A New Stereoselective Synthesis of Phosphiranes

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The synthesis of phosphiranes from primary phosphines and diol ditosylates was found to be stereoselective, and chiral phosphiranes were prepared from optically pure diols. The four optical isomers of 1-mesityl-2,3-dimethylphosphirane, (2*S*,3*S*)-(+)-**3**, (2*R*,3*R*)-(−)-**4**, *anti-cis*-(*meso*)-**5**, and *syn-cis*-(*meso*)-**6**, were all synthesized from mesitylphosphine and the corresponding diol ditosylates. Compound **6** was unstable, but compounds **3**, **4**, and **5** were all isolated in pure form. Their structure assignments were based on the NMR coupling constants J_{P-H} and J_{P-C}. The phosphiranes were transformed into tungsten pentacarbonyl complexes. Tungsten tetracarbonyl−triphenylphosphine complexes (**22**, **23**, **24**) of compounds **3**, **4**, and **5** were synthesized in high yields by the reaction of the phosphiranes and $W(CO)_4(PPh_3)$(THF). The absolute stereochemistry of the phosphiranes **3**, **4**, and **5** was determined by X-ray crystal structure analysis of compounds **22**, **23**, and **24**. Stereochemical effects on NMR coupling constants and mass spectra of the phosphiranes are discussed.

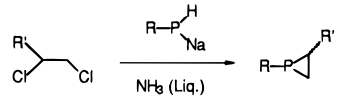
Introduction

The chemistry of phosphiranes is underdeveloped by comparison with that of their oxygen, nitrogen, and sulfur counterparts.[1] Evidence from this laboratory indicates that phosphiranes are good precursors of phosphinidenes R−P, molecules containing monovalent phosphorus atoms.[2,3] The small cone angle at the phosphorus atom of phosphiranes suggests that they could act as ligands that confer interesting properties on metal complexes. Indeed Marinetti, Ricard, and Mathey have employed the "phospha-Wittig" reaction to synthesize phosphirane−metal complexes from oxiranes,[4] including optically active examples from which the first chiral phosphiranes were liberated.[5] Chiral phosphiranes or bisphosphiranes are expected to be useful as ligands in asymmetric catalysis, since the chiral ring carbons would lie very close to tightly complexed phosphorus centers.[6] Preliminary results from the Mathey group on hydrogenation with chiral phosphirane−rhodium complexes have been published.[5]

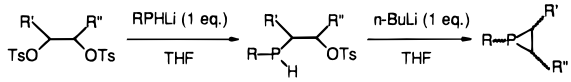
To assist in the study of the properties of chiral phosphiranes, a new, efficient, stereoselective method for the synthesis of phosphiranes has been developed, and representative examples are described here.

When phosphiranes were first prepared by Wagner and his co-workers in 1963, their synthesis was based on the reaction of 1,2-dichloroalkanes and sodium monophosphide in liquid ammonia (Scheme 1).[7] Several other synthetic methods have been reported, but none is efficient and general.[8] Mathey's approaches to phosphiranes, based on the addition of terminal metal phosphinidene complexes to alkenes[9] and the "phospha-Wittig" reaction of phosphorylphosphine complexes with oxiranes,[4,5] are powerful and of considerable interest, but the sequences, including a final decomplexation of the phosphirane from a transition metal, are lengthy, arduous, and expensive.

Scheme 1



Scheme 2



By the methods reported here, gram quantities of pure chiral phosphiranes can be easily obtained. We have found the synthetic approach based on the reaction of a metal phosphide and a diol ditosylate reported by Oshikawa and Yamashita to be very attractive.[10] Its simplicity and directness held promise for practical synthetic utility. After modification of the procedure by reversing the order of addition, this method worked well in the synthesis of 1-mesitylphosphirane **1** and 1-supermesitylphosphirane **2**.[2] If both displacement steps shown in Scheme 2 are

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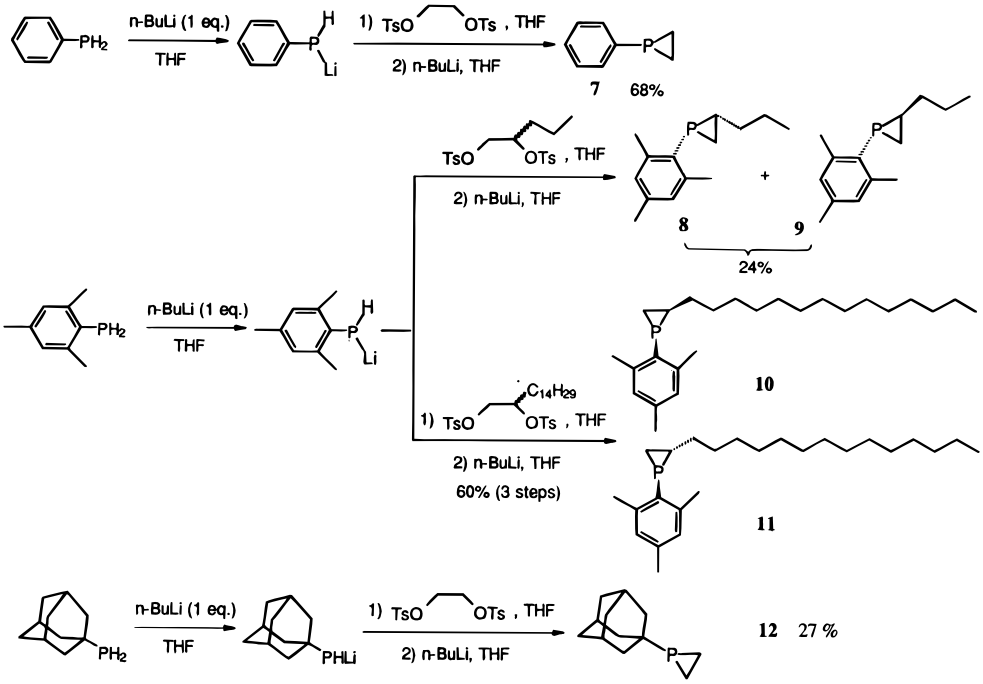
Scheme 3



S_N2 reactions, it is clear that one should be able to make phosphiranes stereoselectively, since the configurations of both chiral carbon centers of the diol ditosylate should be inverted.

The generality of this simple synthetic sequence has been demonstrated by the synthesis of several phosphiranes presented below. Its usefulness in the stereoselective synthesis of phosphiranes is clear from the synthesis of four stereoisomers (**3**−**6**) of 2,3-dimethyl-1-mesitylphosphirane, employed as a model system. The assignment of relative stereochemistry by NMR and the determination of the absolute stereochemistry of the phosphiranes by X-ray diffraction of their tungsten complexes are discussed below.

Results and Discussion

Synthesis of Phosphiranes by Reaction of Primary Phosphines and Diol Ditosylates (Scheme 3). We reported previously the synthesis of 1-mesitylphosphirane **1** and 1-supermesitylphosphirane **2** by our modification of the Oshikawa−Yamashita procedure.[2] A freshly prepared THF solution of monolithium phosphide is added dropwise to a solution of diol distosylate. After the initial displacement of tosylate is complete, a second equivalent of *n*-BuLi is added to metallate the remaining P−H bond and induce cyclization by a second, intramolecular displacement of tosylate. Each stage can be monitored by ^{31}P NMR, and if the reaction is found to be incomplete, a slight excess of *n*-BuLi is added.

A variety of phosphiranes is made available via this procedure, limited only by the availability of the corresponding primary phosphines and by the requirement that the structures of the primary phosphine and the 1,2-ditosylate are such that substitution occurs rather than elimination.

The first synthesis reported of 1-phenylphosphirane (**7**) was by reaction of monosodium phenylphosphide with 1,2-dichloroethane in liquid ammonia,[11] and a later report was of a similar procedure employing ethylene glycol bismesylate.[12] A recent synthesis of 1-phenylphosphirane (**7**) from dilithium phenylphosphide and 1,2-dichloroethane in THF was reported to give a 21% yield.[13]

With the present procedure, 1-phenylphosphirane (**7**) was synthesized in 68% yield and easily purified by vacuum distillation. Low temperatures are not required, and the procedure should be useful on a larger scale.

A mixture of *syn*-1-mesityl-2-propylphosphirane (**8**) and *anti*-1-mesityl-2-propylphosphirane (**9**) was synthesized in an isolated yield of 24%. Pure *anti* isomer **9** was separated by preparative GC, and the less stable *syn* isomer **8** was isolated as a 70:30 mixture with **9**. The *syn*-isomer **8** was recognized from the large coupling of the phosphorus to the two *anti* ring protons ($J_{P-H} = 17.5$ Hz).

Stereochemistry and Coupling Constants. The large inversion barrier for the phosphorus (calculated to be 30−80 kcal/mol)[14] leads to the persistence of phosphirane diastereomers in which substituents on the ring carbons are either *syn* or *anti* to the substituent at phosphorus. Previous studies indicated that for substituents on the ring carbon atoms, such as hydrogen, alkyl, or silyl groups, a large coupling constant (J_{P-H}, J_{P-C}, or J_{P-Si}) will be observed if the substituent is *syn* to the lone pair at phosphorus (*anti* to the P-substituent). If the substituent is *anti* to the lone pair, the coupling constant will be very small or not observable.[15] Examples are shown in Scheme 4.

These generalizations facilitated the characterization of the various diastereomers synthesized in this inves-

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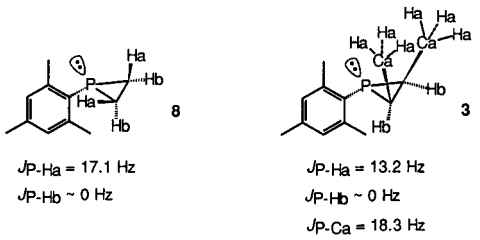
Scheme 4



tigation. The assignments were confirmed by X-ray crystal structure analysis of the corresponding metal complexes.

