Synthesis of 1-Phosphaspiro[2.n]alkanes by Addition of Terminal Phosphinidene Complexes to Exocyclic Olefins[†]

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The phosphinidene complexes PhPW(CO)$_5$ (**1a**) and MePW(CO)$_5$ (**1b**) have been added to exocyclic olefins to yield 1-phosphaspiro[2.n]alkanes (n = 2–5). The molecular structures of the parent phosphirane **10a** and the parent phosphaspiro[2.2]pentane **6a** that result from addition of PhPW-(CO)$_5$ to ethylene and methylenecyclopropane, respectively, have been determined by single-crystal X-ray analyses. The reactivity order for addition of both phosphinidene complexes to exocyclic olefins was determined as methylenecyclopentane (**4**) > methylenecyclobutane (**3**) > methylenecyclohexane (**5**) > methylenecyclopropane (**2**). PhPW(CO)$_5$ is more selective and less reactive in its additions than MePW(CO)$_5$. The relative rates for phosphinidene addition correlate with both ^{13}C NMR chemical shifts of the spiro-carbon and the $^1J_{CH}$ coupling constants of the CH$_2$ group of the 1-phosphaspiro[2.n]alkanes products.

Introduction

The study of small-ring hydrocarbons has had a profound impact on our understanding of chemical bonding and reactivity. The continued accumulation of such knowledge on heterocycles attests to the desire to learn more about the impact of heteroatom substitution. Of the numerous studies that have been dedicated to three-membered ring systems those that include the element phosphorus are the smallest in number, but here also rapid advances are being made. An astonishing array of intriguing polycyclic compounds and even cage structures (*e.g.*, phosphacubanes) have been synthesized recently by several research groups.[1] In this rapidly expanding arena, we address the synthesis of spirophosphiranes. Only few examples have been reported for these compounds, and they include the 1,2-di-[2] and 1,2,3,4-tetraphosphaspiro-[2.2]pentanes.[3]

Our approach employs Mathey's methodology,[4] which entails the addition of an *in situ* generated terminal phosphinidene complex to exocyclic olefins (eq 1). Generally, the precursors to these phosphinidenes are the corresponding 7-phosphanorbornadienes that are decomposed either thermally (with and without catalyst) or photochemically. There is evidence for the carbene-like behavior of the incipient phosphinidene complexes RPM-(CO)$_n$ (R = Ph, CH$_3$, OCH$_3$; M = mainly W, but also Fe and Cr),[4b5,6] but they have yet eluded direct observation. Earlier, we have shown that the stereoselectivity for their

1a = Ph, **1b** = Me
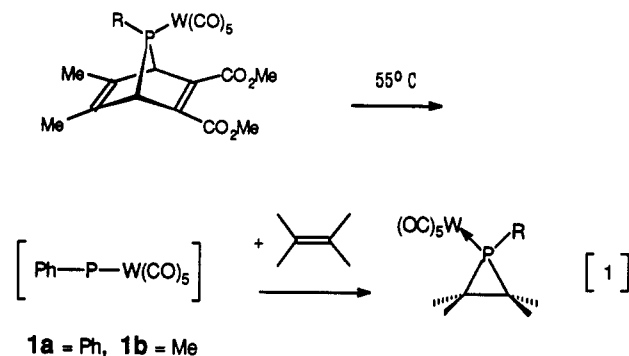
cycloadditions to olefins may differ from those of common carbenes.[7] To broaden the scope of this carbene-like chemistry, we now report on the competitive addition reactivities of two phosphinidenes with methylenecycloalkanes and compare these with the corresponding epoxidation and olefin reactivities toward diarylcarbenium ions.

