti* to the terminal cyclopropane ring. The bond lengths of the phosphirane ring compare well with the values of the W(CO)$_5$-complexed smaller

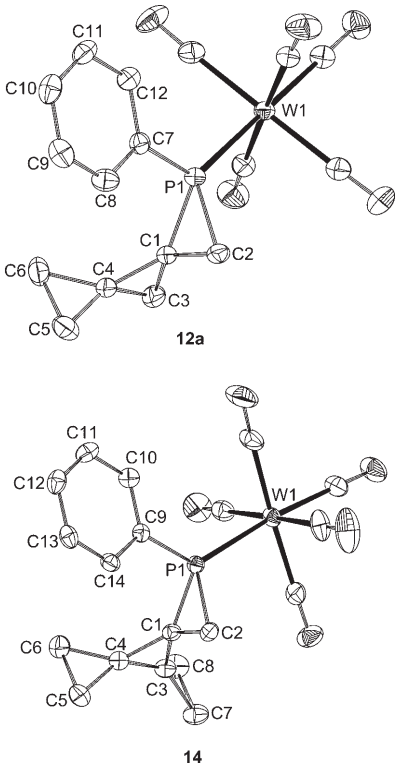



Figure 1. Displacement ellipsoid plot of **12a** (one of the two crystallographically independent molecules is shown) and **14** in the crystal with ellipsoids set at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]; the values for the second molecule are in square brackets. **12a**: C4–C5 1.486(4) [1.475(4)], C4–C6 1.478(4) [1.475(4)], C5–C6 1.528(4) [1.515(4)]; C1-P1-C2 48.41(11) [48.25(12)], C3-C1-C4 59.86(18) [60.33(18)], C5-C4-C6 62.1(2) [61.8(2)]. **14**: C3–C7 1.478(3), C3–C8 1.475(3), C4–C5 1.481(3), C4–C6 1.482(3), C5–C6 1.537(4), C7–C8 1.522(4); C1-P1-C2 48.36(10), C3-C1-C4 59.01(14), C5-C4-C6 62.50(17), C7-C3-C8 62.03(16).

phospha[2]triangulane **4b**[4] (Table 1). Extending the number of cyclopropane rings to three, as in linear **10** or branched methylenetriangulane **11**, gave the corresponding linear and branched phospha[4]triangulanes **13** and **14** (Scheme 1). In the case of **14**, only one isomer can be formed (88 %) of which the X-ray crystal structure is shown in Figure 1, but four diastereomers are feasible for linear **13** (94 %), which depends on the *syn*,*anti* relationship of the phosphirane and terminal spirocyclopropane rings as well as

Table 1. Selected X-ray crystallographic bond lengths for the phosphirane ring of terminal phospha[*n*]triangulanes.

| | **4b**[4] | **12a**[a] | | **14** | **16b**[a] | | **17a** | | av* |
|---|---|---|---|---|---|---|---|---|---|
| P1–C1 | 1.794(6) | 1.799(2) | 1.802(2) | 1.801(2) | 1.796(8) | 1.792(8) | 1.792(6) | 1.792(6) | 1.796 |
| P1–C2 | 1.855(7) | 1.846(3) | 1.846(3) | 1.836(2) | 1.860(8) | 1.850(8) | 1.841(6) | 1.846(6) | 1.846 |
| C1–C2 | 1.508(9) | 1.495(4) | 1.492(4) | 1.490(3) | 1.499(11) | 1.501(11) | 1.503(9) | 1.507(9) | 1.498 |
| C1–C3 | 1.470(1) | 1.504(4) | 1.504(4) | 1.486(3) | 1.505(11) | 1.494(11) | 1.505(8) | 1.505(8) | 1.503[b] |
| C1–C4 | 1.475(10) | 1.462(3) | 1.467(3) | 1.482(3) | 1.468(11) | 1.479(11) | 1.469(9) | 1.461(8) | 1.468[b] |
| C3–C4 | 1.515(10) | 1.480(4) | 1.493(4) | 1.461(3) | 1.494(12) | 1.497(11) | 1.499(9) | 1.497(9) | 1.493[b] |
| P1–W1 | 2.500(2) | 2.5107(7) | 2.4980(7) | 2.5063(5) | 2.497(2) | 2.497(2) | 2.4822(16) | 2.4733(16) | 2.495 |

[a] Both crystallographically independent molecules are given. * Average of **12a**, **14**, **16b**, and **17a**. [b] Excluding **14** because of its symmetrical substituent pattern.

that of the P-substituents. The less congested two major isomers of the four observed by $^{31}$P NMR spectroscopy (ratio 50:36:10:4) were fully characterized (see Experimental Section).

Diphospha[4]triangulanes are accessible by using racemic 1,4-dimethylenespiropentane *rac*-**15** as diene. Reaction of the phosphinidene precursor **8** (CuCl-catalyzed)[12] with only one double bond, with an excess of **15** in toluene at 55 °C (2 h), afforded 5-methylene-1-phosphadispiro[2.0.2.1]heptane **16** (Scheme 2) in 83 % yield as a mixture of four diastereomers ($^{31}$P NMR: ratio 39:31:18:12) of which three could be fully characterized. The structure of the major *anti* isomer **16b**, separated by column chromatography, was ascertained by an X-ray crystal structure determination (Figure 2). The presence of the double bond (1.289(14) Å) is also evident from the $^{1}$H NMR resonances at $\delta = 5.36$ ($^{4}J$(H,H) = 2.4 Hz) and 5.39 ($^{4}J$(H,H) = 1.8 Hz) and the $^{13}$C NMR resonances at $\delta = 101.6$ ($H_2C$=) and 133.7 (=*C*).

Reaction of the remaining double bond in *anti*-**16b** with an excess of **8** (55 °C, CuCl, 3 h) resulted in the smooth formation of the novel linear diphospha[4]triangulane complex

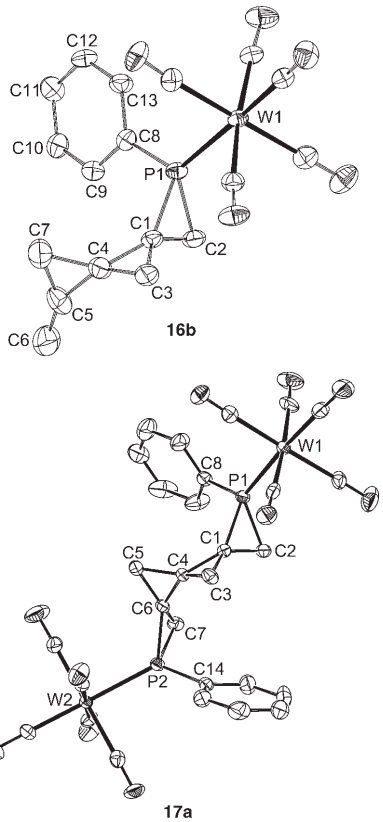
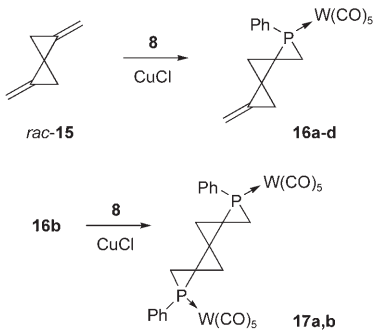



Figure 2. Displacement ellipsoid plot of **16b** (one of the two crystallographically independent molecules is shown) and **17a** in the crystal with ellipsoids set at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]; the values for the second molecule are in square brackets **16b**: C4–C5 1.422(12) [1.423(12)], C4–C7 1.500(13) [1.503(13)], C5–C6 1.289(14) [1.289(14], C5–C7 1.456(14) [1.475(15)]; C1-P1-C2 48.4(4) [48.6(4)], C3-C1-C4 60.3(5) [60.5(5)], C5-C4-C7 59.7(6) [60.5(7)]. **17a**: C1-P1-C2 48.9(3), C6-P2-C7 48.9(3), C3-C1-C4 60.5(4), C4-C5-C6 58.2(4), C4-C6-C5 60.6(4).




Scheme 2.

**17** in 78 % yield in a 10:7 ratio of the *anti*,*anti* and *anti*,*syn* isomers (Scheme 2). *anti*,*anti*-isomer **17a** is easily recognized by its $^{31}$P NMR singlet ($\delta$ −147.9) and *anti*,*syn*-isomer **17b** by its set of doublets ($\delta$ −150.4, −150.5; $^{4}J$(P,P) = 4.5 Hz). Interestingly, the $^{13}$C NMR spectrum of **17a** displays an $A_2X$ system for the central spiro-carbon atom at $\delta^{13}C = 25.4$ ($^{2}J$(C,P) = 5.5 Hz). An X-ray crystal structure confirmed the assignment of this isomer (Figure 2).

Selected structural parameters of four of the novel (di)phospha[*n*]triangulane complexes are given in Table 1. The two different P–C bond lengths (av 1.796 and 1.846 Å) of their terminal phosphirane rings are similar to the values of the $W(CO)_5$-complexed smaller phospha[2]triangulane **4b**[4] with the distal bonds (remote to the spiro-carbon) being longer than the proximal ones (connected to the spiro-carbon). This effect of spirofusion is similar but more pronounced than in the all-carbon triangulanes,[3,14] and likewise is due to rehybridization of the strained spiro-carbon, resulting in less s-character and thus elongation of the distal bonds.[2] The $PhPW(CO)_5$ group also affects the C1-spiro-fused cyclopropane ring, which also has proximal C–C bonds of different length (av 1.503 and 1.468 Å) and a 1.493 Å (av) distal bond. The C1–C2 bonds (av 1.498 Å) of all the structures are of similar length as reported for the parent 1-phenylphosphirane **4a**.[4]

The NMR characteristics of the phospha[*n*]triangulanes also reflect that their $W(CO)_5$-complexed phosphirane rings have similar electronic properties (Table 2). The phosphorus chemical shifts are in the narrow range of $\delta^{31}$P −144 to −155 ppm with $^{1}J$(P,W) coupling constants of 252–261 Hz. The less congested *anti* isomers are always formed predominantly[15] and have the more shielded $^{31}$P NMR resonances[16] that are similar to the $\delta$ −154.8 ppm reported for the parent 1-phenylphospha[2]triangulane complex **4b**.[4] The $^{13}$C resonance of the phosphirane spiro-carbon C1 and carbon C2 are at $\delta$ 25–30 (**4b** 31.2) and $\delta$ 15–18 ppm (**4b** 19.3), respectively. In addition, its two hydrogen atoms resonate at about $\delta^{1}$H 1.7 and 2.0 ppm with $^{2}J$(H,P) coupling constants of $< 1$ and 7.1 Hz, respectively, with the larger one for the more deshielded proton resonance positioned *anti* to the P-$W(CO)_5$ group.