Synthesis of Other Phosphiranes. Phosphiranes with long chain alkyl groups as substituents on carbon can be synthesized as well. A mixture of 1-mesityl-2-*n*-tetradecylphosphiranes (*syn* **10** and *anti* **11**) was formed in 60% combined yield from the reaction of 1,2-hexadecanediol ditosylate and mesityl phosphide. The *syn*-to-*anti* ratio was 0.9:1 on the basis of the integration of the ^{31}P NMR spectrum of the product mixture. Assignment of the stereochemistry of these two isomers was based on the proton-coupled ^{31}P NMR spectra. The chemical shift of the *syn* isomer **10**, −209.95 ppm, can be recognized from the triplet due to coupling to the two *anti* ring-hydrogens with J_{P-H} = 17.7 Hz. The ^{31}P signal for the *anti* isomer **11** at −220.45 ppm appears as a broad singlet.

An alkylphosphirane, 1-admantylphosphirane (**12**), was synthesized in 27% isolated yield by the same procedure.

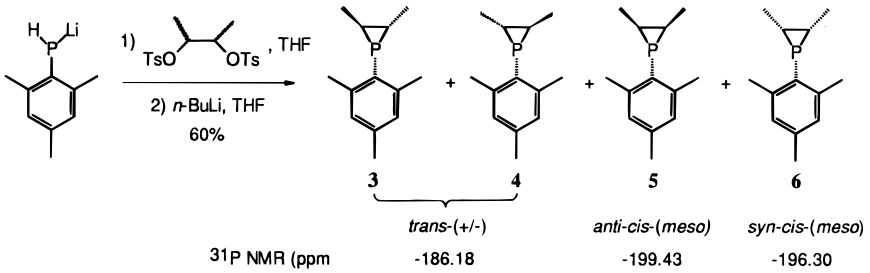
Evidence for Ring Formation by Two S_N2 Processes and the Stereoselective Synthesis of Phosphiranes. Reaction of a mixture of (±)- and *meso*-2,3-butanediol ditosylates with mesitylphosphine yielded all three diastereomers (four optical isomers **3**−**6**: two *meso* compounds **5** and **6** and a pair of enantiomers **3** and **4**) of 1-mesityl-2,3-dimethylphosphirane (Scheme 5), each with a distinct ^{31}P NMR chemical shift. The product mixture (ratio (**3** + **4**):**5**:**6** *ca.* 1:1:1) was isolated in 60% combined yield. The stereochemistries of these isomers were assigned from their proton-coupled ^{31}P NMR spectra. The observation of distinct ^{31}P chemical shifts for the three diastereomers facilitated the examination of the stereochemistry of phosphirane formation.

When a racemic mixture of (±)-2,3-butanediol ditosylate was reacted with phenylphosphide, racemic *trans*-(±)-2,3-dimethyl-1-phenylphosphirane (**13**, **14**) (Scheme 6) was obtained in 90% yield. Since none of the *cis* isomer was detected by ^{31}P NMR even *before* purification, the stereoselectivity appears to be >98%. The stereochemistry of this compound was assigned on the basis of characteristic P−H and P−C coupling patterns in the NMR spectra. The methyl group *anti* to the phenyl group has larger coupling constants with phosphorus (J_{P-H} = 13.5 Hz, J_{P-C} = 17.5 Hz); the *syn* methyl group has small coupling constants with phosphorus (J_{P-H} = 7.4 Hz, J_{P-C} = 0 Hz).

When mesityl phosphide was reacted with (±)-2,3-butanediol ditosylate, a 52% yield of a racemic mixture of *trans*-(±)-1-mesityl-2,3-dimethylphosphiranes **3** and **4** (**Scheme 6**), with no detectable *cis* isomer, was isolated. The stereochemistry was assigned by NMR. The *syn* ring methyl is coupled weakly to phosphorus in the ^{1}H (J_{P-H} = 5.0 Hz) and ^{13}C (J_{P-C} = 0 Hz) spectra, and the *anti* ring methyl is coupled strongly to phosphorus (J_{P-H} = 13.8 Hz and J_{P-C} = 17.7 Hz). Since no *cis* isomer was detected by ^{31}P NMR in the reaction mixture before purification, the stereoselectivity of the displacements forming the P−C bonds appears to be >98%.

With *meso*-2,3-butanediol ditosylate as the starting material, the product of reaction with the mesityl phosphide was revealed by ^{31}P NMR spectroscopy to be a *ca.* 1:1 mixture of two *cis* epimers **5** and **6** (Scheme 7). Before

Scheme 5



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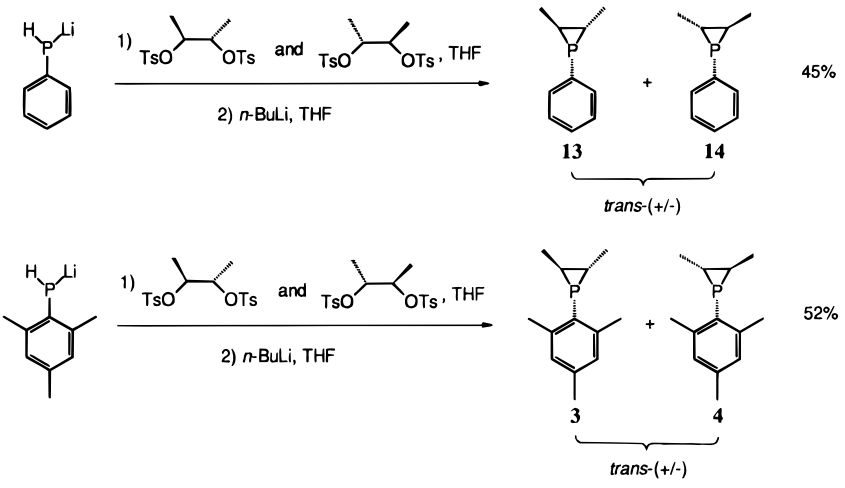
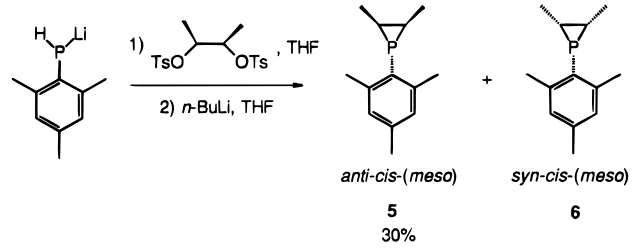
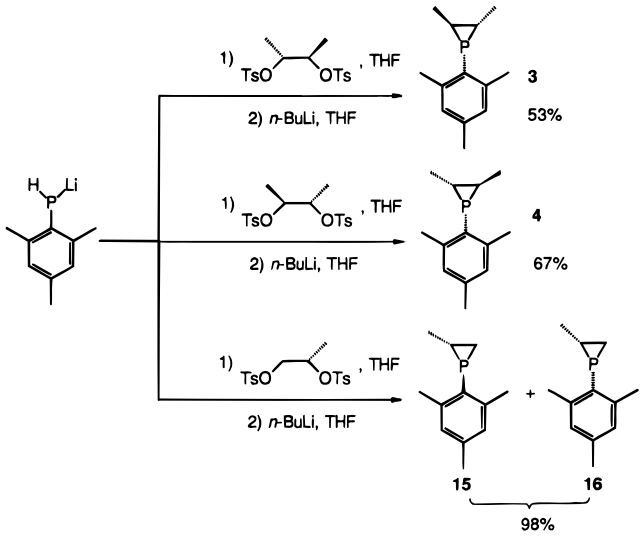


Scheme 7



Scheme 8



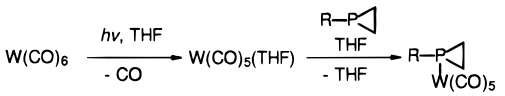
purification, 2.5% of a racemic mixture of *trans* isomers **3** and **4** was detected, giving a stereoselectivity of 97%. The structure of **5** was first assigned by NMR and later confirmed by X-ray crystal structure analysis of a tungsten complex (**22**). The two equivalent ring methyls of **5** are *anti* to the mesityl group, based on the methyl P−H and P−C coupling constants (J_{P-H} = 13.2 Hz and J_{P-C} = 18.3 Hz). The ^{1}H-coupled ^{31}P NMR signal for **5** was split into a clear 1:6:15:20:15:6:1 heptet by coupling with the six ring methyl protons.

Having obtained *trans*-2,3-dimethyl-1-arylphosphiranes from racemic (±)-2,3-butanediol ditosylate and *cis*-2,3-dimethyl-1-arylphosphiranes from *meso*-2,3-butanediol ditosylate with a stereoselectivity of at least 97%, it was clear that phosphirane formation is highly stereoselective, proceding either via two S_N2 inversion steps, as was established from the absolute configurations of the optically active phosphiranes discussed below, or by two retention steps.

Synthesis of Optically Active Phosphiranes. The demonstration that phosphirane formation from phosphines and 2,3-butanediol ditosylates was highly stereoselective suggested that optically active phosphiranes could be synthesized by this procedure (Scheme 8). When optically pure (2*R*,3*R*)-(+)-2,3-butanediol ditosylate was used, (2*S*,3*S*)-(+)-2,3-dimethyl-1-mesitylphosphirane (**3**) of high optical purity was obtained in 53% yield.[16] The relative stereochemistry was assigned by NMR and specific rotation $[\alpha]_D = +24.55°$; the absolute configuration was confirmed by X-ray crystal structure analysis of a tungsten complex (**23**) described below.