Results and Discussion

Competitive relative reactivities for the addition to the exocyclic olefins **2–5** have been determined for both phosphinidene complexes, **1a** and **1b** (eq 1). These are reported in Table I and are based on product distributions as determined from integrated ^{31}P NMR resonances, which are listed in Table II. The reaction products **6–9** are new W(CO)$_5$-complexed phosphaspiro[2.n]alkanes (n = 2–5), all of which have been characterized spectroscopically and in the case of 1-phenyl-1-phosphaspiro[2.2]pentane (**6a**) also by X-ray structure determination. For comparison, we report the X-ray structure of the parent W(CO)$_5$-complexed 1-phenylphosphirane (**10a**). The discussion concentrates first on reactivities and then on structural aspects.

Reactivities. The same methylenecycloalkane reactivity order of **4** > **3** > **5** > **2** is found for the formation of phosphiranes from either of the phosphinidene complexes

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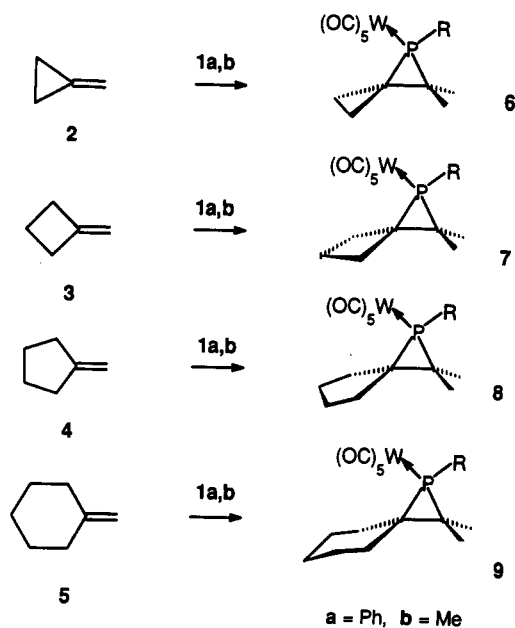
Table I. Relative Reactivities for the Addition of PhPW(CO)$_5$ and MePW(CO)$_5$ to Methylenecycloalkanes

olefins	PhPW(CO)$_5$	MePW(CO)$_5$
methylenecyclopropane	0.38	0.60
methylenecyclobutane	1.22	1.35
methylenecyclopentane	2.14	2.05
methylenecyclohexane	1.00	1.00
cyclohexene	0.26	

Table II. ^{31}P NMR Chemical Shifts (ppm, Toluene) of W(CO)$_5$-Complexed 1-Phospha[2.n]spiroalkanes

	P-substituents	
substrates	PhPW(CO)$_5$	MePW(CO)$_5$
1-phosphaspiro[2.2]pentane	−154.8	−166.2
1-phosphaspiro[2.3]hexane	−153.9	−171.7
1-phosphaspiro[2.4]heptane	−145.8	−165.1
1-phosphaspiro[2.5]octane	−144.5	−164.4

Table III. ^{13}C NMR Chemical Shifts Strain Energies (SE), and Ionization Potentials (IP) for Methylenecycloalkanes

	^{13}C chem. shifts[a] (ppm)		SE[b]	IP[c]
olefins	=CH$_2$	=C	(kcal/mol)	(eV)
methylenecyclopropane	103.1	131.1	41.7	9.57
methylenecyclobutane	105.1	150.3	28.8	9.35
methylenecyclopentane	104.9	153.1	6.3	9.14
methylenecyclohexane	106.9	149.8	1.9	9.13

[a] Reference 12b. [b] Reference 10. [c] Reference 11.

Table IV. ^{13}C NMR Chemical Shifts (ppm) and Coupling Constants (Hz) of Phosphiranes 7a–10a Related to Relative Olefin Reactivities

phosphiranes	log k_x/k_R[a]	spiro-C	$^1J_{CH}$[b]
6a	−0.42	31.2	162.6
7a	0.09	34.0	159.5
8a	0.33	36.9	157.9
9a	0.00	34.3	159.5
corr coeff (r)		0.9767	0.9920

[a] X refers to the methylenecycloalkanes 2–5 and R (reference) to 5. [b] Of the phosphirane CH$_2$ group.