**Spirocyclopropanated bicyclopropylidenes, that is, non-terminal alkenes**: Alkenes with four alkyl substituents are

Table 2. Selected NMR parameters for the phosphirane ring of terminal phospha[*n*]triangulanes.

| | **12a** | **12b** | **13b** | **13d** | **14** | **16b** | **16c** | **16d** | **17a** | **17b** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $^{31}$P | −146.4 | −152.3 | −152.2 | −154.9 | −145.2 | −144.0 | −148.3 | −148.5 | −147.9 | −150.4 | −150.5 |
| $^{1}J$(P,W) | 257.2 | 254.1 | 258.1 | 255.5 | 252.1 | 258.2 | 257.2 | 256.2 | 261.2 | 260.2 | 258.2 |
| $^{13}$C (C1) | 26.5 | 25.7 | 26.7 | 25.6 | 29.6 | 29.0 | 29.1 | 28.3 | 26.3 | 25.6 | 26.1 |
| $^{1}J$(C1,P) | 6.1 | 7.1 | 6.7 | 8.6 | 10.1 | 7.7 | 7.5 | 9.3 | 8.8 | 9.8 | 5.5 |
| $^{13}$C ($C2H_2$) | 17.0 | 17.4 | 16.7 | 16.4 | 15.5 | 17.8 | 17.5 | 17.9 | 15.3 | 15.5 | 16.0 |
| $^{1}J$(C2,P) | ~6 | 6.1 | 6.3 | 6.4 | 5.7 | 5.8 | 6.1 | 6.0 | 6.3 | 6.1 | 6.3 |
| $^{1}$H ($C2H_2$) | 1.79 | ~1.6 | ~1.7 | ~1.7 | 1.62 | 1.83 | 1.70 | 1.65 | 1.59 | 1.75 | ~1.8 |
| | 1.99 | 2.02 | 2.02 | 1.88 | 2.09 | 2.02 | 2.13 | 2.05 | 2.24 | 2.28 | ~1.8 |
| $^{2}J$(H,P) | – | – | – | – | 0.9 | 1.2 | 0.8 | – | ~7 | – | unresolved |
| | 7.1 | 7.1 | 7.1 | 7.1 | 7.0 | 7.4 | 7.0 | ~7 | 7.1 | 6.9 | unresolved |

more reactive toward electrophiles than terminal alkenes, because of their higher nucleophilicity, yet steric factors can hamper the access to the double bond. This is known for the addition of carbenes (e.g. MeCCl)[17] but is less clear for electrophilic phosphinidenes. Reactions of transient R-P=$W(CO)_5$ invariably have first-order kinetics for the uncatalyzed cheletropic elimination from phosphanorbornadiene precursor **8**.[18] Competition reactions showed no discrimination between simple substituted alkenes,[15] but the formation of the phosphaspiroalkanes **4b–e** from methylenecycloalkanes $H_2C{=}C(CH_2)_n$ occurs at different rates ($n=4 > 3 > 5 > 2$) in the presence of CuCl.[4] The catalyst lowers the decomposition temperature for **8** from about 110 to 55 °C and can alter the kinetics of the alkene addition reaction.[19] Recently, a computational study addressed the role of the CuCl catalyst, showing a) that the alkene may complex to it and b) that the active reagent is likely [RP(Cl)$W(CO)_5$]-Cu-L, with L being the alkene or solvent.[20] In this section, the reactivity of spirocyclopropanated bicyclopropylidenes is first compared with that of the methylenecyclopropanes, while the influence of the CuCl catalyst is addressed in the next paragraph.

Bicyclopropylidene[21] is more reactive toward the CuCl-generated phosphinidene complex than both methylenecyclopropane[4] and 2,3-dimethyl-2-butene[15] and was shown to give the phospha[3]triangulane complex **5a**.[5] Adding a second sphere of spirocyclopropane rings gives the more electron-rich alkene **18**,[3] that still allows the formation of a phosphirane, yielding phospha[7]triangulane complex **7**,[11] as confirmed by an X-ray crystal structure determination (Figure 3). It was established that the yield of **7** decreases from 88 to 42% in the presence of CuCl with simultaneous formation of other products, like **19** (6%),[11] which may illustrate the influence of steric factors (Scheme 3). Therefore, the influence of the spirocyclopropane rings on the addition of the CuCl-generated phosphinidene complex to mono- and dispirocyclopropanated bicyclopropylidenes was examined (Scheme 3).

Reaction of **8** with cyclopropylidenespiropentane (**20**) in toluene at 55 °C in the presence of CuCl for one hour gave only the phospha[4]triangulane complex **21** (78%) in a 4:3 ratio of the fully characterized *anti* (**a**) and *syn* diastereomer (**b**). The structure of the less congested *anti* isomer **21a** was ascertained by an X-ray crystal structure determination

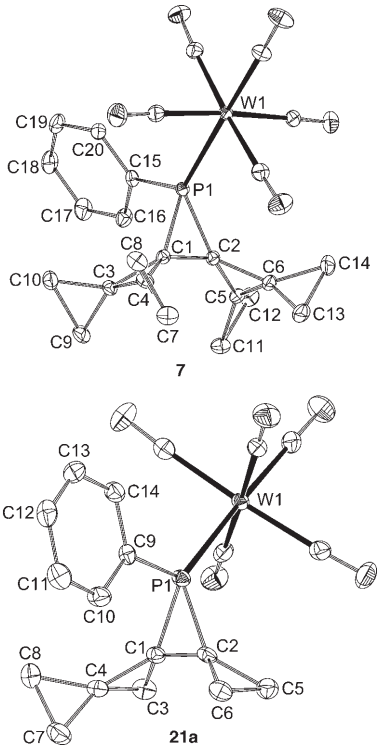
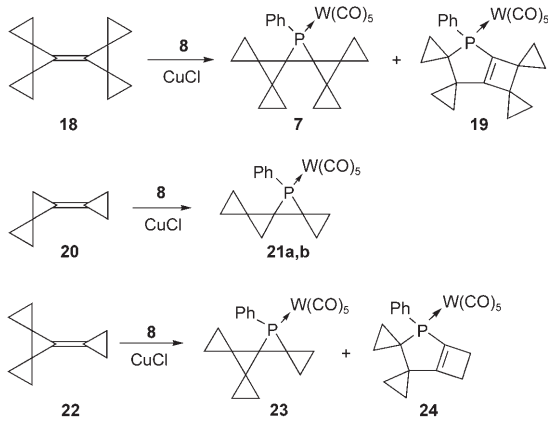



Figure 3. Displacement ellipsoid plot of **7** and **21a** with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] **7**: C3–C9 1.478(3), C3–C10 1.482(3), C4–C7 1.475(3), C4–C8 1.480(3), C5–C6 1.461(3), C5–C11 1.481(3), C5–C12 1.483(3), C6–C13 1.478(3), C6–C14 1.483(3), C7–C8 1.523(3), C9–C10 1.529(3), C11–C12 1.523(3), C13–C14 1.525(3); C3-C1-C4 59.02(13), C9-C3-C10 62.23(14), C7-C4-C8 62.07(15), C5-C2-C6 58.64(13), C11-C5-C12 61.83(15), C13-C6-C14 62.01(15); **21a**: C4–C7 1.487(4), C4–C8 1.473(4), C7–C8 1.521(4), C3-C1-C4 59.86(17), C5-C2-C6 61.10(18), C7-C4-C8 61.85(19).

(Figure 3). The bond lengths in the phosphirane ring compare well with the reported values of the smaller phospha[3]triangulane **5a**[5] (Table 3). The same reaction of **8** (RT, CuCl, 20 h) with 7-cyclopropylidenedispiro[2.0.2.1]-heptane (**22**) afforded the branched phospha[5]triangulane **23** (71%) and 2-phosphabicyclo[3.2.0]heptene **24** (2%) (Scheme 3). This reaction already takes place at room temperature, instead of the usual 55–60 °C,[12] indicating that the bicyclopropylidene with its tetrasubstituted double bond facilitates the CuCl-catalyzed reaction.[19,20] It is also evident




Scheme 3.

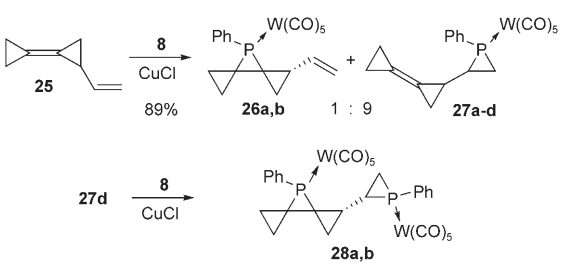
Table 3. Selected X-ray crystallographic bond lengths for the phosphirane ring of phospha[*n*]triangulanes.

| | **4a**[4] | **5a**[5] | **7** | **21a** | **28a**[a] | **28a**[b] |
|---|---|---|---|---|---|---|
| P1–C1 | 1.80(2) | 1.807(8) | 1.8198(19) | 1.821(2) | 1.815(3) | 1.834(3) |
| P1–C2 | 1.83(2) | 1.820(8) | 1.821(2) | 1.816(2) | 1.804(3) | 1.823(3) |
| C1–C2 | 1.50(2) | 1.48(1) | 1.481(3) | 1.470(3) | 1.479(4) | 1.526(4) |
| C1–C3 | | 1.50(1) | 1.487(3) | 1.515(4) | 1.490(3) | |
| C1–C4 | | 1.51(1) | 1.487(4) | 1.468(3) | 1.477(4) | |
| C2–C5 | | 1.48(1) | 1.494(3) | 1.492(4) | 1.484(4) | |
| C2–C6 | | 1.49(1) | 1.489(3) | 1.489(4) | 1.483(4) | |
| C3–C4 | | 1.53(1) | 1.465(3) | 1.489(4) | 1.505(4) | |
| C5–C6 | | 1.51(1) | 1.461(3) | 1.515(4) | 1.507(5) | |
| P1–W1 | 2.504(2) | 2.495(2) | 2.4872(5) | 2.5120(7) | 2.4817(7) | 2.4876(7) |
| C1-P1-C2 | 48.6(7) | 48.1(4) | 47.99(8) | 47.68(11) | 48.25(12) | 49.30(12) |

[a] Disubstituted phosphirane ring. [b] Terminal phosphirane ring.

that the second spirocyclopropane ring influences the phosphinidene addition, in that **22** gives a small amount of by-product that structurally resembles **19**. Before examining the influence of the catalyst, the special reactivity of the tetrasubstituted double bond in a bicyclopropylidene was compared with that of a vinyl substituent.

Reaction of **8** with an excess of ethenylbicyclopropylidene (**25**) in toluene at room temperature in the presence of CuCl gave after 18 h phospha[3]triangulane **26** (two isomers in a 1:1 ratio) and phosphirane **27** in a total yield of 89% (four isomers: 6:11:17:66) in a 1:9 ratio (Scheme 4). Both structure types were fully identified by NMR spectroscopy and show characteristic features, such as the about 40 ppm more shielded $^{31}$P NMR chemical shift for **27** that is




Scheme 4.

common for the parent phosphiranes (e.g. major isomer *anti* **27d**: $\delta^{31}$P = −169.5, *anti* **26a**: $\delta^{31}$P = −127.0) (Table 4). Clearly, the [1+2] cycloaddition of the phosphinidene complex to the singly substituted and less sterically congested double bond is favored over that to the more electron-rich double bond in the bicyclopropylidene moiety, suggesting that steric factors do play a role. However, reaction of the isolated *anti* isomer **27d** with an excess of **8** at the higher temperature of 55 °C (CuCl, 6.5 h), did result in a second addition to give in 62% yield the phosphirane-substituted phospha[3]triangulane complex **28** in a 5:3 ratio of the *anti,anti* (**a**) and *anti*, *syn* isomer (**b**) (Scheme 4), with 12% recovery of the starting substrate **27d**. Isomer **28a** is easily recognized by its set of $\delta^{31}$P NMR singlets ($\delta$ −127.1, $^1J$(P,W) = 258.7 Hz; −164.0, $^1J$(P,W) = 252.6 Hz) and isomer **28b** by its set of doublets ($\delta$ −129.6, $^1J$(P,W) = 259.7 Hz; −166.4, $^1J$(P,W) = 251.6 Hz; $^4J$(P,P) = 4.1 Hz). The assignment of the *anti,anti*-isomer **28a** was confirmed by a single-crystal X-ray structure, depicted in Figure 4, that shows a tightened cyclopropanated phosphirane ring,[5,6] (P–C 1.810 (av); C1–C2 1.479(4)) as compared to the terminal one (P–C 1.829 (av); C1–C2 1.526(4)) (Table 3).

This phosphirane, with spirofused cyclopropanes at both carbons,[5] is similar to the PCC ring of **7** and **17a**. Selected X-ray crystal structural data for these phospha[*n*]triangulanes and the previously reported parent **4a**[4] and **5a**[5] are summarized in Table 3. Phospha[7]triangulane **7** has a P–C bond length of 1.820 Å (av), which is comparable to the average length of the two unlike bonds (av 1.796 and 1.846 Å) of the phospha[*n*]triangulanes with a terminal phosphirane ring (Table 1).

The additional spirofusion on the phosphirane ring is reflected in the NMR data (Tables 2 and 4) and most profoundly in the phosphorus chemical shift of $\delta^{31}$P −120 to −130 ppm ($^1J$(P,W) = 250–260 Hz) that is deshielded by about 25 ppm compared with the terminal spirofused phosphirane complexes and by 55–65 ppm from that of the parent **4a** ($\delta$ −187.6 ppm).[4] The larger phospha[*n*]triangulanes (*n* = 4) have the slightly more deshielded $^{31}$P NMR resonances, thereby showing only a modest influence of the second sphere of spirocyclopropane rings. This influence is also reflected in the $^{13}$C NMR chemical shifts of $\delta$ 23.5–26.5 and 30.0–34.5 ppm for the spirofused phosphirane carbons with first and second sphere spirocyclopropane rings, respectively. The effect is the strongest for phospha[7]triangulane complex **7**[11] with $\delta^{13}$C 34.5 ppm.