The same experiment was carried out with commercially available (2*S*,3*S*)-(−)-2,3-butanediol ditosylate as the starting material, yielding (2*R*,3*R*)-(−)-2,3-dimethyl-1-mesitylphosphirane (**4**) of high optical purity in 67% yield.[16] Again the relative stereochemistry was assigned by NMR and specific rotation $[\alpha]_D = -27.32°$, and the absolute structure was determined later by X-ray crystal structure analysis of a tungsten complex (**24**). These structures confirmed that both carbon centers are inverted during the reaction sequence of two S_N2 reaction processes.

Scheme 9



Reaction of (2*S*)-(−)-1,2-propanediol ditosylate with mesityl phosphide led to the formation of a pair of diastereomers *anti*-(2*R*)- (**15**) (^{31}P NMR δ −216.86 ppm) and *syn*-(2*R*)-1-mesityl-2-methylphosphirane (**16**) (^{31}P NMR δ −208.38 ppm) in 98% combined yield. In this case both 1-P and 2-C are chiral centers. The *anti* to *syn* ratio is 1.3:1 on the basis of the integration of ^{31}P NMR signals. The phosphorus of the *syn* isomer **16** is coupled to two *anti* ring protons, giving rise to a triplet ^{31}P NMR signal with J_{P-H} = 16.0 Hz, and the phosphorus of the *anti* isomer **19a** is coupled to the single *anti* ring proton and to the three methyl protons, giving rise to a quintet ^{31}P NMR signal with J_{P-H} = 14.8 Hz. These isomers could be separated only on a capillary GC column and gave rise to identical mass spectra. While NMR and high-resolution mass spectrometry were performed on mixtures, the peaks in the NMR spectra could be assigned readily on the basis of their coupling constants and intensities.

Synthesis of Phosphirane−Tungsten Pentacarbonyl Complexes. After having synthesized several new phosphiranes, preparation of their metal complexes was undertaken. The complexing ability of phosphiranes should be very high, because their cone angles are very small. Marinetti, Ricard, and Mathey have prepared several W and Mo complexes of phosphiranes via the "phospha-Wittig" reaction and also Rh complexes by complexation of the phosphiranes.[4,5] New phosphirane complexes should be useful as chiral catalysts[5] and as precursors of terminal phosphinidene complexes.[17] X-ray crystal structure analysis of metal complexes facilitated the study of the structure of difficult to crystalize phosphiranes and the determination of the absolute stereochemistry of chiral phosphiranes.

The starting material in these complexation reactions was $W(CO)_6$. Irradiation of $W(CO)_6$ in THF with a medium-pressure mercury lamp afforded a tungsten pentacarbonyl−THF complex.[18] The weakly bound THF ligand can be replaced by many phosphiranes (Scheme 9).

The five tungsten pentacarbonyl−phosphirane complexes shown in Scheme 10, **17**−**21**, have been synthesized in yields of 47−74%. All the new complexes were characterized by NMR and elemental analyses. The phosphirane−tungsten complexes are much more stable than the free phosphiranes and can be handled in air. Tungsten pentacarbonyl complexes of phosphiranes without substituents on the ring carbons were obtained as

(16) While the optical purity was not directly measured, the high degree of stereospecificity (>97%) indicated by the absence of *cis* isomers **5** and **6** implies an optical purity >97%.

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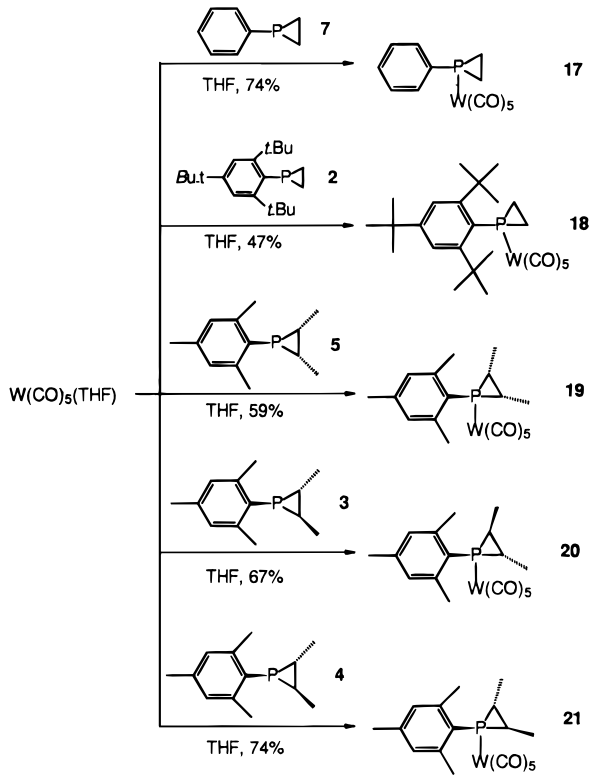
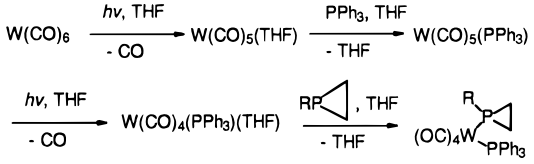
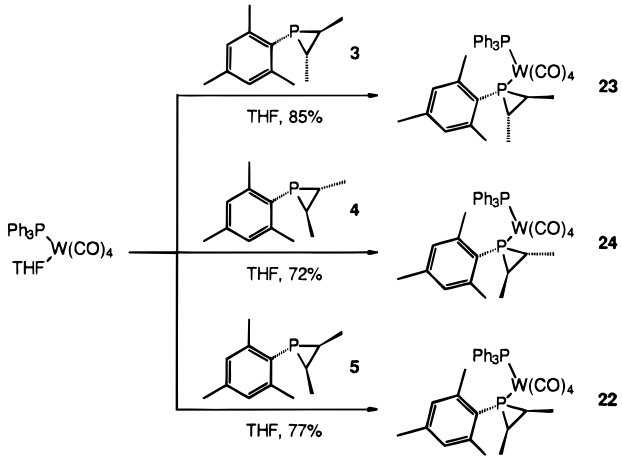
Scheme 10



Scheme 11



Scheme 12



crystals. The tungsten pentacarbonyl complexes of phosphiranes with methyls on the ring carbons were either oils or powders from which single crystals could not be obtained.

(2*S*,3*S*)-(+)-MesP(CHMe)$_2$W(CO)$_5$ (**20**) and (2*R*,3*R*)-(−)-MesP(CHMe)$_2$W(CO)$_5$ (**21**) have identical NMR spectra. Nonequivalent *o*-methyl protons are observed in the ^{1}H spectra, which suggests that the mesityl group cannot rotate freely about the bond between the *ipso* carbon and the phosphorus. In consequence, two different *m*-protons were observed at 6.54 and 6.58 ppm, respectively, and nonequivalent *o*-Ar carbons (141.4, 141.5 ppm) and *m*-Ar carbons (129.0, 129.8 ppm) were observed in the ^{13}C NMR spectrum. An interesting observation was that all the *cis* carbonyls are not equivalent by ^{13}C NMR and appear at 195.6, 196.4, and 197.3 ppm respectively.

Synthesis of Tungsten Phosphirane Triphenylphosphine Tetracarbonyl Complexes. One goal for the synthesis of tungsten−phosphirane complexes was to determine the absolute stereochemistry of the chiral (or pure *meso*) phosphiranes by X-ray diffraction analysis. Having been unable to obtain crystals of the chiral phosphirane−tungsten pentacarbonyl complexes, we decided to replace one CO ligand with triphenylphosphine. It was hoped that the bulky triphenylphosphine ligand would help to produce crystals of X-ray quality. The procedure was similar to that used for the pentacarbonyl complexes. W(CO)$_5$PPh$_3$ was prepared from W(CO)$_6$ in high yield (Scheme 11)[19] and was used as the starting material in the following syntheses.

W(CO)$_4$(PPh$_3$)[(2*S*,3*R*)-*meso*-MesP(CHMe)$_2$] (**22**) was synthesized in 77% yield (Scheme 12), and yellow crystals were obtained. That triphenylphosphine is *cis* to the phosphirane ligand is clear from the phosphorus−phosphorus coupling constant in the ^{31}P NMR spectrum, $J_{P-P} = 24.4$ Hz. If the two phosphine ligands were *trans* to each other, the J_{P-P} should be in the range of 40−70 Hz.[20]

W(CO)$_4$(PPh$_3$)[(2*S*,3*S*)-(+)-MesP(CHMe)$_2$] (**23**) was synthesized in 85% yield as pale yellow crystals. J_{P-P} is 27.4 Hz, suggesting that triphenylphosphine is once again *cis* to the phosphirane ligand. By using the same procedure W(CO)$_4$(PPh$_3$)[(2*R*,3*R*)-(−)-MesP(CHMe)$_2$] (**24**) was synthesized in 72% yield as pale yellow crystals. The NMR spectra of this compound are identical to those of compound **23**.

Crystal Structure Analysis of the Tungsten Phosphirane Triphenylphosphine Tetracarbonyl Complexes. The three stereoisomeric complexes **22**, **23**, and **24** were structurally characterized by X-ray crystallography.

For the complex W(CO)$_4$(PPh$_3$)[(2*S*,3*R*)-*meso*-MesP(CHMe)$_2$ (**22**), the ORTEP drawing (Figure 1, supporting information) clearly reveals the *S* and *R* ring carbon centers. The ORTEP drawing (Figure 2, supporting information) of W(CO)$_4$(PPh$_3$)[(2*S*,3*S*)-(+)-MesP(CHMe)$_2$] (**23**) shows both *S* carbon centers in the phosphirane ring clearly. The two ortho methyls in the mesityl group are inequivalent, and the phenyl ring of mesityl is distorted. These features are consistant with the observed solution NMR spectra. The ORTEP drawing (Figure 3, supporting information) of W(CO)$_4$(PPh$_3$)[(2*R*,3*R*)-(−)-MesP(CHMe)$_2$] (**24**) shows the two R ring carbon centers in the phosphirane. The two ortho methyls on the mesityl group are not equivalent, and the phenyl ring of the mesityl is distorted.