1a or 1b. All olefins react slightly faster than cyclohexene, but the range in reactivities is less than 1 order of magnitude. This similarity in observed reactivities of the olefins is in line with a carbene-like mechanism for the phosphinidene additions. Complex 1b is less selective in its addition to the olefins than complex 1a. This is in accordance with the lower Hammett reaction constant of MePW(CO)$_5$ ($\rho^+ = -0.60$)[5] relative to that of PhPW(CO)$_5$ ($\rho^+ = -0.76$),[6] which were determined from the reaction of styrenes with 1b and 1a, respectively. In a related kinetic epoxidation (CH$_3$CO$_3$H) study, Kas'yan et al.[8] reported reactivities for 3–5 that are similar to our results, with k_{rel} values (relative to 5) of 1.95 for 4 and a slightly smaller 0.62 for 3. Expectantly, these observed relative reactivities of the methylenecycloalkanes toward carbene-like species differ from those of the addition of diarylcarbenium ions (Ar$_2$CHCl, ZnCl$_2$), reported by Mayr and co-workers,[9] who found a ca. 50-fold higher reactivity for 4 as compared to 3 and 5. Neither group reported on the reactivity of 2.

a = Ph, b = Me

Is the reactivity order of the methylenecycloalkanes determined by electronic, steric, or strain factors in the olefins (kinetics) or products (thermodynamics)? In their

epoxidation study Kas'yan et al.[8] did not find a correlation between the olefin reactivities and their strain energies,[9] oxidation potentials,[10] or ^{13}C NMR chemical shifts[11] and nor do we for the phosphinidene reactions (Table III). A correlation with calculated ring strain energies of the olefins is not likely because the ring structure remains intact. A better correlation is expected with olefin π-energies (HOMO), but this expectation is not fulfilled when reported π-ionization energies are used. Because phosphinidenes are slightly electrophilic, stabilization of the partly positive charge could be an important factor and might explain why 4 is the most reactive of the series (cf. Ar$_2$CH$^+$)[9] and 2 the least reactive. A cation center enjoys significant stabilization in a five-membered ring structure, whereas such π-stabilization is reduced in 2 due to the high s-character of the olefinic ring carbon. Kas'yan et al.[8] speculated on a reactivity relationship with both ^{13}C NMR chemical shifts and coupling constants because these reflect to some extent local charge densities. When applied (Table IV) to the phosphinidene additions, we do not find these correlations satisfactory. Of course, it may be argued that the experimental conditions (autoclave and differences in olefin boiling points) render uncertainties in the observed reactivities, but the similarity in the two sets of phosphinidene reactions would seem to eliminate this concern. Instead, we find reasonable correlations of the relative olefin reactivities with both the ^{13}C chemical shifts of the spiro carbon ($\langle r^2 \rangle = 0.9539$, 95% confidence) and the $^1J_{CH}$ coupling constants of the phosphirane CH$_2$ group ($\langle r^2 \rangle = 0.9840$, 95% confidence) of the 1-phosphaspiro[2.n]alkane products. These correlations strongly suggest that the observed phosphinidene addition reactivities of the methylenecycloalkanes are product related and therefore solely controlled by thermodynamics!

To further illustrate the high reactivity for phosphinidene addition to olefins and to obtain a phosphirane for

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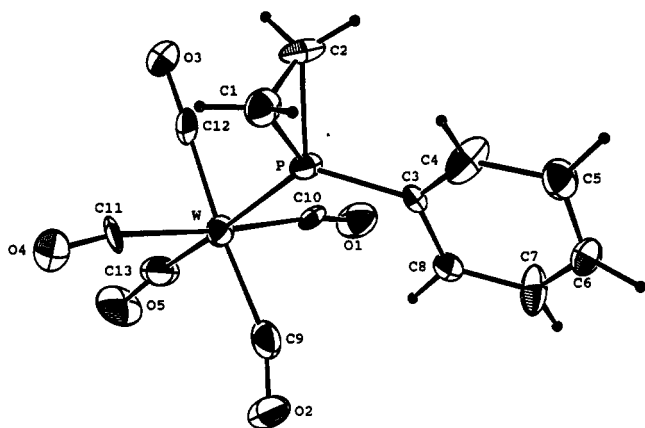
Figure 1. ORTEP drawing with atom-labeling scheme of the molecular crystal structure of 10a.