**CuCl Catalysis**: We return to the role of CuCl in the cycloaddition. Phosphiranes are the major products in all cases,

Table 4. Selected NMR parameters for the phosphirane ring of phospha[*n*]triangulanes.

| | **4a**[5] | **5a**[5] | **7**[11] | **21a** | **21b** | **23** | **26a** | **26b** | **28a**[a] | **28a**[b] | **28b**[a] | **28b**[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^{31}$P | −187.6 | −129.4 | −119.6 | −123.9 | −128.1 | −124.1 | −127.0 | −129.8 | −127.1 | −164.0 | −129.6 | −166.4 |
| $^{1}J$(P,W) | 257.5 | 251.6 | 250.1 | 257.2 | 254.1 | 250.6 | 259.4 | 260.4 | 258.7 | 252.6 | 259.7 | 251.6 |
| $^{13}$C (C1/2) | 10.7 | 26.0 | 34.5 | 30.1 | 30.0 | 32.3 | 31.0 | | 31.8 | 27.4 | 31.4 | 27.3 |
| | | | | 24.8 | 25.3 | 23.5 | 26.5 | | 25.1 | 16.0 | 25.9 | 15.8 |
| $^{1}J$(C1/2,P) | 12.2 | 27.7 | 6.2 | 2.3 | 3.5 | 5.7 | 2.2 | | 3.8 | 16.2 | 5.3 | 15.9 |
| | | | | – | – | – | – | | – | 11.6 | – | 11.4 |

[a] Disubstituted phosphirane ring. [b] Terminal phosphirane ring.

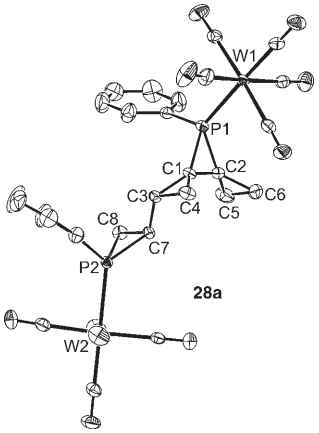
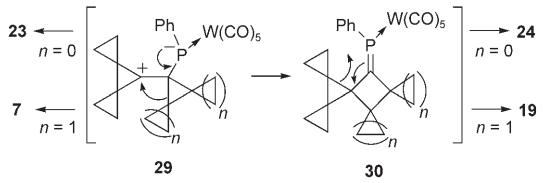



Figure 4. Displacement ellipsoid plot of **28a** with ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C3−C7 1.487(4); C3-C1-C4 60.97(18), C5-C2-C6 61.1(2).

suggesting that transient phosphinidene complex Ph-P=$W(CO)_5$ adds to the C=C bond. However, there are exceptions, namely alkenes **22** and **18** with their full second sphere of spirocyclopropane rings at one and both ends of the double bond, respectively. They gave additional small amounts of the respective 2-phosphabicyclo[3.2.0]hept-1(5)-enes **19** and **24**. An X-ray crystal structure has been reported for **19**.[11] The NMR data of the two products are very similar. Characteristic are the $^{31}$P and two $^{13}$C chemical shifts for the ring C-P-C unit of **19** at $\delta^{31}$P 34.4 ($^{1}J$(P,W) 238.4 Hz), $\delta^{13}$C 34.9 ($^{1}J$(P,C) 39.7 Hz), and 142.5 ppm ($^{1}J$(P,C) 31.2 Hz)[11] and those for **24** at $\delta^{31}$P 34.6 ($^{1}J$(P,W) 234.7 Hz), $\delta^{13}$C 33.1 ($^{1}J$(P,C) 40.2 Hz), and 140.3 ppm ($^{1}J$(P,C) 29.7 Hz). These alkenes, **18** and **22**, but also **10** and **25**, differ from the others in the fact that they react at room temperature within 18–20 h with the phosphinidene precursor **8** instead of the 55–60 °C,[12] which is usually needed for the CuCl-catalyzed cycloadditions. Furthermore, the reactions executed at 55 °C occur rather fast (1–2 h) while the slower second cycloaddition for **16b** (3 h) and **27d** (6.5 h) differ from each other. These observations suggest that the elimination of the phosphinidene complex from the precursor is not necessarily the rate-limiting step, but that the alkene may be involved as well.[19] This notion concurs with a computational analysis,[20] which suggested that the alkene or aromatic solvent interacts with CuCl and that this complex dissociates the precursor to formally give [PhP(Cl)$W(CO)_5$]-Cu-L (L = alkene or solvent) as the active reagent. Phosphirane formation then occurs in an $S_N2$-type addition with a concurrent "chloride shuttle" back to the Cu ion to regenerate the CuCl-L complex. While the products for the uncatalyzed and CuCl-catalyzed reactions are usually the same, they can differ[22] and this was also the case with the alkenes **18** and **22**. Indeed, phosphatriangulane **7** is the sole product formed from **18** in the absence of CuCl.[11] There are two aspects, [PhP(Cl)$W(CO)_5$]-Cu-L is less reactive and bulkier than R-P=$W(CO)_5$ and thus more sensitive to steric constraints, which is the case here. We presume that the C=C bond interacts with the CuCl-L ligated phosphinidene complex under expulsion of the CuCl-L complex, forming zwitterion **29** (Scheme 5). Analogous σ-complexes




Scheme 5.

were identified computationally to precede the formation of the 1,4-addition and C–H insertion products of azulenes.[23] Branched phospha[*n*]triangulanes **7** and **23** will result upon ring closure of the zwitterion, but steric factors may facilitate the well-known cyclopropylcarbinyl to cyclobutyl ring enlargement[24] to form phosphaalkene **30**. The ring expansion preferentially involves the more highly substituted cyclopropane ring, because in this manner the cationic charge can be delocalized the best.[25,26] The reactive P=C bond of **30** enables a subsequent [1,3]-sigmatropic shift[27] that gives the 2-phosphabicyclo[3.2.0]heptenes **19** and **24**.

## Conclusion

Novel, linear and branched mono- and diphospha[*n*]triangulanes have been synthesized in high yields by the CuCl-catalyzed phosphinidene addition to spirocyclopropanated methylenecyclopropanes and bicyclopropylidenes. Single crystal X-ray structure analyses of these remarkably stable products revealed a tightening of the phosphirane ring on spirocyclopropanation. The effect of spirofusion on the electronic

properties of these strained phosphacycles is apparent from the NMR features that show deshielded chemical shifts for the phosphorus and carbon ring atoms. Steric factors play a role when the double bond carries a second sphere of spirocyclopropane rings and causes the formation of 2-phosphabicyclo[3.2.0]heptenes as byproducts. The latter are explained to result from addition of the [PhP(Cl)W(CO)$_5$]-Cu-L (L = alkene or solvent) reagent to the spirocyclopropanated bicyclopropylidene to give an intermediate zwitterion, which can undergo a cyclopropylcarbinyl to cyclobutyl ring expansion followed by a [1,3]-sigmatropic shift.

## 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 (at 298 K) on a Bruker Advance 250 ($^{31}$P; 85% $H_3PO_4$) and a MSL 400 ($^1$H, $^{13}$C) and referenced internally to residual solvent resonances ($^1$H: $\delta$ 7.25 ppm ($CHCl_3$), $^{13}$C{$^1$H}: 77.0 ppm ($CDCl_3$). Isomeric ratios were determined by $^{31}$P NMR spectroscopy. IR spectra were recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer, and high-resolution mass spectra (HR-MS) were measured on a Finnigan Mat 900 mass spectrometer operating at an ionization potential of 70 eV. Melting points were measured on samples in unsealed capillaries and are uncorrected. CuCl (99% purity) was purchased from Acros and stored under nitrogen before use. (5,6-Dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene) pentacarbonyltungsten (**8**),[9,13] methylenespiropentane (**9**),[28] 1-methylenedispiro[2.0.2.1]heptane (**10**),[29] 7-methylenedispiro[2.0.2.1]heptane (**11**),[29,30] 1,4-bismethylenespiropentane (**15**),[31] perspirocyclopropanated bicyclopropylidene **18**,[3] cyclopropylidenespiropentane (**20**),[32] 7-cyclopropylidenedispiro[2.0.2.1]heptane (**22**),[30] and ethenylbicyclopropylidene (**25**)[33] were prepared according to literature procedures.

**(1-Phenyl-1-phosphadispiro[2.0.2.1]hept-1-yl)pentacarbonyltungsten (12)**: Complex **8** (360 mg, 0.55 mmol), methylenespiropentane (**9**) (132 mg, 1.65 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 1 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 19:1 gave **12a** and **b** in a 5:4 ratio (220 mg, 78%) as a pale yellow oil. Fractional recrystallization from pentane at −80 °C followed by recrystallization at −20 °C afforded colorless crystals of the *anti*-isomer **12a**.

***anti*-(1*R*,3*S*)- and (1*S*,3*R*)-Isomer 12a**: m.p. 64 °C; $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta$ = 0.49–0.55 (m, 1H; C*H*), 0.65–0.71 (m, 1H; C*H*), 0.85–0.91 (m, 1H; C*H*), 0.92–0.96 (m, 1H; C*H*), 1.39 (dd, $^2J$(H,H) = 4.1, $^3J$(H,P) = 6.2 Hz, 1H, PCC*H*), 1.77 (dd, $^2J$(H,H) = 4.1, $^3J$(H,P) = 10.2 Hz, 1H, PCC*H*), 1.79 (d, $^2J$(H,H) = 7.6 Hz, 1H; PC*H*), 1.99 (dd, $^2J$(H,H) = 7.6, $^2J$(H,P) = 7.1 Hz, 1H; PC*H*), 7.30–7.38 ppm (m, 5H; Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ = 5.2 (d, $^3J$(C,P) = 4.5 Hz; $CH_2$), 5.9 (s; $CH_2$), 17.0 (d, $^1J$(C,P) = ~6 Hz; P$CH_2$), 17.1 (s; PCC$H_2$), 18.5 (d, $^2J$(C,P) = 5.3 Hz; PC*C*), 26.5 (d, $^1J$(C,P) = 6.1 Hz; P*C*), 128.6 (d, $^3J$(C,P) = 10.5 Hz; *m*-Ph), 130.2 (d, $^4J$(C,P) = 2.5 Hz; *p*-Ph), 131.4 (d, $^2J$(C,P) = 13.4 Hz; *o*-Ph), 132.5 (d, $^1J$(C,P) = 25.6 Hz; *ipso*-Ph), 195.6 (d, $^2J$(C,P) = 8.4, $^1J$(C,W) = 125.5 Hz; *cis*-CO), 197.9 ppm (d, $^2J$(C,P) = 30.0 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −146.4 ppm ($^1J$(P,W) = 257.2 Hz); IR (KBr): $\tilde{\nu}$ = 1932 (s/br, $CO_{eq}$), 1983 (w, $CO_{eq}$), 2074 cm$^{-1}$ (w, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 512 (8) $[M]^+$, 484 (4) $[M-CO]^+$, 456 (9) $[M-2CO]^+$, 428 (8) $[M-3CO]^+$, 400 (32) $[M-4CO]^+$, 372 (100) $[M-5CO]^+$; HR-MS (EI): *m*/*z*: calcd for $C_{17}H_{13}O_5P^{184}W$: 512.00104; found: 511.99819.