NMR Chemical Shifts of Phosphiranes. The ^{31}P NMR chemical shifts of phosphiranes are at very high field, typically in the range of −50 to −350 ppm. This parallels the high-field chemical shifts observed in ^{15}N NMR spectra of aziridines and ^{29}Si NMR spectra of siliranes. The effects of substituents on the ^{31}P chemical shifts of phosphiranes have been explained in both

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Table 1. ^{31}P Chemical Shifts of Phosphiranes

phosphirane	δ (ppm)
phenylphosphirane (**7**)	−237.00
trans-(±)-2,3-dimethyl-1-phenyl-phosphirane (**13**, **14**)	−180.3
1-mesitylphosphirane (**1**)	−240.8
1-mesityl-2-methylphosphirane	−216.86 **15** (*anti*)
15 (*anti*), **16** (*syn*)	−208.38 **16** (*syn*)
1-mesityl-2-propylphosphirane	−219.80 **9** (*anti*)
8 (*syn*), **9** (*anti*)	−209.85 **8** (*syn*)
1-mesityl-2-*n*-tetradecylphosphirane	−220.45 **11** (*anti*)
10 (*syn*), **11** (*anti*)	−209.86 **10** (*syn*)
2,3-dimethyl-1-mesitylphosphirane	−199.43 **5** (*anti*,*cis*)
3, **4** (*trans*), **5** (*anti*,*cis*), **6** (*syn*,*cis*)	−196.30 **6** (*syn*,*cis*)
	−186.18 **3**, **4** (*trans*)

electronic and steric terms.[21] We found that methyl substituents on the carbons of the phosphirane ring lead to a lower field ^{31}P chemical shift. Selected data are shown in Table 1. It should be noted that the chemical shift for the *anti* diastereomer is in each case at higher field than the signal for the *syn* stereoisomer. This observation could be useful in the assignment of stereochemistry.

The ^{13}C resonances of the ring carbons of phosphiranes are also at high field: δ is 0.7 ppm for the parent phosphirane (C_2H_4PH)[4] and 1.2 ppm for adamantylphosphirane **12**. This phenomenon has been observed for other three-membered rings as well.

A large value of the phosphorus−carbon coupling constant (J_{P-C}) is characteristic of phosphiranes. For compounds studied in this laboratory, their range is 30−50 Hz. Coupling constants as large as 82.1 Hz have been reported by others.[18]

Mass Spectra of Phosphiranes. Mass spectra were recorded for all phosphiranes synthesized, and M^+ was generally an ion of significant intensity. Fragment ions corresponding in mass to phosphinidene cations are frequently the base peaks. Selected MS data are given in Table 2.

This fragmantation suggests that phosphiranes are prone to thermal decomposition that extrudes phosphinidenes. This aspect of the work will be reported as a series of pyrolysis experiments and kinetic studies.[22]

Conclusion

In summary, an efficient and general method for the synthesis of phosphiranes was developed and employed to synthesize a series of new compounds. The stereoselectivity of this method was established, and it allows chiral phosphiranes to be conveniently synthesized for the first time. Phosphirane diastereomers can be easily distinguished on the basis of their J_{P-H} and J_{P-C} NMR coupling constants. Phosphiranes can be easily transformed into their tungsten carbonyl complexes. The X-ray crystal structure analysis of the phosphirane−triphenylphosphine−tungsten tetracarbonyl complexes established the absolute stereochemistry of the pure chiral and *meso* phosphiranes unambiguously. The displacement steps in the phosphirane synthesis are all inversions.

Experimental Section

General Methods. Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmosphere glovebox equipped with an He-493 dry-train purifier or by using standard Schlenk or vacuum line techniques. ^{1}H (300 MHz), ^{13}C (75.4 MHz), and ^{31}P (121.4 MHz unless specified as 202.3 MHz) NMR spectra employed C_6D_6 solvent unless otherwise stated. Elemental analyses were performed by Galbraith Analytical Laboratories. Preparative gas chromatography was performed on a chromatograph constructed in this laboratory equipped with dual rhenium−tunsten filaments (Gow-Mac code 13-002). Reaction products were separated on a 5 ft × 0.25 in. aluminum column packed with 5% SE-30 on Chromosorb W 60/80. Typical injection temperatures were between 200 and 280 °C, and typical column temperatures were in the range 100−200 °C. Flash column chromatography was based on a published procedure, with nitrogen as the pressurizing agent.[23] Bottles with screw caps were used to collect the fractions, and the collecting area was blanketed by nitrogen. Yields given are based on the weights of pure products isolated.

Materials. Unless otherwise indicated, all chemicals were of reagent grade quality and used as supplied. Ethyl ether and tetrahydrofuran were distilled from a blue solution of the benzophenone sodium ketyl under nitrogen and used immediately. Pentane, hexane, methylene chloride, and methylcyclohexane were distilled from calcium hydride. Pyridine was distilled from sodium.

Mesitylphosphine. This compound was synthesized by the method of Oshikawa and Yamashita.[24]

(2,4,6-Tri-*tert*-butylphenyl)phosphine. This compound was prepared by the method of Cowley et al.[25]

Admantylphosphine. This compound was synthesized by the procedure of Stetter and Last:[26] ^{31}P NMR δ −82.42 (J_{P-H} = 188.9 Hz); ^{1}H NMR δ 1.4−1.8 (m, 15 H), 2.68 (d, 2 H, J_{P-H} = 188.3 Hz).

The following 2,3-butanediol ditosylates were synthesized from the corresponding diols by the procedure of Corey and Mitra:[27] **(±, *meso*)-2,3-butanediol ditosylate; (±)-2,3-butanediol ditosylate; *meso*-2,3-butanediol ditosylate; (2*S*,3*S*)-(−)-2,3-butanediol ditosylate;[28] (2*R*,3*R*)-(+)-2,3-butanediol ditosylate.[28]**

(*S*)-(−)-Propanediol Ditosylate. This compound was made in 87% yield from (*S*)-(+)-propanediol by the procedure of Fryzuk and Bosnich:[29] ^{1}H NMR δ 0.88 (d, 3 H, J_{H-H} = 6.5 Hz), 1.92 (s, 6 H), 3.73 (m, 2 H), 4.53 (dt, 1 H, J_{H-H} = 6.5 Hz), 6.80 (d, 4 H, J_{H-H} = 7.8 Hz), 7.64 (d, 2 H, J_{H-H} = 8.3 Hz), 7.69 (d, 2 H, J_{H-H} = 8.3 Hz); ^{13}C{^{1}H} NMR δ 16.9, 21.2, 70.7, 75.6, 128.1, 129.9, 130.0, 133.2, 134.4, 144.7, 144.9.

1,2-Pentanediol ditosylate was synthesized in 80% yield by the method of Fryzuk and Bosnich from 1,2-pentanediol:[30] ^{1}H NMR δ 0.56 (t, 3 H, J_{H-H} = 7.3 Hz), 0.85−1.48 (m, 4 H), 1.92 (s, 6 H, 3.85−4.00 (m, 2 H), 4.57 (sextet, 1 H, J_{H-H} = 4.9 Hz), 6.81 (d, 4 H, J_{H-H} = 7.8 Hz), 7.68 (d, 2 H, J_{H-H} = 8.3 Hz), 7.74 (d, 2 H, J_{H-H} = 8.3 Hz); ^{13}C{^{1}H} NMR δ 13.5, 18.1, 21.2, 33.2, 69.9, 78.9, 128.1, 128.2, 129.9, 130.0, 133.3, 134.5, 144.7, 144.9.

1,2-Hexadecanediol ditosylate was synthesized in 85% yield by the same method from 1,2-hexadecanediol:[29] ^{1}H NMR δ 0.90−1.42 (m, 29 H), 1.88 (s, 6 H), 3.93 (m, 2 H), 4.57 (bs, 1 H), 6.76 (d, 4 H, J_{H-H} = 5.6 Hz), 7.67 (d, 2 H, J_{H-H} = 7.7 Hz), 7.73 (d, 2 H, J_{H-H} = 7.6 Hz).