Table V. Comparison of X-ray Crystallographic Data (Bond Distances (Å) and Angles (deg)) of W(CO)₅-Complexed Phosphiranes and the Microwave Structure of Phosphirane

substrates	10a[a]	11[b]	12[c]	13[d]	10c[e]
C(1)–C(2)	1.50(2)	1.49(1)	1.51(1)	1.49(2)	1.502
C(1)–P	1.83(2)	1.81(1)	1.83(1)	1.82(1)	1.867
C(2)–P	1.80(2)	1.78(1)	1.82(1)	1.80(1)	1.867
P–W	2.504(2)	2.455(2)	2.506(2)	2.486(1)	
P–R	1.80(1)	2.037(3)	1.85(2)	1.667(8)	1.428
C(1)–P–C(2)	48.6(7)	49.2(5)	49.1(4)	48.5(5)	47.4
R–P–W	122.9(3)	118.4(1)		125.9(2)	

[a] This work, R = Ph. [b] Reference 14, R = Cl. [c] Reference 15, R = 1-L-menthyl. [d] Reference 16, R = 2,2,6,6-tetramethylpiperidyl. [e] Reference 17, R = H.

structural comparisons, we reacted the parent olefin, ethylene, by passing it through a solution containing 1a, heated at 55 °C. This reaction yielded the parent W(CO)₅-complexed phosphirane 10a in a simpler and more gentle procedure than the reported synthesis from ethoxyacetylene using a sealed tube at 130 °C.[13]

Solid-State Structures of W(CO)₅ Complexes of Phosphirane 6a and 1-Phosphaspiro[2.2]pentane. The important X-ray structural features of 10a (Figure 1) are summarized in Table V together with those of the 1-chloro- (11),[14] 1-L-menthyl- (12),[15] and 2,2,6,6-tetramethylpiperidyl- (13)[16] derivatives and the microwave spectroscopic data of the parent phosphirane C₂PH₅ (10c).[17] All these phosphiranes have essentially the same C–C bond lengths. The P–C bonds are also of the same length for all W(CO)₅-complexed structures with an average distance of 1.81 Å but differ from those (1.867 Å) of the uncomplexed phosphirane 10c. The P–W and P–R distances differ significantly among the structures. Whereas the P–W bond lengths are the same (average 2.505(3) Å) for the P-hydrocarbon substituted phosphiranes 10a and 12, shorter P–W bonds are found when the phosphorus is substituted with the more electronegative Cl (11) and piperidyl (13) groups or when the phosphorus is part of a phosphirene, e.g., 2.496 Å in (1,2,3-triphenylphosphirene)pentacarbonyltungsten.[18] The P–R bond length
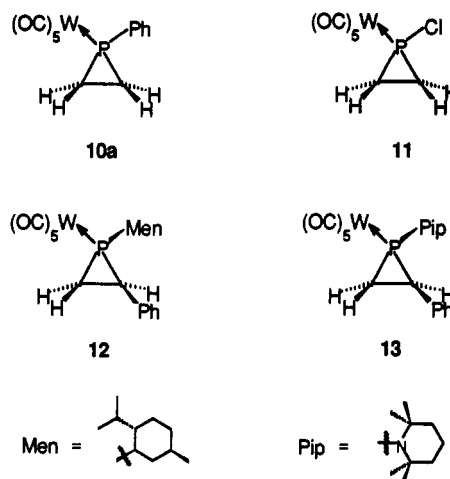
is of course strongly dependent on the substituent R, and the 0.05 Å difference in P–C bond lengths between the phenyl (10a) and alkyl (12) substituents is noted even though it falls within the error limits of 12. It is, however, evident that W(CO)₅ complexation and P-phenyl substitution have a significant stabilizing influence on the phosphirane ring.