***syn*-(1*R*,3*R*)- and (1*S*,3*S*)-Isomer 12b**: $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta$ = 0.85–0.91 (m, 1H; C*H*), 0.91–0.97 (m, 1H; C*H*), 1.08–1.14 (m, 1H; C*H*), 1.20–1.25 (m, 1H; C*H*), 1.58–1.62 (m, 2H; PC*H*, PCC*H*), 1.68 (dd, $^2J$(H,H) = 4.0, $^3J$(H,P) = 11.1 Hz, 1H; PCC*H*), 2.02 (dd, $^2J$(H,H) = 7.4, $^2J$(H,P) = 7.1 Hz, 1H; PC*H*), 7.39–7.44 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.52–7.57 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ = 5.2 (d, $^3J$(C,P) = 1.8 Hz; $CH_2$), 6.2 (d, $^3J$(C,P) = 3.4 Hz; $CH_2$), 16.4 (d, $^2J$(C,P) = 3.5 Hz; PC$CH_2$), 17.4 (d, $^1J$(C,P) = 6.1 Hz; P$CH_2$), 19.3 (s; PC*C*), 25.7 (d, $^1J$(C,P) = 7.1 Hz; P*C*), 128.7 (d, $^3J$(C,P) = 10.4 Hz; *m*-Ph), 130.2 (d, $^4J$(C,P) = 2.3 Hz; *p*-Ph), 131.4 (d, $^2J$(C,P) = 13.1 Hz; *o*-Ph), 134.6 (d, $^1J$(C,P) = 25.4 Hz; *ipso*-Ph), 195.7 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.6 Hz; *cis*-CO), 197.8 ppm (d, $^2J$(C,P) = 29.8 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −152.3 ppm ($^1J$(P,W) = 254.1 Hz).

**(1-Phenyl-1-phosphatrispiro[2.0.0.2.1.1]non-1-yl)pentacarbonyltungsten (13)**: Complex **8** (450 mg, 0.69 mmol), 1-methylenedispiro[2.0.2.1]heptane (**10**) (183 mg, 1.72 mmol), and CuCl (10 mg, 0.1 mmol) were stirred in toluene (4 mL) at room temperature for 18 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 9:1 gave a 4:50:10:36 mixture of isomers **13a**, **b**, **c** and **d** (350 mg, 94%) as a pale yellow oil. Recrystallization from pentane at −80 °C afforded a 10:7 isomeric mixture of the main isomers **13b** and **13d**.

**Compound 13a**: $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −147.3 ppm ($^1J$(P,W) = 258.2 Hz).

***anti*-(1*R*,3*S*,4*R*)- and (1*S*,3*R*,4*S*)-Isomer 13b**: $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta$ = 0.76–0.96 (m, 5H; C$H_2$, PCCC*H*), 1.23–1.27 (m, 2H; PCC*H*, PCCC*H*), 1.68–1.73 (m, 1H; PC*H*), 1.81 (dd, $^2J$(H,H) = 4.4, $^3J$(H,P) = 10.0 Hz, 1H; PCC*H*), 2.02 (dd, $^2J$(H,H) = 7.4, $^2J$(H,P) = 7.1 Hz, 1H; PC*H*), 7.34–7.45 ppm (m, 5H; Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ = 4.0 (s; $CH_2$), 5.1 (d, $^4J$(C,P) = 1.2 Hz; $CH_2$), 11.7 (d, $^3J$(C,P) = 4.6 Hz; PCC*C*H), 14.7 (s; PCC*C*), 16.1 (s; PC*C*H), 16.7 (d, $^1J$(C,P) = 6.3 Hz; P$CH_2$), 22.4 (d, $^2J$(C,P) = 8.8 Hz; PC*C*), 26.7 (d, $^1J$(C,P) = 6.7 Hz; P*C*), 128.5 (d, $^3J$(C,P) = 10.8 Hz; *m*-Ph), 130.3 (d, $^4J$(C,P) = 2.7 Hz; *p*-Ph), 131.7 (d, $^2J$(C,P) = 13.9 Hz; *o*-Ph), 132.0 (d, $^1J$(C,P) = 24.9 Hz; *ipso*-Ph), 195.7 (d, $^2J$(C,P) = 8.4, $^1J$(C,W) = 125.5 Hz; *cis*-CO), 197.7 ppm (d, $^2J$(C,P) = 30.2 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −152.2 ppm ($^1J$(P,W) = 258.1 Hz); MS (70 eV): (mixture of **13b** and **13d**): *m*/*z* (%): 538 (6) $[M]^+$, 482 (2) $[M-2CO]^+$, 454 (5) $[M-3CO]^+$, 426 (22) $[M-4CO]^+$, 398 (88) $[M-5CO]^+$; HR-MS (EI) calcd for $C_{19}H_{15}O_5P^{184}W$: 538.01672; found: 538.01741.

**Compound 13c**: $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −152.3 ppm ($^1J$(P,W) = 254.4 Hz).

***syn*-(1*R*,3*R*,4*S*)- and (1*S*,3*S*,4*R*)-Isomer 13d**: $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta$ = 0.69–0.73 (m, 1H, C*H*), 0.76–0.96 (m, 3H; C$H_2$), 1.44 (dd, $^2J$(H,H) = 4.3, $^3J$(H,P) = 1.7 Hz, 1H; PCC*H*), 1.46, 1.47, 1.60, 1.61 (AB type, $^2J$(H,H) = 4.3 Hz, 2H; PCCC$H_2$), 1.68–1.73 (m, 2H; PC*H*, PCC*H*), 1.88 (dd, $^2J$(H,H) = 7.3, $^2J$(H,P) = 7.1 Hz, 1H; PC*H*), 7.34–7.45 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.52–7.57 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ = 4.2 (s; $CH_2$), 4.8 (d, $^4J$(C,P) = 2.1 Hz; $CH_2$), 12.7 (d, $^3J$(C,P) = 3.9 Hz; PCCC*H*), 14.5 (d, $^3J$(C,P) = 3.2 Hz; PCC*C*), 15.2 (d, $^2J$(C,P) = 3.6 Hz; PC*C*H), 16.4 (d, $^1J$(C,P) = 6.4 Hz; P$CH_2$), 23.1 (s; PC*C*), 25.6 (d, $^1J$(C,P) = 8.6 Hz; P*C*), 128.7 (d, $^3J$(C,P) = 10.4 Hz; *m*-Ph), 130.2 (d, $^4J$(C,P) = 2.4 Hz; *p*-Ph), 131.5 (d, $^2J$(C,P) = 13.1 Hz; *o*-Ph), 134.6 (d, $^1J$(C,P) = 25.3 Hz; *ipso*-Ph), 195.7 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.5 Hz; *cis*-CO), 197.9 ppm (d, $^2J$(C,P) = 30.0 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −154.9 ppm ($^1J$(P,W) = 255.5 Hz).

**(1-Phenyl-1-phosphatrispiro[2.0.2.0.2.0]non-1-yl)pentacarbonyltungsten (14)**: Complex **8** (400 mg, 0.61 mmol), 7-methylenedispiro[2.0.2.1]heptane (**11**) (97 mg, 0.92 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 1 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 9:1 gave **14** (290 mg, 88%) as a pale yellow oil. Recrystallization from pentane at −20 °C afforded colorless crystals. M.p. 61–62 °C; $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta$ = 0.34–0.38 (m, 1H; C*H*), 0.57–0.62 (m, 1H; C*H*), 0.62–0.66 (m, 1H; C*H*), 0.70–0.73 (m, 1H; C*H*), 0.73–0.76 (m, 1H; C*H*), 0.88–0.95 (m, 2H; C*H*), 1.20–1.30 (m, 1H; C*H*), 1.62 (dd, $^2J$(H,H) = 7.8, $^2J$(H,P) = 0.9 Hz, 1H; PC*H*), 2.09 (dd, $^2J$(H,H) = 7.8, $^2J$(H,P) = 7.0 Hz, 1H; PC*H*), 7.36–7.48 ppm (m, 5H; Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ = 4.4 (d, $^3J$(C,P) = 3.8 Hz; $CH_2$), 4.7, 5.0 (2s; $CH_2$), 5.9 (d, $^3J$(C,P) = 2.8 Hz; $CH_2$), 15.5 (d, $^1J$(C,P) = 5.7 Hz; P$CH_2$), 22.5 (s; PC*C*), 22.5 (d, $^2J$(C,P) = 5.7 Hz; PC*C*), 29.6 (d, $^1J$(C,P) = 10.1 Hz; P*C*), 128.6 (d, $^3J$(C,P) = 10.4 Hz; *m*-Ph), 130.2 (d, $^4J$(C,P) = 2.3 Hz; *p*-Ph), 131.3 (d, $^2J$-

(C,P) = 13.1 Hz; *o*-Ph), 132.9 (d, $^1J$(C,P) = 25.9 Hz; *ipso*-Ph), 195.7 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.5 Hz; *cis*-CO), 198.0 ppm (d, $^2J$(C,P) = 29.8 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -145.2$ ppm ($^1J$(P,W) = 252.1 Hz); IR (KBr): $\tilde{\nu} = 1917$ (s/br, $CO_{eq}$), 1983 (w, $CO_{eq}$), 2070 $cm^{-1}$ (m, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 538 (10) $[M]^+$, 482 (3) $[M-2CO]^+$, 454 (16) $[M-3CO]^+$, 426 (28) $[M-4CO]^+$; HR-MS (EI): *m*/*z*: calcd for $C_{19}H_{15}O_5P^{184}W$: 538.01672; found: 538.01581; elemental analysis calcd (%) for $C_{19}H_{15}O_5P^{184}W$: C 42.41, H 2.81; found: C 41.68, H 2.89.

**(1-Phenyl-1-phospha-5-methylenedispiro[2.0.2.1]hept-1-yl)pentacarbonyltungsten (16)**: Complex **8** (450 mg, 0.69 mmol), *rac*-1,4-dimethylenespiropentane (**15**) (191 mg, 2.07 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 2 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 19:1 gave a 12:39:31:18 mixture of isomers of **16a**, **b**, **c** and **d** (300 mg, 83 %) as a pale yellow oil. Compound **16b** could be separated by sequential column chromatography over silica gel eluting with pentane/dichloromethane 19:1. Colorless crystals were obtained from pentane at −20 °C. Those of **16c** could be isolated by fractional recrystallization of the remaining mixture from pentane at −80 °C followed by recrystallization at −20 °C. NMR data of the *syn* isomer **16d** could be obtained from the residual mixture of isomers.

***syn*-(1*S*,3*S*,4*S*)- and (1*R*,3*R*,4*R*)-Isomer 16a**: $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -142.5$ ppm ($^1J$(P,W) = 257.8 Hz).

***anti*-(1*R*,3*S*,4*R*)- and (1*S*,3*R*,4*S*)-Isomer 16b**: m.p. 47–48 °C; $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.08$–1.11 (dddd, $^2J$(H,H) = 8.4, $^4J$(H,H) = 2.4, $^4J$(H,H) = 1.8, $^4J$(H,H) = 0.7 Hz, 1H; C*H*), 1.50 (ddd, $^2J$(H,H) = 8.4, $^4J$(H,H) = 2.4, $^4J$(H,H) = 1.8 Hz, 1H; C*H*), 1.61 (ddd, $^2J$(H,H) = 4.2, $^3J$(H,P) = 6.8, $^4J$(H,H) = 0.7 Hz, 1H; PCC*H*), 1.83 (dd, $^2J$(H,H) = 7.7, $^2J$(H,P) = 1.2 Hz, 1H; PC*H*), 2.02 (dd, $^2J$(H,H) = 7.7, $^2J$(H,P) = 7.4 Hz, 1H; PC*H*), 2.11 (dd, $^2J$(H,H) = 4.2, $^3J$(H,P) = 9.9 Hz, 1H; PCC*H*), 5.36 (t, $^4J$(H,H) = 2.4 Hz, 1H; =C*H*), 5.39 (t, $^4J$(H,H) = 1.8 Hz, 1H; =C*H*), 7.28–7.41 ppm (m, 5H; Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta = 9.5$ (d, $^3J$(C,P) = 4.6 Hz; *C*$H_2$), 17.8 (d, $^1J$(C,P) = 5.8 Hz; P*C*$H_2$), 19.5 (s; PCC$H_2$), 19.5 (s; PCC), 29.0 (d, $^1J$(C,P) = 7.7 Hz; P*C*), 101.6 (s; =$CH_2$), 128.6 (d, $^3J$(C,P) = 10.9 Hz; *m*-Ph), 130.5 (d, $^4J$(C,P) = 2.5 Hz; *p*-Ph), 131.3 (d, $^1J$(C,P) = 25.8 Hz; *ipso*-Ph), 131.6 (d, $^2J$(C,P) = 14.0 Hz; *o*-Ph), 133.7 (s; =*C*), 195.5 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.5 Hz; *cis*-CO), 197.6 ppm (d, $^2J$(C,P) = 30.4 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -144.0$ ($^1J$(P,W) = 258.2 Hz); IR (KBr): $\tilde{\nu} = 1925$ (s/br, $CO_{eq}$), 2074 $cm^{-1}$ (m, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 524 (4) $[M]^+$, 468 (8) $[M-2CO]^+$, 440 (3) $[M-3CO]^+$, 412 (12) $[M-4CO]^+$, 384 (52) $[M-5CO]^+$; HR-MS (EI): *m*/*z*: calcd for $C_{18}H_{13}O_5P^{184}W$: 524.00104; found: 524.00082.