1-Phenylphosphirane (7). A solution of phenylphosphine (3.0 g, 27.2 mmol) in 100 mL of THF was placed in a 250 mL-flask equipped with a magnetic stirring bar and a rubber septum and cooled to 0 °C with ice water. A hexane solution of *n*-BuLi (18 mL, 1.6 M, 28.8 mmol) was added by syringe over 15 min. The mixture was allowed to warm to room temperature and was stirred for 30 min, producing a solution of fresh monolithium phosphide. The solution of PhPHLi was added dropwise over a 1 h period to a stirred solution of

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Table 2. Selected MS Data for Phosphiranes

phosphirane and ionization mode	M^+ mass and relative intensity	"$R-P^+$" mass and relative intensity
phenylphosphirane (**7**) (EI)	136 (66)	108 (100)
trans-(±)-2,3-dimethyl-1-phenylphosphirane (**13**, **14**) (EI)	164 (57)	108 (100)
1-mesitylphosphirane (**1**) (EI)	178 (38)	150 (100)
1-mesityl-2-methylphosphirane **15** (*anti*), **16** (*syn*) (EI)	192 (48)	150 (100)
1-mesityl-2-propylphosphirane **8** (*syn*), **9** (*anti*) (EI)	220 (21)	150 (100)
2,3-dimethyl-1-mesitylphosphirane **3**, **4** (*trans*), **5** (*anti*,*cis*), **6** (*syn*,*cis*) (EI)	206 (37)	150 (100)
1-adamantylphosphirane (**12**) (EI)	194 (7)	166 (0.8)
1-supermesitylphosphirane (**2**) (CI)	304 (1.2)	276 (16)

ethylene glycol ditosylate (11.9 g, 32 mmol) in 150 mL of THF at 0 °C in a 500 mL flask. When addition was complete, the mixture was allowed to warm room temperature. After a further 2 h the reaction mixture was again cooled to 0 °C, and a hexane solution of *n*-BuLi (20 mL, 1.6 M, 32 mmol) was added by syringe over 15 min. After addition was complete, the reaction mixture was warmed to room temperature. After a further 3 h, ^{31}P NMR indicated that the reaction was complete. THF was removed in vacuo, and the residue was mixed with 100 mL of pentane and filtered to remove lithium tosylate. After evaporation of pentane from the filtrate, the residue was distilled in vacuo (50−60 °C/1 Torr), yielding 1-phenylphosphirane (**7**) (2.5 g, 68%) as a colorless liquid: ^{31}P NMR (202.3 MHz) δ −237.0 (lit. δ −234,[7] −236[13]); ^{1}H NMR δ 0.87−0.95 (m, 2 H), 1.00−1.06 (m, 2 H), 6.8−7.0 (m, 3 H), 7.15−7.25 (m, 2 H) (lit.[7] δ 0.3−1.0 (4 H)), 6.5−7.2 (5 H); ^{13}C-{^{1}H} δ 10.0 (d, J_{P-C} = 39.8 Hz), 128.4, 128.5, 128.7 (bs), 131.9 (d, J_{P-C} = 19.4 Hz); exact mass determination for C_7H_9P (M^+), calcd 136.0442, found 136.0448.

1-Mesityl-2-propylphosphirane (*syn* 8, *anti* 9). The same procedure was followed with a solution of mesitylphosphine (2.0 g, 13.2 mmol) in 150 mL of THF, a hexane solution of *n*-butyllithium (5.5 mL, 2.5 M, 13.8 mmol), and a solution of 1,2-pentanediol ditosylate (5.8 g, 14.0 mmol) in 100 mL of THF. After 2 h, the reaction mixture was again cooled to −5 to 0 °C, and another equivalent of *n*-BuLi (6 mL, 2.5 M, 15.0 mmol) was added. After a further 10 h at room temperature, a pair of phosphirane diastereomers, **8** and **9** (1:1 ratio), were the only products observable by ^{31}P NMR, which indicated that the reaction was complete. Solvent was removed in vacuo, and the remaining material was mixed with 150 mL of pentane and filtered to remove lithium tosylate. After evaporation of the hexane from the filtrate, the residue was chromatographed on silica gel with pentane eluent, yielding a mixture of 1-mesityl-2-propylphosphiranes **8** and **9** (0.7 g, 24%) as a colorless oil. The low yield was due to oxidation during workup. The two diastereomers were separated by preparative gas chromatography on a 5 × $^1/_4$ in. o.d. aluminum column with a packing consisting of 5% SE-30 on 60/80 mesh Chromosorb W operated at 150 °C. The *anti* isomer **9** was obtained in pure form, but the *syn* isomer **8** was collected as a 70:30 mixture with the *anti* isomer **9**. *syn*-1-Mesityl-2-propylphosphirane (**8**): ^{31}P δ −209.85 (t, J_{P-H} = 17.5 Hz); ^{1}H NMR δ 0.57 (m, 1 H), 0.72 (t, 3 H, J_{H-H} = 7.4 Hz), 0.82 (m, 1 H), 1.24−1.60 (m, 4 H), 1.79 (m, 1 H), 2.06 (s, 3 H), 2.45 (bs, 6H), 6.67 (s, 2 H); ^{13}C{^{1}H} NMR δ 14.0, 15.5 (d, J_{P-C} = 37.4 Hz), 21.0, 22.7 (bd, J_{P-C} = 15.0 Hz), 24.4, 24.6 (d, J_{P-C} = 44.3 Hz), 33.3, 129.4 (bs), 132.4 (d, J_{P-C} = 44.3 Hz), 137.1, 143.0 (bs); exact mass determination for $C_{14}H_{21}P$ (M^+), calcd 220.1381, found 220.1383. ***anti*-1-Mesityl-2-propylphosphirane (9):** ^{31}P NMR δ −219.80 (poorly resolved multiplet due to coupling with several protons of propyl group as well as with single *anti* ring proton); ^{1}H NMR δ 0.87 (t, 3 H, J_{H-H} = 7.0 Hz), 1.05 (m, 1 H), 1.20 (m, 1 H), 1.30−1.60 (m, 5 H), 2.08 (s, 3 H), 2.46 (s, 6 H), 6.67 (s, 2 H); ^{13}C{^{1}H} NMR δ 14.3, 20.9 (d, J_{P-C} = 39.0 Hz), 21.0, 22.5 (d, J_{P-C} = 8.9 Hz), 23.4 (d, J_{P-C} = 6.1 Hz), 29.1 (d, J_{P-C} = 37.9 Hz), 36.8 (d, J_{P-C} = 16.3), 128.8, 136.2 (d, J_{P-C} = 40.6 Hz), 137.1, 142.2 (d, J_{P-C} = 9.6 Hz); exact mass determination for $C_{14}H_{21}P$ (M^+), calcd 220.1381, found 220.1383.

1-Mesityl-2-*n*-tetradecylphosphirane (10, 11). The same procedure was followed with a solution of mesitylphosphine (1.5 g, 9.9 mmol) in 120 mL of THF, a hexane solution of *n*-butyllithium (6.3 mL, 1.6 M, 10.1 mmol), and a solution of hexadecanediol ditosylate (6.3 g, 11.1 mmol) in 100 mL of THF. After 1.5 h at room temperature, monitoring of the reaction mixture by ^{31}P NMR indicated the formation of $MesPHCH_2$-$CH(OTs)(CH_2)_{13}CH_3$ and $CH_2(OTs)CH(MesPH)(CH_2)_{13}CH_3$: ^{31}P NMR (THF) δ −98.7 to −101.6 (four peaks). The reaction mixture was again cooled to −5 to 0 °C, and another equivalent of *n*-BuLi (8 mL, 1.6 M, 12.8 mmol) was added dropwise over 15 min. After addition was complete, the reaction mixture was allowed to warm to room temperature. After a further 10 h, a pair of phosphirane diastereomers **10** and **11** were the only products observable by ^{31}P NMR, which indicated that the reaction was complete. Solvent was removed in vacuo, and the remaining material was mixed with 400 mL of cyclohexane/pentane (1:2) and filtered to remove lithium tosylate. After evaporation of the hexane from the filtrate, the residue was chromatographed on silica gel with pentane/ether (9:1) eluent (R_f = 0.51), yielding 1-mesityl-2-*n*-tetradecylphosphirane (**10** + **11**) (2.2 g, 60%) as a white wax. Both **10** and **11** decomposed in the GC at *ca.* 200−210 °C, forming hexadecene as the major product, but a mass spectrum of the mixture of stereoisomers was obtained *via* a solid sample probe: ^{31}P NMR ($CDCl_3$) δ −209.86 (*syn* **10**, J_{P-H} = 17.7 Hz), −220.45 (*anti* **11**); ^{1}H NMR δ 0.89 (t, 3 H, J_{H-H} = 6.6 Hz), 1.26 (s, 26 H), 2.22 (s, 3 H), 2.49 (s, 6 H), 6.78 (s, 1 H); exact mass determination for $C_{25}H_{43}P$ (M^+), calcd 374.3102, found 374.3071.

1-Admantylphosphirane (12). The same procedure was employed with admantylphosphine (1.0 g, 5.95 mmol) and ethylene glycol ditosylate (2.3 g, 6.2 mmol). When reaction was complete, THF was removed in vacuo, and the residue was mixed with 100 mL of pentane and filtered to remove lithium tosylate. After evaporation of pentane from the filtrate, the residue was transfered into a drybox and was chromatographed on silica gel with pentane as eluent, yielding 1-adamantylphosphirane (0.30 g, 27%) as a colorless oil. **12** is unstable toward air and silica gel, and the low yield of isolated product was due to decomposition and oxidation during isolation. ^{31}P NMR analysis of the crude reaction mixture indicated a high yield. After purification **12** was stable for months in the freezer: ^{31}P NMR δ −208.16; ^{1}H NMR δ 0.52 (dm, 2 H, J_{P-H} = 16.5 Hz), 0.82 (m, 2 H), 1.14−1.73 (m, 15 H); ^{13}C{^{1}H} NMR δ 1.2 (d, J_{P-C} = 42.9 Hz), 29.0 (d, J_{P-C} = 7.8 Hz), 37.0, 40.7 (d, J_{P-C} = 12.7 Hz); exact mass determination for $C_{12}H_{19}P$ (M^+) calcd 194.1224, found 194.1222.