The asymmetric unit in racemic W(CO)₅-complexed 1-phosphaspiro[2.2]pentane (P1̄ unit cell, which has a center of symmetry) consists of two molecular structures 6a (Figure 2) and 6a'. These structures differ largely in a slight rotation of the W(CO)₅ group and a twisting in the phosphaspiro[2.2]pentane unit (i.e., 90.5(5)° for 6a and 91.6(5)° for 6a'). These small distortions, which are possibly due to packing effects, also induce small differences in bond lengths between 6a and 6a'; full structural analyses of the crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. For simplicity, we employ 6a–6a' averaged (av) bond distances and angles (Table VI) in comparison with the aforementioned phosphiranes (Table V). The P–Cl (1.794(6) Å) and P–C2 (1.854(7) Å) bond lengths of the phosphirane ring of 6a(av) are noticeably different from each other, which thereby underscores the spiro-group substituent effect on Cl(1′); i.e., distal bonds are longer than lateral bond distances. Especially, the distal P–C2 bond is elongated as compared to, e.g., 10a and is similar to the 1.867-Å P–C bond length of the parent C₂PH₅ phosphirane 10c. The structural parameters of the ClC3C4 cyclopropane unit of 6a(av) are very similar to those of spiropentane (–163 °C, uncorrected),[19] which has distal C–C bonds distances of 1.527 Å and lateral C–C bond distances of 1.477 Å.

Conclusion. Methylenecycloalkanes react with W(CO)₅complexed phenyl- and methylphosphinidenes to yield in a convenient manner 1-phosphaspiro[2.n]-alkanes. The reactivity order of the olefins, as determined from competitive reactions, is 4 > 3 > 5 > 2 with a spread of less than 1 order of magnitude. This reactivity order correlates with ¹³C NMR parameters of the spirophosphirane products. Of the two phosphinidenes, MePW-(CO)₅ is the most reactive and least selective one. The

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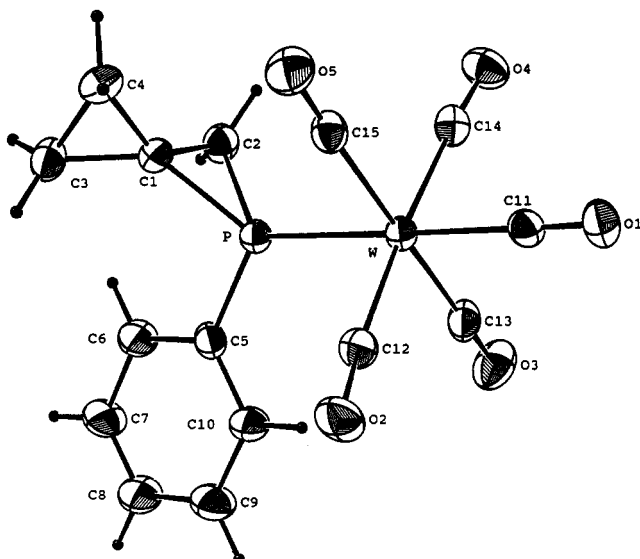(19) Boese, R.; Bläser, D.; Gomann, K.; Brinker, U. H. J. Am. Chem. Soc. 1989, 111, 1501.

Figure 2. ORTEP drawing with atom-labeling scheme of the molecular structure of **6a**.

Table VI. Average Bond Distances (Å) and Angles (deg) for 6a and 6a'

atoms	distance/angle	atoms	distance/angle
W–P	2.500(2)	P–C(1)–C(2)	67.8(3)
P–C(1)	1.794(6)	P–C(2)–C(1)	63.6(3)
P–C(2)	1.855(7)	C(1)–P–C(2)	48.6(3)
C(1)–C(2)	1.508(9)	C(1)–C(3)–C(4)	59.0(5)
C(1)–C(3)	1.475(10)	C(1)–C(4)–C(3)	59.1(5)
C(1)–C(4)	1.470(1)	C(3)–C(1)–C(4)	62.0(5)
C(3)–C(4)	1.515(10)		

first X-ray structure of the prototypic 1-phosphaspiro-[2.2]alkane **6a** has been determined. The prototypic phosphirane **10a** can also readily be synthesized from reaction of incipient PhPW(CO)₅ with gaseous ethylene. Comparison of its X-ray structure with those of differently substituted phosphiranes suggests that both the W(CO)₅ and *P*-phenyl group are stabilizing.