***anti*-(1*R*,3*S*,4*S*)- and (1*S*,3*R*,4*R*)-Isomer 16c**: $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.45$–1.54 (m, 2H, C*H*), 1.70 (dd, $^2J$(H,H) = 7.7, $^2J$(H,P) = 0.8 Hz, 1H; PC*H*), 1.85 (dd, $^2J$(H,H) = 4.2, $^3J$(H,P) = 10.8 Hz, 1H; PCC*H*), 1.92 (dd, $^2J$(H,H) = 4.2, $^3J$(H,P) = 2.1 Hz, 1H; PCC*H*), 2.13 (dd, $^2J$(H,H) = 7.7, $^2J$(H,P) = 7.0 Hz, 1H; PC*H*), 5.51–5.53 (m, 2H; =$CH_2$), 7.40–7.45 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.51–7.57 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta = 9.4$ (d, $^3J$(C,P) = 2.3 Hz; *C*$H_2$), 17.5 (d, $^1J$(C,P) = 6.1 Hz; P*C*$H_2$), 19.3 (d, $^2J$(C,P) = 3.5 Hz; PC*C*$H_2$), 20.5 (s; PC*C*), 29.1 (d, $^1J$(C,P) = 7.5 Hz; P*C*), 102.7 (s; =*C*$H_2$), 128.8 (d, $^3J$(C,P) = 10.5 Hz; *m*-Ph), 130.4 (d, $^4J$(C,P) = 2.2 Hz; *p*-Ph), 131.4 (d, $^2J$(C,P) = 13.3 Hz; *o*-Ph), 132.9 (d, $^3J$(C,P) = 3.6 Hz; =*C*), 134.2 (d, $^1J$(C,P) = 25.3 Hz; *ipso*-Ph), 195.6 (d, $^2J$(C,P) = 8.4, $^1J$(C,W) = 125.6 Hz; *cis*-CO), 197.7 ppm (d, $^2J$(C,P) = 30.7 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -148.3$ ppm ($^1J$(P,W) = 257.2 Hz).

***syn*-(1*S*,3*S*,4*R*)- and (1*R*,3*R*,4*S*)-Isomer 16d**: $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.65$ (d, $^2J$(H,H) = 7.5 Hz, 1H; PC*H*), 1.71–1.74 (m, 1H; C*H*), 1.78–1.82 (m, 2H; PCC*H*, C*H*), 1.99–2.07 (m, 1H, $^3J$(H,P) = 4.1 Hz, PCC*H*), 2.05 (d, $^2J$(H,H) = 7.5, $^2J$(H,P) = ~7 Hz, 1H; PC*H*), 5.29 (t, $^4J$(H,H) = 2.4 Hz, 1H; =C*H*), 5.40 (t, $^4J$(H,H) = 1.7 Hz, 1H; =C*H*), 7.41–7.45 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.52–7.58 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta = 10.5$ (d, $^3J$(C,P) = 4.3 Hz; *C*$H_2$), 17.9 (d, $^1J$(C,P) = 6.0 Hz; P*C*$H_2$), 18.9 (d, $^2J$(C,P) = 3.8 Hz; PC*C*$H_2$), 20.4 (s; PC*C*), 28.3 (d, $^1J$(C,P) = 9.3 Hz; P*C*), 101.4 (d, $^4J$(C,P) = 1.4 Hz; =$CH_2$), 128.8 (d, $^3J$(C,P) = 10.4 Hz; *m*-Ph), 130.4 (d, $^4J$(C,P) = 2.4 Hz; *p*-Ph), 131.3 (d, $^2J$(C,P) = 13.0 Hz; *o*-Ph), 132.7 (d, $^3J$(C,P) = 2.2 Hz; =*C*), 134.4 (d, $^1J$(C,P) = 25.6 Hz; *ipso*-Ph), 195.5 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.4 Hz; *cis*-CO), 197.6 ppm (d, $^2J$(C,P) = 30.4 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -148.5$ ppm ($^1J$(P,W) = 256.2 Hz).

**1,6-Di(pentacarbonyltungstino)-1,6-diphenyl-1,6-diphosphadispiro-[2.0.0.2.1.1]nonane (17)**: Compound **16b** (88 mg, 0.17 mmol), complex **8** (219 mg, 0.33 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (1 mL) at 55 °C for 3 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 9:1 gave **17a** and **b** in a 10:7 ratio (127 mg, 78 %) as a colorless solid. Fractional recrystallization from pentane/$CH_2Cl_2$ at 0 °C afforded colorless crystals of **17a**.

***anti*,*anti*-17a**: m.p. 198 °C (decomp); $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta =$ 0.95 (dd, $^3J$(H,P) = 6.5, $^2J$(H,H) = 4.9 Hz, 2H; PCC*H*), 1.59 (d, $^2J$(H,H) = 7.7 Hz, 2H; PC*H*), 1.76 (dd, $^3J$(H,P) = 9.9, $^2J$(H,H) = 4.9 Hz, 2H; PCC*H*), 2.24 (dd, $^2J$(H,P) = 7.1, $^2J$(H,H) = 7.7 Hz, 2H; PC*H*), 7.40–7.46 ppm (m, 10H; Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta = 15.1$ (m, $^{(2+3)}J$(C,P) = 4.6 Hz; PCC*H*), 15.3 (d, $^{(1+4)}J$(C,P) = 6.3 Hz; P*C*$H_2$), 25.4 (t, $^2J$(C,P) = 5.5 Hz; PC*C*), 26.3 (d, $^{(1+3)}J$(C,P) = 8.8 Hz; P*C*), 128.8 (d, $^3J$(C,P) = 10.8 Hz; *m*-Ph), 130.8 (m, $^4J$(C,P) = 2.3 Hz; *p*-Ph), 131.4 (d, $^2J$(C,P) = 13.9 Hz; *o*-Ph), 131.5 (d, $^1J$(C,P) = 26.3 Hz; *ipso*-Ph), 195.3 (d, $^2J$(C,P) = 8.4, $^1J$(C,W) = 125.4 Hz; *cis*-CO), 197.3 ppm (d, $^2J$(C,P) = 31.1 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -147.9$ ($^1J$(P,W) = 261.2 Hz); IR (KBr): $\tilde{\nu} = 1917$ and 1935 (s/br, $CO_{eq}$), 1991 (w, $CO_{eq}$), 2074 $cm^{-1}$ (m, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 956 (8) $[M]^+$, 900 (1) $[M-2CO]^+$, 844 (16) $[M-4CO]^+$, 788 (20) $[M-6CO]^+$, 732 (40) $[M-8CO]^+$, 676 (100) $[M-10CO]^+$; HR-MS (EI): *m*/*z*: calcd for $C_{29}H_{18}O_{10}P_2{}^{184}W_2$: 955.93945; found: 955.93875; elemental analysis calcd (%) for $C_{29}H_{18}O_{10}P_2{}^{184}W_2$: C 36.43, H 1.90; found: C 36.12, H 1.95.

***anti*,*syn*-17b**: $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.05$ (dd, $^3J$(H,P) = 1.5, $^2J$(H,H) = 4.6 Hz, 1H; PCC*H*), 1.58 (dd, $^3J$(H,P) = 10.8, $^2J$(H,H) = 4.7 Hz, 1H; PCC*H*), 1.75 (d, $^2J$(H,H) = 8.1 Hz, 1H; PC*H*), 1.80 (dd, $^3J$(H,P) = 6.5, $^2J$(H,H) = 5.0 Hz, 1H; PCC*H*), 1.81–1.87 (m, 2H; PC*H*), 2.00 (dd, $^3J$(H,P) = 9.6, $^2J$(H,H) = 5.0 Hz, 1H; PCC*H*), 2.28 (dd, $^2J$(H,P) = 6.9, $^2J$(H,H) = 8.2 Hz, 1H; PC*H*), 7.38–7.48 ppm (m, 10H; Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta = 14.2$ (dd, $^2J$(C,P) = 3.9 Hz; PC*C*H), 15.5 (d, $^1J$(C,P) = 6.1 Hz; P*C*$H_2$), 16.0 (d, $^1J$(C,P) = 6.3 Hz; P*C*$H_2$), 16.1 (d, $^2J$(C,P) = 3.1 Hz; PC*C*H), 25.6 (d, $^1J$(C,P) = 9.8 Hz; P*C*), 26.1 (d, $^1J$(C,P) = 5.5 Hz; P*C*), 26.4 (dd, $^2J$(C,P) = 2.1, $^2J$(C,P) = 8.9 Hz; PC*C*), 128.7 (d, $^3J$(C,P) = 10.5 Hz; *m*-Ph), 128.9 (d, $^3J$(C,P) = 10.4 Hz; *m*-Ph), 130.5 (d, $^4J$(C,P) = 2.3 Hz; *p*-Ph), 130.6 (d, $^4J$(C,P) = 2.4 Hz; *p*-Ph), 131.2 (d, $^2J$(C,P) = 13.0 Hz; *o*-Ph), 131.4 (d, $^2J$(C,P) = 13.4 Hz; *o*-Ph), 131.7 (d, $^1J$(C,P) = 25.4 Hz; *ipso*-Ph), 133.8 (d, $^1J$(C,P) = 26.1 Hz; *ipso*-Ph), 195.3 (d, $^2J$(C,P) = 8.1, $^1J$(C,W) = 125.4 Hz; *cis*-CO), 195.5 (d, $^2J$(C,P) = 8.0, $^1J$(C,W) = 125.4 Hz; *cis*-CO), 197.3 (d, $^2J$(C,P) = 30.4 Hz; *trans*-CO), 197.4 ppm (d, $^2J$(C,P) = 30.6 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -150.4$ ($^1J$(P,W) = 260.2, $^4J$(P,P) = 5.1 Hz), −150.5 ppm ($^1J$(P,W) = 258.2, $^4J$(P,P) = 4.1 Hz).

**Synthesis of 7 and 19**: Complex **8** (0.65 g, 1.00 mmol), perspirocyclopropanated bicyclopropylidene **18** (0.22 g, 1.20 mmol) and CuCl (10 mg, 0.1 mmol) were stirred at room temperature for 20 h in toluene (4 mL). Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 19:1 yielded both **7** (0.26 g, 42 %) and **19** (40 mg, 6 %) as pale yellow solids. Recrystallization of **7** from hexane at −20 °C and **19** from diethyl ether at −5 °C afforded colorless crystals for both.