(±,*meso*)-2,3-Dimethyl-1-mesitylphosphiranes (a mixture of 3, 4, 5, and 6). A similar procedure was employed with a solution of mesitylphosphine (2.0 g, 13.2 mmol) in 120 mL of THF and a hexane solution of *n*-BuLi (8.3 mL, 1.6 M, 13.3 mmol). Formation of monolithium mesityl phosphide was indicated by ^{31}P NMR (THF) δ −155.3 ppm (d, J_{P-H} = 168 Hz). The solution of monolithium mesityl phosphide was added dropwise over 30 min to a stirred solution of 2,3-butanediol ditosylate (5.6 g, 14.0 mmol) in 200 mL of THF cooled to 0 °C in a 500 mL flask. After 3 h at room temperature, the reaction mixture was again cooled to 0 °C, and another equivalent of *n*-BuLi (9 mL, 1.6 M, 14.4 mmol) was added dropwise over 15 min. After 5−10 h at room temperature, monitoring the appearance of the phosphirane product by ^{31}P NMR indicated that the reaction was complete (product ratio **3**,**4**:**5**:**6** *ca.* 1:1:1). Solvent was removed in vacuo, and the remaining material was mixed with 200 mL of pentane and filtered to remove lithium tosylate. After evaporation of the pentane from the filtrate, the residue was chromatograped as described above. **6** largely decomposed during workup. A mixture of stereoisomeric 2,3-dimethyl-1-mesitylphosphiranes **3**−**6** was obtained in 60% yield. These isomers could not be separated, and the mixture was subjected to NMR spectros-

copy: ^{31}P NMR δ −196.30 (t, J_{H-P} = 19 Hz, *syn-cis*, **6** minor), −199.43 (heptet, J_{P-H} = 13.0 Hz), *anti-cis* **5**), −186.18 (bs, *trans*-(±) **3**, **4**); ^{1}H NMR δ 0.90−1.50 (m, 1 H), 1.62 (m, 1 H), 0.99−1.30 (m, 6 H), 2.08 (s, 3 H), 2.44 (s, 6 H), 6.68 (s, 2 H); ^{13}C{^{1}H} NMR δ 12.4 (d, J_{P-C} = 18.9 Hz), 15.2, 18.3 (d, J_{P-C} = 17.6 Hz), 20.6, 21.8 (d, J_{P-C} = 8.9 Hz), 28.5 − 29.4, 128.8, 129.4, 136.9, 142.2 (d, J_{P-C} = 9.4 Hz), 143.2 (d, J_{P-C} = 9.4 Hz).

***trans*-(±)-2,3-Dimethyl-1-phenylphosphirane (13, 14).** The same procedure was employed with a THF solution of phenylphosphine (3.0 g, 27.2 mmol), a hexane solution of *n*-BuLi (18 mL, 1.6 M, 28.8 mmol), and a solution of 2,3-butanediol ditosylate (racemic mixture, 13.0 g, 32.0 mmol) in 150 mL of THF. After 3 h at room temperature, the reaction mixture was treated at 0 °C with a hexane solution of *n*-BuLi (20 mL, 1.6 M, 32 mmol). After 10 h at room temperature, ^{31}P NMR indicated that the reaction was complete. THF was removed in vacuo, and the residue was mixed with 150 mL of pentane and filtered to remove lithium tosylate. After evaporation of pentane from the filtrate, the product was obtained upon vacuum distillation in 90% yield as a colorless liquid. Product of high purity was obtained by chromatography as described above (2.0 g, 45%). The product is readily oxidized, but if the compound is very pure or in solution, it can be stored in a freezer under N_2 for months. **13**, **14**: ^{31}P NMR δ −180.3; ^{1}H NMR δ 0.91 (dd, 3 H, J_{P-H} = 7.4 Hz, J_{H-H} = 7.4 Hz), 0.95−1.10 (m, 1 H), 1.18 (dd, 3 H, J_{P-H} = 13.5 Hz, J_{H-H} = 6.4 Hz), 1.41−1.50 (m, 1 H), 6.95−7.00 (m, 3 H), 7.24−7.30 (m, 2 H); ^{13}C{^{1}H} NMR δ 15.7, 18.9 (d, J_{P-C} = 17.5 Hz), 26.2 (d, J_{P-C} = 35.4 Hz), 27.3 (d, J_{P-C} = 41.2 Hz), 128.2 (d, J_{P-C} = 7.7 Hz), 128.7 − 129.3, 134.3 (d, J_{P-C} = 14.9 Hz), 137.3 (d, J_{P-C} = 42.2 Hz); exact mass determination for $C_{10}H_{13}P$ (M^+), calcd 164.0755, found 164.0756.

(±)-2,3-Dimethyl-1-mesitylphosphirane (racemic mixture of 3 and 4). The same procedure was followed with mesitylphosphine (**16**) (2.0 g, 13.2 mmol) and (±)-2,3-butanediol ditosylate (5.6 g, 14.0 mmol) as starting materials. When reaction was complete, THF was removed in vacuo, and the remaining material was mixed with 200 mL of pentane and filtered to remove lithium tosylate. After evaporation of the pentane from the filtrate, the residue was chromatographed on silica gel with pentane eluent (R_f = 0.35). Pure product (1.4 g, 52%) was obtained as a colorless oil: ^{31}P δ −186.20; ^{1}H NMR δ: 1.01 (dd, 3 H, J_{P-H} = 5.0 Hz, J_{H-H} = 6.2 Hz), 1.10−1.35 (m, 2 H), 1.27 (dd, 3 H, J_{P-H} = 13.8 Hz, J_{H-H} = 6.3 Hz), 2.08 (s, 3 H), 2.42 (bs, 6 H), 6.69 (s, 2 H); ^{13}C{^{1}H} δ 15.6, 18.7 (d, J_{P-C} = 17.7 Hz), 21.0, 22.5 (bd, J_{P-C} = 37.6 Hz), 29.1 (d, J_{P-C} = 34.3 Hz), 29.5 (d, J_{P-C} = 43.0 Hz), 129.3 (bs), 132.1 (d, J_{P-C} = 43.7 Hz), 136.9, 143.2; UV (cyclohexane) λ_{max} 284 nm (ϵ = 1.564 × 10^3), 275 nm (ϵ = 1.631 × 10^3), shoulder 246 nm (ϵ = 8.985 × 10^3); exact mass determination (EI) for $C_{13}H_{19}P$ (M^+), calcd 206.1244, found 206.1220. Anal. Calcd for $C_{13}H_{19}P$: C, 75.70; H, 9.28. Found: C, 74.77; H, 9.39.

***meso-anti-cis*-1-Mesityl-2,3-dimethylphosphirane (5).** The same procedure was followed with mesitylphosphine (**16**) (2.0 g, 13.2 mmol) and *meso*-2,3-butanediol ditosylate (5.6 g, 14.0 mmol). Chromatography on silica gel with pentane eluent (R_f = 0.38), yielded *meso-anti*-1-mesityl-2,3-dimethylphosphirane (**5**) (0.8 g, 30%) as a colorless oil. *meso-syn-cis*-1-Mesityl-2,3-dimethylphosphirane (**6**) was present in the crude mixture in a nearly 1:1 ratio with the *meso-anti-cis* isomer **5**, but **6** decomposed completely during workup, and phosphinidene oligomers were observed as decomposition products. **5**: ^{31}P{^{1}H} δ −199.56; ^{31}P NMR δ (heptet, J_{P-H} = 13.0 Hz); ^{1}H NMR δ 1.26 (dd, 6 H, J_{P-H} = 13.2 Hz, J_{H-H} = 5.5 Hz), 1.62 (m, 2 H), 2.08 (s, 3 H), 2.45 (s, 6 H), 6.67 (s, 2 H); ^{13}C{^{1}H} NMR δ 12.8 (d, J_{P-C} = 18.3 Hz), 20.1, 22.2 (d, J_{P-C} = 9.0 Hz), 29.3 (d, J_{P-C} = 36.3 Hz), 128.8, 136.3 (d, J_{P-C} = 38.6 Hz), 136.9, 142.2 (d, J_{P-C} = 9.2 Hz); exact mass determination for $C_{13}H_{19}P$ (M^+), calcd 206.1224, found 206.1229.

(2*S*,3*S*)-(+)-1-Mesityl-2,3-dimethylphosphirane (3). The same procedure was followed with mesitylphosphine (1.4 g, 9.2 mmol) and (2*R*,3*R*)-(+)-2,3-butanediol ditosylate (4.3 g, 10.8 mmol). Distillation under high vacum and column chromatography yielded (2*S*,3*S*)-(+)-1-mesityl-2,3-dimethylphosphirane (**3**) (1.0 g, 53%) as a colorless oil: NMR data are identical with those for the racemic mixture; exact mass determination for $C_{13}H_{19}P$ (M^+), calcd 206.1224, found 206.1222; [a]$_D$ = 24.55, *c* = 3.86, methylcyclohexane.

(2*R*,3*R*)-(−)-Mesityl-2,3-dimethylphosphirane (4). The same procedure was followed with mesitylphosphine (2.0 g, 13.2 mmol) and (2*S*,3*S*)-(−)-2,3-butanediol ditosylate (6.3 g, 15.8 mmol). Distillation under high vacum yielded (2*R*,3*R*)-(−)-1-mesityl-2,3-dimethylphosphirane (**4**) (1.8 g, 67%) as a colorless oil: NMR data are identical with those for the racemic mixture; exact mass determination for $C_{13}H_{19}P$ (M^+), calcd 206.1224, found 206.1223; [a]$_D$ = −27.32, *c* = 3.45, methylcyclohexane.