Experimental Section

NMR spectra were recorded on a GE NT-300 wide-bore spectrometer. Chemical shifts are referenced in ppm to internal (CH₃)₄Si for the ¹H and ¹³C NMR spectra and to external 85% H₃PO₄ for the ³¹P NMR spectra. Downfield shifts are reported as positive. IR spectra were recorded on a Nicolet IR44 spectrometer. Mass spectra were recorded on a HP 5985 at 70 eV. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. All materials were handled under an atmosphere of dry, high-purity nitrogen. Reagents and solvents were used as purchased, except for THF, which was distilled from sodium–benzophenone prior to use, and toluene, which was dried over molecular sieves. The methylenecycloalkanes were purchased from Aldrich and Fluka Chemical Co. and were used without further purification. Chromatographic separations were performed on silica gel columns (230–400 mesh, EM Science). The synthesis of [5,6-dimethyl-2,3-bis(methoxy-carbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyl-tungsten (**1a**) and the 7-methyl derivative (**1b**) are described in ref 4b.

General Procedure for the Competition Reactions. Two mmol each of two methylenecycloalkanes were transferred at −40 to −60 °C to a precooled autoclave filled with 5 mL of dry toluene and a magnetic stirrer. To this was added 130 mg (0.2 mmol) of complex **1a** or 110 mg (0.2 mmol) of complex **1b** and 10 mg (0.1 mmol) CuCl, after which the reaction mixture was placed under a nitrogen atmosphere. The sealed autoclave was

heated for 2 h at 60 °C for complex **1a** and for 40 min at 55 °C for complex **1b**. After cooling and removal of CuCl by filtration, aliquots of the reaction mixtures were subjected to ³¹P NMR analysis. Relative phosphirane product ratios were determined from integration of the ³¹P resonances. All competition reactions were executed in duplicate with several cross-checks for a total of 18 reactions.

(1-Phenyl-1-phosphaspiro[2.2]pentane)penta-carbonyltungsten (6a). Complex **1a** (1.0 g, 1.53 mmol) and methylenecyclopropane (0.56 mL, 8 mmol) in 20 mL of toluene with CuCl (100 mg, 1.0 mmol) were heated at 60 °C for 2 h in an autoclave. Filtration of the reaction mixture, evaporation to dryness, and chromatography over silica with hexane–benzene (4:1) as eluent gave 0.46 g (62%) of a colorless solid: mp 57–58 °C; ³¹P NMR (C₆D₆) δ −154.8; ¹³C NMR (C₆D₆) δ 9.5 (t, ³*J*(PC) = 2.63 Hz, ¹*J*(CH) = 163.0 Hz), 11.1 (t, ¹*J*(CH) = 163.8 Hz), 19.3 (t, *J*(CP) = 6.9 Hz, ¹*J*(CH) = 162.6 Hz), 21.2 (d, ³*J*(CP) = 2.85 Hz, C), 128.8, 130.3, and 131.8 (Ph), 195.6 (cis CO), 197.7 (trans CO); MS (¹⁸⁴W) *m/z* (relative intensity) 486 (M, 19), 374 (M − 4CO, 40), 346 (M − 5CO, 100), 292 (PhPW, 61). Anal. Calcd for C₁₅H₁₁O₅PW: C, 37.04; H, 2.26. Found: C, 36.82; H, 2.29.