**(15-Phenyl-15-phosphahexaspiro[2.0.2.0.0.0.2.0.2.0.1]pentadec-15-yl)pentacarbonyltungsten (7)**: m.p. 178–179 °C (decomp); $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.60$–0.68 (m, 4H; C$H_2$), 0.75–0.80 (m, 2H; C$H_2$), 0.85–0.96 (m, 6H; C$H_2$), 0.96–1.02 (m, 2H; C$H_2$), 1.22–1.28 (m, 2H; C$H_2$), 7.25–7.39 ppm (m, 5H; Ph*H*); $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta = 4.4$ (d, $^3J$(C,P) = 4.0 Hz; *C*$H_2$), 4.7 (d, $^3J$(C,P) = 3.3 Hz; *C*$H_2$), 7.1 (d, $^3J$(C,P) = 2.1 Hz; *C*$H_2$), 7.4 (s; *C*$H_2$), 21.8 (d, $^2J$(C,P) = 5.3 Hz; PC*C*), 21.9 (d, $^2J$(C,P) = 1.2 Hz; PC*C*), 34.5 (d, $^1J$(C,P) = 6.2 Hz; P*C*), 128.2 (d, $^3J$(C,P) = 10.2 Hz; *m*-Ph), 130.0 (d, $^4J$(C,P) = 2.6 Hz; *p*-Ph), 131.9 (d, $^2J$(C,P) = 13.1 Hz; *o*-Ph), 132.9 (d, $^1J$(C,P) = 19.9 Hz; *ipso*-Ph), 195.9 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.4 Hz; *cis*-CO), 198.9 ppm (d, $^2J$(C,P) = 29.5 Hz; *trans*-CO); $^{31}$P{$^1$H} NMR (101.3 MHz, $CDCl_3$): $\delta = -119.6$ ppm ($^1J$(P,W) = 250.1 Hz); IR (KBr): $\tilde{\nu} = 1923$, 1942 (s/br, $CO_{eq}$), 1985 (w, $CO_{eq}$),

2072 $cm^{-1}$ (m, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 616 (4) $[M]^+$; HR-MS (EI, 70 eV): *m*/*z*: calcd for $C_{25}H_{21}O_5P^{184}W$: 616.06366; found: 616.06655.

**{2-Phenyl-2-phospha-3:3,4:4,6:6,7:7-tetrakisethanobicyclo[3.2.0]hept-1(5)-en-2-yl}pentacarbonyltungsten (19)**: m.p. 146–148 °C; $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 0.23–0.29 (m, 1H; C$H_2$), 0.33–0.42 (m, 2H; C$H_2$), 0.51–0.59 (m, 2H; C$H_2$), 0.61–0.71 (m, 6H; C$H_2$), 0.79–0.83 (m, 2H, C$H_2$) 0.91–0.98 (m, 2H; C$H_2$), 1.10–1.14 (m, 1H, C$H_2$), 7.40–7.44 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.50–7.56 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 6.3, 6.6, 7.7, 7.8, 7.9, 8.8 (s; *C*$H_2$), 10.1 (d, $^2J$(C,P) = 2.9 Hz; PC*C*$H_2$), 10.4 (d, $^2J$(C,P) = 7.1 Hz; PC*C*$H_2$), 30.6 (d, $^2J$(C,P) = 7.7 Hz; PC*C*), 34.9 (d, $^1J$(C,P) = 39.7 Hz; P*C*), 35.2 (d, $^2J$(C,P) = 22.1 Hz; P(C=)*C*), 35.8 (d, $^3J$(C,P) = 4.2 Hz; PC=C*C*), 128.5 (d, $^3J$(C,P) = 9.6 Hz; *m*-Ph), 130.3 (d, $^4J$(C,P) = 2.1 Hz; *p*-Ph), 131.4 (d, $^2J$(C,P) = 12.3 Hz; *o*-Ph), 136.3 (d, $^1J$(C,P) = 32.5 Hz; *ipso*-Ph), 142.5 (d, $^1J$(C,P) = 31.2 Hz; P*C*=C), 172.0 (d, $^2J$(C,P) = 5.8 Hz; PC=*C*), 196.8 (d, $^2J$(C,P) = 7.1, $^1J$(C,W) = 125.4 Hz; *cis*-CO), 199.3 ppm (d, $^2J$(C,P) = 21.1 Hz; *trans*-CO); $^{31}$P{$^1$H} NMR (101.3 MHz, $CDCl_3$): $\delta$ = 34.4 ppm ($^1J$(P,W) = 238.4 Hz); IR (KBr): $\tilde{\nu}$ = 1908, 1933 (s/br, $CO_{eq}$), 1977 (w, $CO_{eq}$), 2068 $cm^{-1}$ (m, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 616 (2) $[M]^+$; HR-MS (EI, 70 eV): *m*/*z*: calcd for $C_{25}H_{21}O_5P^{184}W$: 616.06366; found: 616.06445.

**(8-Phenyl-8-phosphatrispiro[2.0.0.2.1.1]non-8-yl)pentacarbonyltungsten (21)**: Complex **8** (369 mg, 0.55 mmol), cyclopropylidenespiropentane (**20**) (117 mg, 1.10 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (4 mL) at 55 °C for 1 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 19:1 gave **21a** and **b** in a 4:3 ratio (220 mg, 78%) as a pale yellow oil. Fractional recrystallization from pentane at −20 °C afforded colorless crystals of both isomers.

***anti*-(4*R*,9*R*)- and (4*S*,9*S*)-Isomer 21a**: m.p. 99 °C; $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta$ = 0.43–0.48 (m, 1H; C*H*), 0.76–0.91 (m, 3H; C*H*), 0.93–1.00 (m, 1H; PCC*H*), 1.13 (dd, $^2J$(H,H) = 4.3, $^2J$(H,P) = 7.0 Hz, 1H, PCC*H*C), 1.35–1.46 (m, 2H; PCC*H*), 1.47–1.53 (m, 1H; PCC*H*), 1.67 (dd, $^2J$(H,H) = 4.3, $^2J$(H,P) = 10.9 Hz, 1H; PCC*H*C), 7.35–7.46 ppm (m, 5H; Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ = 3.9 (d, $^3J$(C,P) = 4.6 Hz; *C*$H_2$), 4.7 (s; *C*$H_2$), 7.4 (d, $^2J$(C,P) = 3.6 Hz; PC*C*$H_2$), 8.9 (s; PC*C*$H_2$), 15.0 (s; PC*C*$H_2$C), 18.0 (d, $^2J$(C,P) = 5.3 Hz; PC*C*), 24.8 (s; P*C*), 30.1 (d, $^1J$(C,P) = 2.3 Hz; P*C*), 128.4 (d, $^3J$(C,P) = 10.5 Hz; *m*-Ph), 130.2 (d, $^4J$(C,P) = 2.6 Hz; *p*-Ph), 132.2 (d, $^2J$(C,P) = 13.5 Hz; *o*-Ph), 132.6 (d, $^1J$(C,P) = 21.5 Hz; *ipso*-Ph), 195.6 (d, $^2J$(C,P) = 8.4, $^1J$(C,W) = 125.4 Hz; *cis*-CO), 197.8 ppm (d, $^2J$(C,P) = 29.4 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −123.9 ppm ($^1J$(P,W) = 257.2 Hz); IR (KBr): $\tilde{\nu}$ = 1914 and 1931 (s/br, $CO_{eq}$), 1987 (w, $CO_{eq}$), 2072 $cm^{-1}$ (m, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 538 (2) $[M]^+$, 454 (3) $[M-3CO]^+$, 426 (6) $[M-4CO]^+$, 398 (20) $[M-5CO]^+$; HR-MS (EI): *m*/*z*: calcd for $C_{19}H_{15}O_5P^{184}W$: 538.01672; found: 538.01570; elemental analysis calcd (%) for $C_{19}H_{15}O_5P^{184}W$: C 42.41, H 2.81; found: C 42.24, H 2.82.

***syn*-(4*S*,9*R*)- and (4*R*,9*S*)-isomer 21b**: m.p. 74–75 °C; $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta$ = 0.77–0.84 (m, 1H; C*H*), 0.95–1.07 (m, 2H; C*H*), 1.10–1.20 (m, 2H; C*H*, PCC*H*), 1.22–1.30 (m, 2H; PCC*H*), 1.32 (dd, $^2J$(H,H) = 4.2, $^2J$(H,P) = 2.6 Hz, 1H; PCC*H*C), 1.34–1.44 (m, 1H; PCC*H*), 1.51 (dd, $^2J$(H,H) = 4.2, $^2J$(H,P) = 11.9 Hz, 1H; PCC*H*C), 7.38–7.46 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.56–7.64 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ = 4.1 (d, $^3J$(C,P) = 2.4 Hz; *C*$H_2$), 5.2 (d, $^3J$(C,P) = 3.7 Hz; *C*$H_2$), 8.0 (d, $^2J$(C,P) = 3.5 Hz; PC*C*$H_2$), 8.2 (s; PC*C*$H_2$), 14.9 (d, $^2J$(C,P) = 3.8 Hz; PC*C*$H_2$C), 18.8 (s; PC*C*), 25.3 (s; P*C*), 30.0 (d, $^1J$(C,P) = 3.5 Hz; P*C*), 128.5 (d, $^3J$(C,P) = 10.5 Hz; *m*-Ph), 130.2 (d, $^4J$(C,P) = 2.6 Hz; *p*-Ph), 132.3 (d, $^2J$(C,P) = 13.4 Hz; *o*-Ph), 134.0 (d, $^1J$(C,P) = 20.7 Hz; *ipso*-Ph), 195.7 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.4 Hz; *cis*-CO), 197.7 ppm (d, $^2J$(C,P) = 29.4 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −128.1 ppm ($^1J$(P,W) = 254.1 Hz); IR (KBr): $\tilde{\nu}$ = 1937 (s/br, $CO_{eq}$), 1987 (w, $CO_{eq}$), 2072 $cm^{-1}$ (w, $CO_{ax}$).

**Synthesis of 23 and 24**: Complex **8** (0.33 g, 0.50 mmol), 7-cyclopropylidenedispiro[2.0.2.1]heptane (**22**) (0.13 g, 1.00 mmol) and CuCl (10 mg, 0.1 mmol) were stirred at room temperature for 20 h in toluene (4 mL). Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 9:1 yielded **23** and **24** as a pale yellow solid. Fractional recrystallization from pentane at 0 °C afforded colorless crystals of **23** (200 mg, 71%). **24** was obtained as a colorless oil (5 mg, 2%) after sequential column chromatography over silica gel eluting with pentane/dichloromethane 9:1.

**(11-Phenyl-11-phosphatetraspiro[2.0.2.0.0.2.1]undec-11-yl)pentacarbonyltungsten (23)**: m.p. 93 °C; $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta$ = 0.19–0.24 (m, 1H; C*H*), 0.49–0.57 (m, 1H; C*H*), 0.58–0.64 (m, 2H; C*H*), 0.76–0.86 (m, 2H; C*H*), 0.96–1.02 (m, 1H; C*H*), 1.10–1.27 (m, 3H; C*H*, PCC$H_2$), 1.47–1.61 (m, 2H; PCC$H_2$), 7.35–7.40 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.48–7.54 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ = 3.0 (d, $^3J$(C,P) = 4.0 Hz; *C*$H_2$), 3.5 (d, $^3J$(C,P) = 1.6 Hz; *C*$H_2$), 3.9 (s; *C*$H_2$), 4.6 (d, $^3J$(C,P) = 3.2 Hz; *C*$H_2$), 6.8 (s; PC*C*$H_2$), 6.9 (d, $^2J$(C,P) = 3.3 Hz; PC*C*$H_2$), 20.8 (d, $^2J$(C,P) = 1.7 Hz; PC*C*), 21.5 (d, $^2J$(C,P) = 5.6 Hz; PC*C*), 23.5 (s; P*C*(C$H_2$)$_2$), 32.2 (d, $^1J$(C,P) = 5.7 Hz; P*C*), 128.4 (d, $^3J$(C,P) = 10.5 Hz; *m*-Ph), 130.2 (d, $^4J$(C,P) = 2.6 Hz; *p*-Ph), 132.0 (d, $^2J$(C,P) = 13.2 Hz; *o*-Ph), 133.1 (d, $^1J$(C,P) = 21.0 Hz; *ipso*-Ph), 195.7 (d, $^2J$(C,P) = 8.4, $^1J$(C,W) = 125.5 Hz; *cis*-CO), 197.9 ppm (d, $^2J$(C,P) = 29.4, $^1J$(C,W) = 149.6 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −124.1 ppm ($^1J$(P,W) = 250.6 Hz); IR (KBr): $\tilde{\nu}$ = 1915, 1933 (s/br, $CO_{eq}$), 1979 (m, $CO_{eq}$), 2072 $cm^{-1}$ (m, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 564 (13) $[M]^+$, 508 (2) $[M-2CO]^+$, 480 (7) $[M-3CO]^+$, 452 (19) $[M-4CO]^+$, 424 (100) $[M-5CO]^+$; HR-MS (EI): *m*/*z*: calcd for $C_{21}H_{17}O_5P^{184}W$: 564.03235; found: 564.03512.