(2*R*)-1-Mesityl-2-methylphosphiranes 15, 16. The same procedure was followed with mesitylphosphine (0.8 g, 5.3 mmol) and (2*S*)-(−)-1,2-propanediol ditosylate (3.0 g, 8.0 mmol). A mixture of (2*R*)-1-mesityl-2-methylphosphirane diastereomers **15**, **16** (1.0 g, 98%) was obtained by chromatography as a colorless oil that could not be separated. Spectra of the mixture were recorded. ***anti*-(2*R*)-1-Mesityl-2-methylphosphirane (15):** ^{31}P NMR δ 216.86 (p, J_{P-H} = 14.8 Hz); ^{1}H NMR δ 0.7−1.5 (m, 3 H), 1.21 (dd, 3 H, J_{P-H} = 13.9 Hz, J_{H-H} = 6.5 Hz), 2.08 (s, 3 H), 2.43 (s, 6 H), 6.65 (s, 2 H); ^{13}C-{^{1}H} NMR δ 18.9 (d, J_{P-C} = 18.3 Hz), 19.1 (d, J_{P-C} = 44.0 Hz), 21.0, 22.4 (d, J_{P-C} = 9.0 Hz), 23.2 (d, J_{P-C} = 37.0 Hz), 128.8, 136.1 (d, J_{P-C} = 39.8 Hz), 137.0, 142.1 (d, J_{P-C} = 9.4 Hz); exact mass determination for $C_{12}H_{17}P$ (M^+), calcd 192.1068, found 192.1071. ***syn*-(2*R*)-1-Mesityl-2-methylphosphirane (16):** ^{31}P NMR δ 208.38 (t, J_{P-H} = 16.0 Hz); ^{1}H NMR δ 0.70−1.50 (m, 3 H), 0.97 (dd, 3 H, J_{P-H} = 5.0 Hz, J_{H-H} = 6.2 Hz), 2.08 (s, 3 H), 2.43 (bs, 6 H), 6.65 (s, 2 H); ^{13}C{^{1}H} NMR δ 16.0, 18.8 (d, J_{P-C} = 37.8 Hz), 21.0, 22.4 (d, J_{P-C} = 9.0 Hz), 22.4 (d, J_{P-C} = 39.2 Hz), 129.3 (bs), 132.0 (d, J_{P-C} = 44.5 Hz), 137.0, 143.1 (bs); exact mass determination for $C_{12}H_{17}P$ (M^+), calcd 192.1068, found 192.1071.

PhP(CH$_2$CH$_2$)W(CO)$_5$ (17). A solution of W(CO)$_6$ (0.78 g, 2.22 mmol) in 200 mL of THF was placed in a Pyrex photolysis tube (o.d. = 4.5 cm, length = 22 cm) with a magnetic stirring bar and degassed with three freeze−pump−thaw cycles. The mixture was irradiated for 6 h with a medium-pressure mercury lamp with stirring. Phenylphosphirane (**7**) (0.3 g, 2.2 mmol) in 20 mL of THF was placed in a 500 mL flask equipped with a rubber septum and a magnetic stirring bar. The freshly prepared yellow-orange THF solution of W(CO)$_5$(THF) was transfered to this reaction flask with a double needle with stirring at room temperature. After being stirred a further 10 h, the mixture turned from orange to nearly colorless, and ^{31}P NMR indicated the reaction was complete. Solvent was removed under vacuo, and the remaining material was mixed with 40 mL of pentane and filtered to remove the residue. After evaporation of the pentane from the filtrate, the residue was recrystallized from pentane/ether (9:1), yielding white crystalline product **17** (0.75 g, 74%): ^{31}P NMR δ −187.78 (J_{P-W} = 256.9 Hz); ^{1}H NMR δ 0.82 (m, 2 H), 0.89−0.95 (m, 2 H), 6.84−7.02 (m, 5 H); ^{13}C{^{1}H} NMR δ 10.7 (d, J_{P-C} = 12.4 Hz), 128.8 (d, J_{P-C} = 10.4 Hz), 130.3 (d, J_{P-C} = 2.4 Hz, 131.4 (d, J_{P-C} = 13.3 Hz), 196.0 (d, J_{P-C} = 8.4 Hz), 198.0 (d, J_{P-C} = 30.2 Hz). Anal. Calcd for $C_{13}H_9O_5PW$: C, 33.92; H, 1.97. Found: C, 33.97; H, 2.06.

Mes*P(CH$_2$CH$_2$)W(CO)$_5$ (18). The same procedure was followed with a solution of W(CO)$_6$ (0.5 g, 1.42 mmol) in 150 mL of THF and a solution of 1-supermesitylphosphirane (**2**) (0.43 g, 1.41 mmol) in 50 mL of THF. Product was extracted with 50 mL of pentane and 10 mL of ether and recrystallized from pentane/ether (9:1) at −20 °C, giving dark brown crystals of **18** (0.42 g, 47%): ^{31}P NMR δ −201.62 (J_{P-W} = 258.7 Hz); ^{1}H NMR δ 1.00−1.20 (m, 4 H), 1.18 (s, 9 H), 1.58 (s, 18 H), 7.28 (d, 2 H, J_{P-H} = 3.7 Hz); ^{13}C{^{1}H} NMR δ 22.4 (d, J_{P-C} = 11.1 Hz), 31.1, 34.8 (d, J_{P-C} = 2.9 Hz), 36.2, 39.9 (s), 123.5 (d, J_{P-C} = 7.2 Hz), 150.8 (d, J_{P-C} = 2.3 Hz), 157.8 (d, J_{P-C} = 4.2 Hz), 198.0 (d, J_{P-C} = 7.1 Hz), 198.4. Anal. Calcd for $C_{25}H_{33}O_5PW$: C, 47.79; H, 5.29. Found: C, 47.49; H, 5.73.

(2*S*,3*R*)-*meso*-MesP(CHMe)$_2$W(CO)$_5$ (19). The same procedure was followed with a solution of W(CO)$_6$ (0.20 g, 0.57 mmol) in 100 mL of THF and a solution of *meso*-(2*S*,3*R*)-*anti-cis*-MesP(CHMe)$_2$ (**5**) (0.1 g, 0.49 mmol) in 10 mL of THF. The product was extracted with 100 mL of pentane and chromatographed on silica gel with pentane−ether (95:5) as eluent, yielding **19** as a light pink powder (0.16 g, 59%): ^{31}P NMR δ

−162.75 (J_{P-W} = 254.2 Hz); ^{1}H NMR δ 1.05 (ddd, 6 H, J_{P-H} = 17.9 Hz, J_{H-H} = 6.4 Hz, $J_{H'-H}$ = 2.1 Hz), 1.25−1.33 (m, 2 H), 1.96 (s, 3 H), 2.35 (s, 6 H), 6.54 (d, 2 H, J_{P-H} = 3.4 Hz); ^{13}C{^{1}H} NMR δ 11.0 (d, J_{P-C} = 3.0 Hz), 20.9, 21.5 (d, J_{P-C} = 8.6 Hz), 26.7 (d, J_{P-C} = 12.7 Hz), 129.3 (d, J_{P-C} = 7.0 Hz), 132.4 (d, J_{P-C} = 33.0 Hz), 139.8, 140.7 (d, J_{P-C} = 8.3 Hz), 196.0 (d, J_{P-C} = 8.0 Hz), 197.5 (d, J_{P-C} = 28.4 Hz). Anal. Calcd for $C_{18}H_{19}O_5PW$: C, 40.78; H, 3.61. Found: C, 40.82; H, 3.73.

(2*S*,3*S*)-(+)-MesP(CHMe)$_2$W(CO)$_5$ (20). The same procedure and the same amounts of materials were used for the preparation of **20** from **3**. Pure **20** (0.18 g, 67%) was obtained as a pale yellow oil: ^{31}P NMR δ −156.18 (J_{P-W} = 252.5 Hz); ^{1}H NMR δ 0.69−0.80 (m, 1 H), 0.81 (dd, 3 H, J_{P-H} = 13.4 Hz, J_{H-H} = 6.4 Hz), 1.00−1.11 (m, 1 H), 1.19 (dd, 3 H, J_{P-H} = 18.1 Hz, J_{H-H} = 6.7 Hz), 1.97 (s, 3 H), 2.31 (s, 3 H), 2.40 (s, 3 H), 6.54 (s, 1 H), 6.58 (s, 1 H); ^{13}C{^{1}H} NMR δ 15.4 (d, J_{P-C} = 3.9 Hz), 16.8, 20.9, 21.8 (d, J_{P-C} = 7.8 Hz, 22.2 (d, J_{P-C} = 7.7 Hz), 27.7 (d, J_{P-C} = 9.7 Hz), 30.7 (d, J_{P-C} = 15.7 Hz), 129.0 (d, J_{P-C} = 7.1 Hz), 129.8 (d, J_{P-C} = 6.8 Hz), 139.9, 141.4 (d, J_{P-C} = 9.6 Hz), 141.9 (d, J_{P-C} = 8.1 Hz), 195.6 (d, J_{P-C} = 8.1 Hz), 196.4 (d, J_{P-C} = 8.1 Hz), 197.3 (d, J_{P-C} = 7.8 Hz), 198.1 (d, J_{P-C} = 28.4 Hz). Anal. Calcd for $C_{18}H_{19}O_5PW$: C, 40.78; H, 3.61. Found: C, 40.75; H, 3.87.

(2*R*,3*R*)-(−)-MesP(CHMe)$_2$W(CO)$_5$ (21). The same procedure and same amounts of materials were used for the preparation of **21** from **4**. Pure **21** (0.20 g, 74%) was obtained as a pale yellow oil: ^{31}P NMR δ −156.16 (J_{P-W} = 252.4 Hz); ^{1}H NMR δ 0.69−0.75 (m, 1 H), 0.80 (dd, 3 H, J_{P-H} = 13.4 Hz, J_{H-H} = 6.4 Hz), 0.99−1.10 (m, 1 H), 1.18 (dd, 3 H, J_{P-H} = 18.0 Hz, J_{H-H} = 6.7 Hz), 1.96 (s, 3 H), 2.31 (s, 3 H), 2.40 (s, 3 H), 6.54 (d, 1 H, J_{P-H} = 2.6 Hz), 6.58 (s, 1 H); ^{13}C{^{1}H} NMR δ 15.4 (d, J_{P-C} = 3.8 Hz), 16.8, 20.9, 21.8 (d, J_{P-C} = 8.0 Hz), 22.2 (d, J_{P-C} = 7.8 Hz), 27.7 (d, J_{P-C} = 9.9 Hz), 30.7 (d, J_{P-C} = 15.7 Hz), 129.0 (d, J_{P-C} = 7.1 Hz), 129.8 (d, J_{P-C} = 6.8 Hz), 139.8, 141.4 (d, J_{P-C} = 9.2 Hz), 141.9 (d, J_{P-C} = 7.9 Hz), 195.6 (d, J_{P-C} = 8.1 Hz), 196.4 (d, J_{P-C} = 8.2 Hz), 197.3 (d, J_{P-C} = 8.0 Hz), 198.1 (d, J_{P-C} = 28.0 Hz). Anal. Calcd for $C_{18}H_{19}O_5PW$: C, 40.78; H, 3.61. Found: C, 41.04; H, 3.90.