(1-Phenyl-1-phosphaspiro[2.3]hexane)penta-carbonyltungsten (7a). The same reaction with methylenecyclobutane gave, after purification on silica gel (hexane), 100 mg (20%) of a colorless solid: mp 34–35 °C; ³¹P NMR (C₆D₆) δ −153.9; ¹³C NMR (C₆D₆) δ 17.6 (t, ³*J*(PC) = 7.1 Hz, ¹*J*(CH) = 138.0 Hz), 23.0 (t, *J*(CP) = 10.9 Hz, ¹*J*(CH) = 159.5 Hz), 29.2 (t, *J*(CP) = 2.7 Hz, ¹*J*(CH) = 137.3 Hz), 31.6 (t, *J*(CH) = 137.5 Hz), 34.0 (³*J*(CP) = 20.0 Hz, C), 128.8, 130.1, and 132.1 (Ph). Anal. Calcd for C₁₆H₁₃O₅PW: C, 38.40; H, 2.60. Found: C, 38.58; H, 2.64.

(1-Phenyl-1-phosphaspiro[2.4]heptane)penta-carbonyltungsten (8a). The same reaction with methylenecyclopentane gave, after purification on silica gel, 150 mg (29%) of a colorless solid: mp 63–64 °C; ³¹P NMR (C₆D₆) δ −145.9; ¹³C NMR (C₆D₆) δ 21.7 (t, ³*J*(PC) = 12.0 Hz, ¹*J*(CH) = 157.9 Hz), 26.0 (t, *J*(CP) = 1.7 Hz, ¹*J*(CH) = 134.8 Hz), 26.2 (t, *J*(CP) = 3.8 Hz, ¹*J*(CH) = 132.9 Hz), 34.4 (t, *J*(CH) = 132.0 Hz), 36.9 (³*J*(CP) = 6.0 Hz, C), 37.2 (³*J*(CP) = 16.8 Hz, C), 128.8, 130.0, 132.3 (Ph), 196.0 (cis CO), 198.0 (trans CO). Anal. Calcd for C₁₇H₁₅O₅PW: C, 39.68; H, 2.92. Found: C, 39.83; H, 2.96.

(1-Phenyl-1-phosphaspiro[2.5]octane)penta-carbonyltungsten (9a). The same reaction with methylenecyclohexane gave, after purification on silica gel, 200 mg (38%) of a colorless solid: mp 58–59 °C; ³¹P NMR (C₆D₆) δ −144.0; ¹³C NMR (C₆D₆) δ 21.9 (t, *J*(CP) = 12.5 Hz, ¹*J*(CH) = 159.5 Hz), 25.5 (t, ¹*J*(CH) = 122.8 Hz, two carbons), 25.7 (t, ³*J*(CP) = 5.5 Hz, *J*(CH) = 126.5 Hz), 32.8 (³*J*(CP) = 16.5 Hz, *J*(CH) = 130.6 Hz), 34.3 (³*J*(CP) = 16.5 Hz, C), 35.7 (t, *J*(CP) = 6.5 Hz, ¹*J*(CH) = 125 Hz), 128.0, 130.0, 132.2 (Ph), 196.5 (²*J*(CP) = 9.1 Hz, cis CO), 198.2 (²*J*(CP) = 28.9 Hz, trans CO). Anal. Calcd for C₁₈H₁₇O₅-PW: C, 40.91; H, 3.22. Found: C, 41.00; H, 3.24.

(1-Phenylphosphirane)pentacarbonyltungsten (10a). Ethylene gas was bubbled through a toluene solution containing 0.65 g (1 mmol) of **1a** and 70 mg (0.7 mmol) of CuCl at 55 °C for 2–3 h. The resulting black solution was filtered to remove CuCl, concentrated, and chromatographed on silica gel with hexane-benzene (4:1) to yield 0.25 g (54%) of **6a** as a colorless solid: mp 77–77.5 °C; ³¹P NMR (C₆D₆) δ −187.6 (¹*J*PW) = 257.5 Hz); ¹³C NMR (C₆D₆) δ 10.7 (d, *J*(CP) = 12.2 Hz, ¹*J*(CH) = 163.2 Hz, CH₂), 128.8, 130.3, 131.1 (Ph), 195.9 (d, ²*J*(CP) = 6.5 Hz, cis CO), 197.92 (²*J*(CP) = 33.0 Hz, trans CO); ¹H NMR (C₆D₆) δ 0.80–0.86 (m, 2H, CH₂), 0.89–1.00 (m, 2H, CH₂), 6.88–7.05 (m, 5H, Ph); MS (¹⁸⁴W) *m/z* (relative intensity) 460 (M, 20), 348 (M − 4CO, 100), 320 (M − 5CO, 58), 292 (PhPW, 90). Anal. Calcd for C₁₃H₉O₅-PW: C, 33.91; H, 1.96. Found: C, 34.00; H, 1.99.