**{2-Phenyl-2-phospha-3:3,4:4-bisethanobicyclo[3.2.0]hept-1(5)-en-2-yl}-pentacarbonyltungsten (24)**: $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ = 0.21–0.31 (m, 2H; PCCC*H*, PCC*H*), 0.32–0.40 (m, 1H; PCC*H*), 0.49–0.55 (m, 1H; PCC*H*), 0.62–0.74 (m, 3H; PCCC*H*), 0.90–0.99 (m, 1H, PCC*H*), 2.79–2.91 (m, 2H; =CC*H*), 2.96–3.12 (m, 2H, =CC*H*), 7.40–7.51 ppm (m, 5H; Ph*H*); $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): $\delta$ = 7.7, 8.9 (s; PCC*C*$H_2$), 10.8 (d, $^2J$(C,P) = 3.1 Hz; PCC$H_2$), 11.1 (d, $^2J$(C,P) = 7.4 Hz; PC*C*$H_2$), 28.5 (d, $^2J$(C,P) = 2.5 Hz; P(C=)C$H_2$), 28.7 (d, $^3J$(C,P) = 15.8 Hz; PC=C*C*$H_2$), 31.4 (d, $^2J$(C,P) = 8.2 Hz; PC*C*), 33.1 (d, $^1J$(C,P) = 40.2 Hz; P*C*), 128.6 (d, $^3J$(C,P) = 9.6 Hz; *m*-Ph), 130.4 (d, $^4J$(C,P) = 2.1 Hz; *p*-Ph), 131.6 (d, $^2J$(C,P) = 12.2 Hz; *o*-Ph), 136.0 (d, $^1J$(C,P) = 32.3 Hz; *ipso*-Ph), 140.3 (d, $^1J$(C,P) = 29.7 Hz; P*C*=C), 170.6 (d, $^2J$(C,P) = 4.4 Hz; PC=*C*), 196.7 (d, $^2J$(C,P) = 7.1, $^1J$(C,W) = 125.4 Hz; *cis*-CO), 199.5 ppm (d, $^2J$(C,P) = 21.0 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = 34.6 ppm ($^1J_{P,W}$ = 234.7 Hz); MS (70 eV): *m*/*z* (%): 564 (10) $[M]^+$, 508 (2) $[M-2CO]^+$, 480 (5) $[M-3CO]^+$, 452 (4) $[M-4CO]^+$, 424 (20) $[M-5CO]^+$; HR-MS (EI): calcd for $C_{21}H_{17}O_5P^{184}W$: 564.03235; found: 564.03554.

**Synthesis of 26 and 27**: Complex **8** (600 mg, 0.92 mmol), ethenylbicyclopropylidene (**25**) (293 mg, 2.76 mmol) and CuCl (10 mg, 0.1 mmol) were stirred in toluene (4 mL) at room temperature for 18 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 19:1 gave a mixture of six phosphirane isomers (440 mg, 89%) as a pale yellow oil. This mixture consisted of 9% of the phospha[3]triangulane isomers **26a** and **b** (1:1 ratio) and 91% of the phosphiranes **27** (four isomers 6:11:17:66). Colorless crystals of **27d** could be isolated by fractional recrystallization from hexane at −80 °C followed by recrystallization at −80 °C. **26a** could be separated from the remaining isomers by subsequent column chromatography over silica gel eluting with pentane/dichloromethane 19:1 and recrystallization at −80 °C.

**(1-Ethenyl-7-phenyl-7-phosphadispiro[2.0.2.1]hept-7-yl)pentacarbonyltungsten (26)**

***anti*-(1*R*,3*S*,7*S*)- and (1*S*,3*R*,7*R*)-Isomer 26a**: $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta$ = 0.90–1.02 (m, 1H; C*H*), 1.02–1.08 (m, $^2J$(H,H) = 5.3 Hz, 1H; C*H*), 1.15–1.25 (m, 1H; C*H*), 1.40–1.50 (m, 1H; C*H*), 1.50–1.61 (m, 1H; C*H*), 1.74–1.81 (m, $^2J$(H,H) = 5.3 Hz, 1H; C*H*), 2.37–2.43 (m, 1H; PCC*H*), 5.08–5.11 (m, 1H; =C$H_2$), 5.24–5.28 (m, 2H; =C$H_2$, =C*H*), 7.42–7.46 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.56–7.62 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta$ = 7.6 (d, $^2J$(C,P) = 3.4 Hz; *C*$H_2$), 9.8 (s; *C*$H_2$), 17.3 (s; *C*$H_2$), 26.5 (s; P*C*), 27.1 (d, $^2J$(C,P) = 3.1 Hz; PCC*C*H), 31.0 (d, $^1J$(C,P) = 2.2 Hz; P*C*), 115.9 (s; =C$H_2$), 128.5 (d, $^3J$(C,P) = 10.9 Hz; *m*-Ph), 130.4 (d, $^4J$(C,P) = 2.7 Hz; *p*-Ph), 132.7 (d, $^1J$(C,P) = 21.6 Hz; *ipso*-Ph), 133.1 (d, $^2J$(C,P) = 14.2 Hz; *o*-Ph), 137.6 (s; =C*H*), 195.5 (d, $^2J$(C,P) = 8.3 Hz; *cis*-CO), 197.5 ppm (d, $^2J$(C,P) = 29.5 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −127.0 ppm ($^1J$(P,W) = 259.4 Hz).

***syn*-(1*R*,3*S*,7*R*)- and (1*S*,3*R*,7*S*)-Isomer 26b**: $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = −129.8 ppm ($^1J$(P,W) = 260.4 Hz).

**(1-Phenyl-2-bicyclopropylidenylphosphiranyl)pentacarbonyltungsten (27)**

**Compound 27a**: $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -165.7$ ppm ($^1J$(P,W) = 257.8 Hz).

**Compound 27b**: $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -167.7$ ppm ($^1J$(P,W) = 258.0 Hz).

**Compound 27c**: $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -167.7$ ppm ($^1J$(P,W) = 252.8 Hz).

***anti*-(1*S*,2*S*,4*R*)- and (1*R*,2*R*,4*S*)-Isomer 27d**: m.p. 61 °C; $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.73$–0.81 (m, 2H; =CC*H*), 1.01–1.13 (m, 2H; =CC*H*), 1.13–1.20 (m, 1H; PCCC$H_2$), 1.32–1.37 (m, 1H; PCC*H*), 1.40–1.46 (m, 1H; PCCC$H_2$), 1.52–1.58 (m, 1H; PC$H_2$), 1.64–1.70 (m, 1H; PC*H*), 1.70–1.76 (m, 1H; PC$H_2$), 7.35–7.42 (m, 3H; *m*-Ph*H*, *p*-Ph*H*), 7.50–7.62 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta =$ 2.8, 3.0 (2s; =C($CH_2$)$_2$), 10.4 (d, $^3J$(C,P) = 5.0 Hz; PCC$CH_2$), 14.7 (d, $^1J$(C,P) = 11.8 Hz; P$CH_2$), 16.3 (d, $^2J$(C,P) = 4.0 Hz; PC*C*H), 28.5 (d, $^1J$(C,P) = 16.3 Hz; P*C*H), 112.9 (s; =*C*($CH_2$)$_2$), 113.3 (d, $^3J$(C,P) = 6.2 Hz; PCC*C*=), 128.8 (d, $^3J$(C,P) = 10.0 Hz; *m*-Ph), 130.2 (d, $^4J$(C,P) = 2.1 Hz; *p*-Ph), 132.6 (d, $^1J$(C,P) = 30.8 Hz; *ipso*-Ph), 132.8 (d, $^2J$(C,P) = 11.6 Hz; *o*-Ph), 195.8 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.7 Hz; *cis*-CO), 198.4 ppm (d, $^2J$(C,P) = 29.9 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -169.5$ ppm ($^1J$(P,W) = 253.0 Hz); IR (KBr): $\tilde{\nu} = 1923$ (s/br, $CO_{eq}$), 1985 (w, $CO_{eq}$), 2072 cm$^{-1}$ (w, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 538 (3) [*M*]$^+$, 482 (6) [*M*−2CO]$^+$, 454 (8) [*M*−3CO]$^+$, 426 (23) [*M*−4CO]$^+$, 398 (85) [*M*−5CO]$^+$; HR-MS (EI): *m*/*z*: calcd for $C_{19}H_{15}O_5P^{184}W$: 538.01672; found: 538.01634.

**{1-(1′-Phenyl-1′-pentacarbonyltungstenphosphiran-2-yl)-7-phenyl-7-phosphadispiro[2.0.2.1]hept-7-yl}pentacarbonyltungsten (28)**: Compound **27d** (55 mg, 0.10 mmol), complex **8** (133 mg, 0.20 mmol) and CuCl (10 mg, 0.1 mmol) were heated in toluene (1 mL) at 55 °C for 6.5 h. Evaporation to dryness and chromatography of the residue over silica gel eluting with pentane/dichloromethane 4:1 yielded **28a** and **b** in a 5:3 ratio (60 mg, 62 %) as a pale yellow oil; 12 % of **27d** (7 mg) could be recovered. Subsequent chromatography on silica gel eluting with pentane/dichloromethane 9:1 and recrystallization from hexane/$CH_2Cl_2$ at 0 °C afforded colorless crystals of both isomers of **28**.

***anti*,*anti*-(*R*,*R*-Phosphiranyl-1*R*,3*S*,7*S*)- and (*S*,*S*-phosphiranyl-1*S*,3*R*,7*R*)-isomer 28a**: m.p. 150 °C (decomp); $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.85$–0.98 (m, 2H; PC*H*, PCC*H*), 0.99–1.04 (m, 2H; C$H_2$), 1.44–1.62 (m, 1H; PC$H_2$; m, 4H; C$H_2$), 1.67 (ddd, $^2J$(H,H) = 8.7 Hz, 1H; PC$H_2$), 7.38–7.45 (m, 8H; Ph*H*), 7.47–7.53 ppm (m, 2H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta = 8.2$ (d, $^2J$(C,P) = 3.3 Hz; *C*$H_2$), 9.7 (s; *C*$H_2$), 16.0 (d, $^1J$(C,P) = 11.6 Hz; P*C*$H_2$), 16.4 (s; *C*$H_2$), 24.2 (d, $^{(2+2}J$(C,P) = 3.5 Hz; PC*C*H), 25.1 (s; P*C*), 27.4 (d, $^1J$(C,P) = 16.2 Hz; P*C*H), 31.8 (dd, $^1J$(C,P) = 3.8, $^3J$(C,P) = 9.6 Hz; P*C*), 128.6 (d, $^3J$(C,P) = 10.5 Hz; *m*-Ph), 129.1 (d, $^3J$(C,P) = 10.0 Hz; *m*-Ph), 130.5 (d, $^4J$(C,P) = 2.6 Hz; *p*-Ph), 130.8 (d, $^4J$(C,P) = 2.1 Hz; *p*-Ph), 130.9 (d, $^1J$(C,P) = 29.8 Hz; *ipso*-PhPC$H_2$), 132.2 (d, $^2J$(C,P) = 13.4 Hz; *o*-Ph), 132.4 (d, $^2J$(C,P) = 12.0 Hz; *o*-Ph), 133.7 (d, $^1J$(C,P) = 22.3 Hz; *ipso*-Ph), 195.3 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.6 Hz; *cis*-CO), 195.6 (d, $^2J$(C,P) = 8.2, $^1J$(C,W) = 125.7 Hz; *cis*-CO), 197.2 (d, $^2J$(C,P) = 29.9 Hz; *trans*-CO), 197.8 ppm (d, $^2J$(C,P) = 30.8 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -127.1$ ($^1J$(P,W) = 258.7 Hz; *P*[3]triangulane), −164.0 ppm ($^1J$(P,W) = 252.6 Hz; *P*CC); IR (KBr): $\tilde{\nu} = 1919$, 1936 (s/br, $CO_{eq}$), 1983, 1993 (s/br, $CO_{eq}$), 2074 cm$^{-1}$ (m, $CO_{ax}$); elemental analysis calcd (%) for $C_{30}H_{20}O_{10}P_2{}^{184}W_2$: C 37.14, H 2.08; found: C 36.55, H 2.27.