W(CO)$_5$PPh$_3$.[17] The procedure employed for the synthesis of **17** was followed with a solution of $W(CO)_6$ (3.0 g, 8.53 mmol) in 250 mL of THF. PPh_3 (2.3 g, 8.78 mmol) was reacted with freshly prepared $W(CO)_5$THF. After the reaction was complete, solvent was removed under vacuo, and the remaining material was mixed with 200 mL of hexane and filtered to remove the dark residue. After evaporation of the hexane from the filtrate, the residue was recrystallized from a mixture of hexane and ether (8:2) at −5 to −10 °C. Then 0.6 g of $W(CO)_6$ was recovered as white needles, and light yellow crystals of $W(CO)_5PPh_3$ (3.3 g, 82.5%) were obtained. Column chromatography on silica gel can also be used to purify $W(CO)_5PPh_3$, if there is large amount of unreacted $W(CO)_6$ present.

W(CO)$_4$(PPh$_3$)[(2*S*,3*R*)-*meso*-MesP(CHMe)$_2$] (22). In a typical experiment a solution of $W(CO)_5$ (PPh_3) (0.2 g, 0.34 mmol) in 120 mL of THF was placed in a Pyrex photolysis tube (o.d. = 4.5 cm, length = 22 cm) with a magnetic stirring bar, a nitrogen inlet to the bottom of the tube, and a nitrogen outlet on the top. With stirring and nitrogen bubbling through the reaction solution, the mixture was irradiated for 3 h with a medium-pressure mercury lamp. The reaction was conveniently monitored by TLC (silica gel) with a mixture of pentane and ether (9:1) as eluent. *meso-anti-cis*-MesP(CHMe)$_2$ (**5**) (0.07 g, 0.34 mmol) was placed in a 250 mL flask equipped with a rubber septum and a magnetic stirring bar. The freshly prepared yellow-orange THF solution of $W(CO)_4(PPh_3)$(THF) was transfered to the reaction flask with a double needle with stirring. After a further 5 h with stirring, the mixture turned from orange to light yellow or nearly colorless, and TLC analysis suggested that the reaction was complete. Solvent was removed under vacuo, and the remaining material was mixed with 150 mL of hexane and filtered to remove the dark residue. After evaporation of the hexane from the filtrate, the residue was chromatographed on silica gel with hexane/ether (9:1) eluent, yielding $W(CO)_4(PPh_3)$[(2*S*,3*R*)-*meso*-MesP(CHMe)$_2$] (**22**) (0.20 g, 77%) of high purity. This was recrystallized from a mixture of pentane and ether (1:1) at −5 to −10 °C. X-ray quality light yellow crystals of **22** were obtained: ^{31}P NMR δ −169.18 (dd, 1 P, J_{P-P} = 24.4 Hz, J_{P-W} = 240.8 Hz, P(CHMe)$_2$), 21.28 (dd, 1 P, J_{P-P} = 24.4 Hz, J_{P-W} = 238.0 Hz, Ph_3P); ^{1}H NMR ($CDCl_3$) δ 1.29 (dd, *6 H*, J_{P-H} = 16.5 Hz, J_{H-H} = 6.1 Hz), 1.71 (m, 2 H), 2.23 (s, 3 H), 2.29 (s, 6 H), 6.77 (d, 2 H, J_{P-H} = 2.7 Hz), 7.26−7.39 (m, 15 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 11.4 (s), 21.0, 22.1 (d, J_{P-C} = 7.0 Hz), 28.1 (d, J_{P-C} = 12.6 Hz), 128.0 (d, J_{P-C} = 9.5 Hz), 129.0 (m), 129.7, 133.5 (d, J_{P-C} = 12.0 Hz), 136.6 (d, J_{P-C} = 37.1 Hz), 138.9, 141.3 (d, J_{P-C} = 8.7 Hz), 201.7 (m), 203.7 (d, J_{P-C} = 16.9 Hz). Anal. Calcd for $C_{35}H_{34}O_4P_2W$: C, 54.99; H, 4.48. Found: C, 55.01; H, 4.46.

W(CO)$_4$(PPh$_3$)[(2*S*,3*S*)-(+)-MesP(CHMe)$_2$] (23). The same procedure and same amounts of starting materials were used for the preparation of **23** from **3**. Product was extracted with 150 mL of pentane/ether (8:2) and recrystallized from a mixture of pentane and ether (1:1) at −5 to 10 °C. X-ray quality light yellow crystals of **23** were obtained (0.22 g, 85%): ^{31}P NMR ($CDCl_3$) δ −155.27 (dd, 1 P, J_{P-P} = 27.4 Hz, J_{P-W} = 241.5 Hz, P(CHMe)$_2$), 22.36 (dd, 1 P, J_{P-P} = 27.4 Hz, J_{P-W} = 236.5 Hz, Ph_3P); ^{1}H NMR ($CDCl_3$) δ 0.86 (m, 1 H), 1.01−1.17 (m, 6 H), 1.53 (s, 1 H), 2.24 (s, 3 H), 2.29 (s, 3 H), 2.38 (s, 3 H), 6.77 (d, 2 H, J_{P-H} = 13.2 Hz), 7.32−7.36 (m, 9 H), 7.40−7.47 (m, 6 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 15.5 (d, J_{P-C} = 3.4 Hz), 16.4, 21.0, 22.0 (d, J_{P-C} = 7.5 Hz), 22.6 (d, J_{P-C} = 6.4 Hz), 29.4 (d, J_{P-C} = 8.9 Hz), 30.8 (d, J_{P-C} = 19.3 Hz), 128.2 (d, J_{P-C} = 9.2 Hz), 128.5 (m) 129.5 (m), 129.7, 133.5 (d, J_{P-C} = 11.78 Hz), 136.4 (d, J_{P-C} = 35.6 Hz), 138.9, 141.2 (d, J_{P-C} = 9.9 Hz), 142.4 (d, J_{P-C} = 7.4 Hz), 202.0 (m), 203.5 (m). Anal. Calcd for $C_{35}H_{34}O_4P_2W$: C, 54.99; H, 4.48. Found: C, 54.32; H, 3.96.

W(CO)$_4$(PPh$_3$)[(2*R*,3*R*)-(−)-MesP(CHMe)$_2$] (24). The same experimental procedure was followed as in the synthesis of **22**. A solution of $W(CO)_5(PPh_3)$ (0.3 g, 0.51 mmol) in 200 mL of THF was used to prepare $W(CO)_4(PPh_3)$(THF). (2*R*,3*R*)-MesP(CHMe)$_2$ (**4**) (0.11 g, 0.53 mmol) was reacted with the freshly prepared $W(CO)_4(PPh_3)$(THF) in THF. Product was extracted with 150 mL of hexane and chromatographed on silica gel with hexane/ether (9:1) eluent. Pure $W(CO)_4(PPh_3)$-[(2*R*,3*R*)-(−)-MesP(CHMe)$_2$] (**24**) (0.28 g, 72%) was obtained. The material was recrystallized from a mixture of pentane and ether (1:1) at −5 to −10 °C giving X-ray quality light yellow crystals: ^{31}P NMR ($CDCl_3$) δ −155.28 (dd, 1 P, J_{P-P} = 27.4 Hz, J_{P-W} = 240.8 Hz, P(CHMe)$_2$), 22.36 (dd, 1 P, J_{P-P} = 27.4 Hz, J_{P-W} = 238.0 Hz, Ph_3P); ^{1}H NMR ($CDCl_3$) δ 0.87 (m, 1 H), 1.02−1.17 (m, 6 H), 1.55−1.62 (m, 1 H), 2.24 (s, 3 H), 2.30 (s, 3 H), 2.38 (s, 3 H), 6.77 (d, 2 H, J_{P-H} = 13.1 Hz), 7.33−7.35 (m, 9 H), 7.41−7.48 (m, 6 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 15.5 (d, J_{P-C} = 3.1 Hz), 16.4, 21.0, 22.0 (d, J_{P-C} = 7.8 Hz), 22.6 (d, J_{P-C} = 6.7 Hz), 29.5 (d, J_{P-C} = 9.1 Hz), 30.8 (d, J_{P-C} = 18.1 Hz), 128.2 (d, J_{P-C} = 9.2 Hz), 128.5 (m), 129.5 (m), 129.7, 133.5 (d, J_{P-C} = 12.0 Hz), 136.4 (d, J_{P-C} = 37.1 Hz), 138.9, 141.2 (d, J_{P-C} = 9.7 Hz), 142.4 (d, J_{P-C} = 7.2 Hz), 201.8 (m), 203.5−204.0 (m). Anal. Calcd for $C_{35}H_{34}O_4P_2W$: C, 54.99; H, 4.48. Found: C, 54.92; H, 4.17.

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Supporting Information Available: ^{1}H and ^{13}C NMR peak assignments, IR absorptions, and MS fragmentation patterns. Data acquisition details for X-ray structure determinations and ORTEP drawings for **22**, **23**, and **24** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. The author has deposited atomic coordinates for structures **22**, **23**, and **24** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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