X-ray Structure Determination of 6a and 10a. Structure Solution and Refinement. Well-formed single crystals, attached to glass fibers with epoxy cement, were mounted on an Enraf-Nonius CAD4 diffractometer. Least-squares refinement of 25 well-centered reflections (25 ≤ θ ≤ 35) yielded precision lattice constants for each crystal. Intensity data were collected at room temperature using Ni-filtered monochromatized Cu-Kα radiation (λ = 1.5418 Å) with an ω/2θ scan mode (scan speed 0.67 min, background/scan ratio = 0.5)) up to 2θ = 152. Three reflections were measured periodically during data collection to monitor crystal decay. The data were processed using the Enraf-

Nonius MolEN software on a VAX/VMS. Intensities were corrected for Lorentz and polarization effects; a linear decay correction and an empirical absorption correction were also applied. Variances were assigned based on standard counting statistics, with the addition of an instrumental uncertainty term $0.02F_o{}^2$. The structures were solved by standard Patterson and difference Fourier techniques and refined by weighted full-matrix least-squares methods. The final models contain anisotropic thermal parameters for all non-hydrogen atoms and isotropic hydrogens atoms in calculated positions riding on their attached carbon atoms. The final difference Fourier maps contained maximum $\Delta\rho$ values near the W atom, with no peaks interpretable as extra atoms. The atomic scattering factors were taken from the *International Tables for Crystallography*. **Crystal and intensity data:** $C_{15}H_{11}O_5PW$ (**6a, 6a'**), MW = 486.08, triclinic unit cell, a = 10.935 (4) Å, b = 12.184 (2) Å, c = 12.936 (6) Å, α = 93.61 (3)°, β = 107.02 (4)°, γ = 82.68 (3)°, V = 1634.5 Å³, space group $P\bar{1}$, Z = 4, D_c = 1.975 g/cm³, crystal dimensions 0.31 × 0.37 × 0.49 mm, reflections measured with indices ranges $-13 \leq h \leq 13$, $0 \leq k \leq 15$, $-16 \leq l \leq 16$, 6956 unique reflections from which 6439 were observed having $I > 3\sigma(I)$, 398 parameters, R = 4.17%, R_w = 5.87%, GOF = 2.486, T_{max} = 98.56%, T_{min} = 85.06%, $\Delta\rho_{max}$ = 1.611 e Å⁻³, Δ/σ_{max} = 0.01. $C_{13}H_9O_5PW$ (**10a**), MW = 460.04, orthorhombic unit cell, a = 12.598 (3) Å, b = 13.869 (3), Å, c = 8.530 (1) Å, V = 1490.3 Å³, space group $Pna2_1$, Z = 4, D_c = 2050 g/cm³, crystal dimensions 0.11 × 0.27 × 0.55 mm, reflections measured with indices ranges $-15 \leq h \leq 0$, $0 \leq k \leq 17$, $-10 \leq l \leq 0$, 1638 unique reflections from which 1439 were observed having $I > 3\sigma(I)$, 181 parameters, R = 6.76%, R_w = 7.96%, GOF = 1.721 T_{max} = 98.33%, T_{min} = 69.6%, $\Delta\rho_{max}$ = 2.103 e Å⁻³, Δ/σ_{max} = 0.03.