***anti*,*syn*-(*R*,*R*-Phosphiranyl-1*R*,3*S*,7*R*)- and (*S*,*S*-phosphiranyl-1*S*,3*R*,7*S*)-isomer 28b**: m.p. 170 °C; $^1$H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.82$–0.89 (m, 1H; PC*H*), 1.08–1.12 (m, 1H; PCC*H*), 1.19 (m, $^3J$(H,P) = 5.2 Hz, 1H; C$H_2$), 1.21–1.38 (m, 3H; C$H_2$), 1.41–1.54 (m, 2H; C$H_2$), 1.67 (m, $^2J$(H,P) = 1.0 Hz, 1H; PC$H_2$), 1.97 (m, $^2J$(H,P) = 8.4 Hz, 1H; PC$H_2$), 7.37–7.41 (m, 6H; *m*-Ph*H*, *p*-Ph*H*), 7.48–7.54 ppm (m, 4H; *o*-Ph*H*); $^{13}$C{$^1$H} NMR (100.62 MHz, $CDCl_3$): $\delta = 8.4$ (d, $^2J$(C,P) = 3.6 Hz; *C*$H_2$), 9.9 (s; *C*$H_2$), 15.2 (d, $^2J$(C,P) = 4.6 Hz; *C*$H_2$), 15.8 (d, $^1J$(C,P) = 11.4 Hz; P$CH_2$), 25.4 (d, $^2J$(C,P) = 3.6 Hz; PCC*H*), 25.9 (s; P*C*), 27.3 (dd, $^1J$(C,P) = 15.9, $^3J$(C,P) = 2.3 Hz; P*C*H), 31.4 (dd, $^1J$(C,P) = 5.3, $^3J$(C,P) = 10.0 Hz; P*C*), 128.6 (d, $^3J$(C,P) = 10.7 Hz; *m*-Ph), 128.9 (d, $^3J$(C,P) = 10.1 Hz; *m*-Ph), 130.5 (d, $^4J$(C,P) = 2.7 Hz; *p*-Ph), 130.7 (d, $^4J$(C,P) = 2.1 Hz; *p*-Ph), 130.8 (d, $^1J$(C,P) = 30.0 Hz; *ipso*-PhPC$H_2$), 132.5 (d, $^2J$(C,P) = 13.7 Hz; *o*-Ph), 132.5 (d, $^2J$(C,P) = 11.8 Hz; *o*-Ph), 132.6 (d, $^1J$(C,P) = 21.1 Hz; *ipso*-Ph), 195.4 (d, $^2J$(C,P) = 8.3, $^1J$(C,W) = 125.5 Hz; *cis*-CO), 195.7 (d, $^2J$(C,P) = 8.2, $^1J$(C,W) = 125.7 Hz; *cis*-CO), 197.1 (d, $^2J$(C,P) = 29.9 Hz; *trans*-CO), 197.9 ppm (d, $^2J$(C,P) = 30.6 Hz; *trans*-CO); $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta = -129.6$ ($^1J$(P,W) = 259.7, $^4J$(P,P) = 4.1 Hz; *P*[3]triangulane), −166.4 ppm ($^1J$(P,W) = 251.6, $^4J$(P,P) = 4.1 Hz; *P*CC); IR (KBr): $\tilde{\nu} = 1898$, 1917 and 1927 (s/br, $CO_{eq}$), 2072 cm$^{-1}$ (m, $CO_{ax}$); MS (70 eV): *m*/*z* (%): 970 (20) [*M*]$^+$, 914 (5) [*M*−2CO]$^+$, 858 (12) [*M*−4CO]$^+$, 802 (24) [*M*−6CO]$^+$, 746 (42) [*M*−8CO]$^+$, 690 (55) [*M*−10CO]$^+$; HR-MS (EI): *m*/*z*: calcd for $C_{30}H_{20}O_{10}P_2{}^{184}W_2$: 969.95520; found: 969.95191.

**Crystal structure determinations**: X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator ($\lambda = 0.71073$ Å). The structures were solved with automated Patterson Methods[34] (compounds **7**, **12a**, **14**, **16b**, **21a**, and **28a**) or Direct Methods[35] (compound **17a**) and refined with SHELXL-97[36] on $F^2$ of all reflections. Geometry calculations, drawings and checking for higher symmetry were performed with the PLATON[37] package.

**Compound 7**: $C_{25}H_{21}O_5PW$, $F_w = 616.24$, colourless needle, $0.51 \times 0.24 \times 0.21$ mm$^3$, monoclinic, $P2_1/c$ (no. 14), $a = 8.0553(1)$, $b = 17.0487(2)$, $c = 18.6096(3)$ Å, $\beta = 114.6694(12)°$, $V = 2322.45(6)$ Å$^3$, $Z = 4$, $\rho = 1.762$ g cm$^{-3}$; $T = 110(2)$ K; 54513 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max} = 0.81$ Å$^{-1}$. An analytical absorption correction was applied ($\mu = 5.08$ mm$^{-1}$, 0.15–0.40 correction range). 10119 reflections were unique ($R_{int} = 0.049$). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. 353 parameters were refined with no restraints. *R*1/*wR*2 [$I > 2\sigma(I)$]: 0.0188/0.0416. *R*1/*wR*2 [all refl.]: 0.0412/0.0533. $S = 0.603$. Residual electron density between −1.32 and 1.63 e Å$^{-3}$.

**Compound 12a**: $C_{17}H_{13}O_5PW$, $F_w = 512.09$, colourless plate, $0.18 \times 0.13 \times 0.06$ mm$^3$, monoclinic, $P2_1/c$ (no. 14), $a = 9.8460(1)$, $b = 9.2242(1)$, $c = 38.9935(3)$ Å, $\beta = 97.1897(3)°$, $V = 3513.60(6)$ Å$^3$, $Z = 8$, $\rho = 1.936$ g cm$^{-3}$; $T = 150(2)$ K; 44020 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å$^{-1}$. An analytical absorption correction was applied ($\mu = 6.69$ mm$^{-1}$, 0.32–0.79 correction range). 7989 reflections were unique ($R_{int} = 0.041$). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. 497 parameters were refined with no restraints. *R*1/*wR*2 [$I > 2\sigma(I)$]: 0.0211/0.0432. *R*1/*wR*2 [all refl.]: 0.0310/0.0461. $S = 1.026$. Residual electron density between −1.19 and 1.03 e Å$^{-3}$.

**Compound 14**: $C_{19}H_{15}O_5PW$, $F_w = 538.13$, colourless block, $0.33 \times 0.15 \times 0.15$ mm$^3$, monoclinic, $C2/c$ (no. 15), $a = 24.8645(2)$, $b = 10.0503(1)$, $c = 18.0840$ Å, $\beta = 122.9428(4)°$, $V = 3792.50(7)$ Å$^3$, $Z = 8$, $\rho = 1.865$ g cm$^{-3}$; $T = 150(2)$ K; 32020 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å$^{-1}$. An analytical absorption correction was applied ($\mu = 6.20$ mm$^{-1}$, 0.21–0.43 correction range). 4335 reflections were unique ($R_{int} = 0.039$). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. 275 parameters were refined with no restraints. *R*1/*wR*2 [$I > 2\sigma(I)$]: 0.0165/0.0365. *R*1/*wR*2 [all refl.]: 0.0192/0.0374. $S = 1.097$. Residual electron density between −1.03 and 0.68 e Å$^{-3}$.

**Compound 16b**: $C_{18}H_{13}O_5PW$, $F_w = 524.10$, colourless needle, $0.36 \times 0.09 \times 0.06$ mm$^3$, triclinic, $P\bar{1}$ (no. 2), $a = 9.9006(10)$, $b = 14.0474(12)$, $c = 14.652(2)$ Å, $\alpha = 64.984(8)$, $\beta = 79.165(9)$, $\gamma = 89.522(8)°$, $V = 1807.9(3)$ Å$^3$, $Z = 4$, $\rho = 1.926$ g cm$^{-3}$; $T = 150(2)$ K; 41602 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max} = 0.59$ Å$^{-1}$. An analytical absorption correction was applied ($\mu = 6.50$ mm$^{-1}$, 0.24–0.86 correction range). The crystal appeared to be non-merohedrally twinned with a twofold rotation about the a-axis as twin operation. This twin relationship was taken into account for the integration[38] and merging[39] of the reflections and the HKLF5 refinement.[40] 11455 reflections were unique ($R_{int} = 0.071$). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map

and refined as rigid groups. 452 parameters were refined with no restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0422/0.1208. $R1/wR2$ [all refl.]: 0.0746/0.1343. S = 1.084. Twin fraction 0.1862(5). Residual electron density between −1.36 and 2.04 e Å$^{-3}$.

**Compound 17a**: $C_{29}H_{18}O_{10}P_2W_2$, $F_w$ = 956.07, colourless needle, 0.42 × 0.12 × 0.12 mm$^3$, monoclinic, $P2_1$ (no. 4), $a$ = 6.3432(4), $b$ = 21.233(2), $c$ = 11.6997(8) Å, $\beta$ = 98.997(7)°, $V$ = 1556.4(2) Å$^3$, $Z$ = 2, $\rho$ = 2.040 g cm$^{-3}$; $T$ = 150(2) K. 18806 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å$^{-1}$. An absorption correction based on multiple measured reflections was applied ($\mu$ = 7.54 mm$^{-1}$, 0.18–0.41 correction range). 7049 reflections were unique ($R_{int}$ = 0.026). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined as rigid groups. 388 parameters were refined with 1 restraint. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0296/0.0667. $R1/wR2$ [all refl.]: 0.0359/0.0699. $S$ = 1.018. Flack $x$ parameter[41] −0.024(8). Residual electron density between −1.79 and 1.26 e Å$^{-3}$.

**Compound 21a**: $C_{19}H_{15}O_5PW$, $F_w$ = 538.13, colourless needle, 0.20 × 0.08 × 0.04 mm$^3$, triclinic, $P\bar{1}$ (no. 2), $a$ = 9.1520(1), $b$ = 9.2457(1), $c$ = 11.7216(2) Å, $\alpha$ = 79.5224(9), $\beta$ = 72.9620(8), $\gamma$ = 84.7207(7)°, $V$ = 931.71(2) Å$^3$, $Z$ = 2, $\rho$ = 1.918 g cm$^{-3}$; $T$ = 150(2) K; 16007 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å$^{-1}$. An analytical absorption correction was applied ($\mu$ = 6.31 mm$^{-1}$, 0.39–0.77 correction range). 4172 reflections were unique ($R_{int}$ = 0.045). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. 275 parameters were refined with no restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0192/0.0386. $R1/wR2$ [all refl.]: 0.0236/0.0397. $S$ = 1.054. Residual electron density between −0.84 and 0.98 e Å$^{-3}$.

**Compound 28a**: $C_{30}H_{20}O_{10}P_2W_2$ + disordered solvent, $F_w$ = 970.10[*], yellowish needle, 0.42 × 0.18 × 0.18 mm$^3$, monoclinic, $C2/c$ (no. 15), $a$ = 30.9063(16), $b$ = 11.9175(8), $c$ = 20.6181(11) Å, $\beta$ = 117.985(7)°, $V$ = 6706.2(8) Å$^3$, $Z$ = 8, $\rho$ = 1.922 g cm$^{-3}$[*]; $T$ = 150(2) K; 49557 reflections were measured up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å$^{-1}$. An absorption correction based on multiple measured reflections was applied ($\mu$ = 7.00 mm$^{-1}$[*], 0.17–0.28 correction range). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Phenyl hydrogen atoms were refined as rigid groups, all other hydrogen atoms were refined freely with isotropic displacement parameters. The crystal structure contains large voids (545 Å$^3$/unit cell) filled with disordered $CH_2Cl_2$ solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the PLATON program[37] resulting in 152 electrons/unit cell. 437 parameters were refined with no restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0190/0.0370. $R1/wR2$ [all refl.]: 0.0297/0.0386. $S$ = 1.030. Residual electron density between −0.64 and 0.76 e Å$^{-3}$. [*] Derived quantities do not contain the contribution of the disordered solvent.

CCDC-212086 (**7**), -269693 (**12a**), -269694 (**14**), -269695 (**16b**), -269696 (**17a**), -269697 (**21a**) and -269698 (**28a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/.

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