RR02652-01) and the 500-MHz NMR was purchased with funds from NIH (RR04733) and NSF (CHE-8814866). We would like thank John Wright for technical assistance.

Registry No. 5, 137039-59-9; **5(Cr)**, 137039-65-7; **6**, 137039-60-2; **6(Cr)**, 137039-66-8; **7**, 137039-61-3; **7(Cr)**, 137039-67-9; **8**, 3450-15-5; **9**, 137039-62-4; **10**, 2715-54-0; **11**, 635-81-4; **12**, 65870-23-7; **13**, 31366-07-1; **14**, 17314-92-0; **15**, 137039-63-5; **16**, 137039-64-6; $Fe(CO)_5$, 13463-40-6; $Cr(CO)_6$, 13007-92-6; triaminechromium tricarbonyl, 14974-11-9; 3-hexyne, 928-49-4; 1,2,4-triethylbenzene, 877-44-1.

Use of Prochiral Phosphaalkene Complexes in the Synthesis of Optically Active Phosphines

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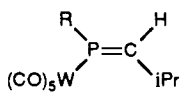
Contribution from the Laboratoire de Chimie du Phosphore et des Métaux de Transition, CNRS UM 13, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France. *Received June 19, 1991*

Abstract: Prochiral L-menthyl phosphaalkene complexes were prepared from "phospha-Wittig" reagents, $[MenP(H)-P(O)(OR)_2]M(CO)_5$ (M = Mo, W), and several aldehydes. Their catalytic hydrogenation using RhL_2^+ catalysts and their [2 + 4] cycloaddition with cyclopentadiene proceeded with full diastereoselectivity. A molecular model of such a phosphaalkene complex showed that a preferred conformation exists that minimizes the combined interactions of the isopropyl substituent of the L-menthyl group with the complexing group and the phosphavinylic C–H bond. In this conformation, only the *si* face of the phosphaalkene is free for the incoming reagents. Both hydrogenation and [2 + 4] cycloaddition with cyclopentadiene selectively take place on this face as demonstrated by the X-ray crystal structure analysis of two of the resulting complexes. A two-step procedure was devised for the conversion of $[MenPH_2]Mo(CO)_5$ into optically pure phosphines. In the first step, the primary phosphine complex was phosphorylated, the resulting phospha-Wittig reagent was allowed to react with an aldehyde, and the phosphaalkene complex thus formed was trapped by cyclopentadiene. The decomplexation of the resulting molybdenum complex was carried out by heating with diphos. An optically pure 2-L-menthyl-2-phospha-5-norbornene was thus prepared.

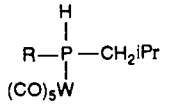
Prochiral phosphaalkenes or phosphaalkene complexes are a potential source of optically active P^{III} species provided that face selectivity can be achieved during the additions or cycloadditions onto the P=C double bond. We have recently devised a versatile route to phosphaalkene complexes via the so-called phospha-Wittig reaction.[1,2] Prochiral P=C double bonds thus became easily accessible, and we were naturally led to investigate the synthesis of optically active P^{III} ligands from these P^{II} complexes.

Results and Discussion

In a previous work,[3] we have described the catalytic hydrogenation of phosphaalkene P–$W(CO)_5$ complexes using Rh(diphos)X (X = Cl, PF_6) as the catalyst. Using prochiral phosphaalkene complexes **1** and $[RhL_2^*]^+PF_6^-$ (L_2^* = chiraphos, dipamp, diop) as the catalyst, we first carried out a series of hydrogenation experiments under the standard conditions.[3b] We never observed a significant ee in the resulting P^{III} complexes **2**.



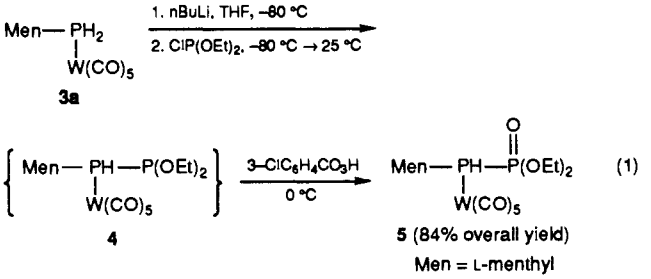
1a: R = Ph
b: R = cyclohexyl



2

Since the synthesis of carbonyl C-substituted phosphaalkene complexes was hampered by their instability,[4] it was impossible to create a second coordination site in the phosphaalkene complex in order to increase the face selectivity as in the case of dehydroaminoacids.[5] We thus decided to change our approach and to incorporate the optically active group into the structure of the phosphaalkene complex. During our preliminary study of the catalytic hydrogenation of the P=C double bond,[3] we noted that the speed of the reaction was much more sensitive to the steric bulk of the substituents at phosphorus than to the steric bulk of the substituents at carbon. It was thus logical to introduce the optically active group as a substituent at phosphorus where it could better influence the catalytic process.

In a first step, the L-menthyl phospha-Wittig reagent **5** was prepared as follows (eq 1):



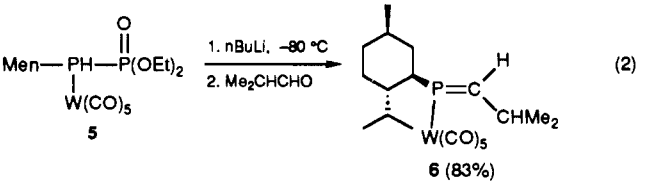
3a

4

5 (84% overall yield)
Men = L-menthyl

(1)

This route to phospha-Wittig reagents is described more in depth elsewhere.[1c] It gives better yields of **5** than the other possible routes.[1a,b] This reagent was then used to prepare the *P*-menthyl phosphaalkene complex **6** (eq 2):

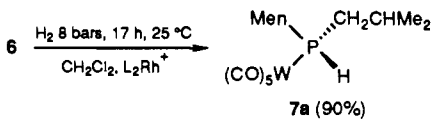


5

6 (83%)

(2)

The hydrogenation experiments were carried out under the standard experimental conditions[3] (eq 3):



7a (90%)

(3)

(1) (a) Marinetti, A.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1382. (b) Marinetti, A.; Bauer, S.; Ricard, L.; Mathey, F. *Organometallics* **1990**, *9*, 793. (c) Bauer, S.; Marinetti, A.; Mathey, F. *Heteroatom. Chem.* **1991**, *2*, 277.
(2) Le Floch, P.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1990**, *112*, 2407. Le Floch, P.; Mathey, F. *Synlett* **1990**, 171.
(3) (a) de Vaumas, R.; Marinetti, A.; Mathey, F. *J. Organomet. Chem.* **1991**, *413*, 411. (b) de Vaumas, R. Ph.D. Thesis, Ecole Polytechnique, 1991.
(4) Marinetti, A.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1990**, 153.
(5) For recent reviews, see: Ojima, I.; Clos, N.; Bastos, C.; *Tetrahedron* **1989**, *45*, 6901. Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. Blystone, S. L. *Chem. Rev.* **1989**, *89*, 1663.

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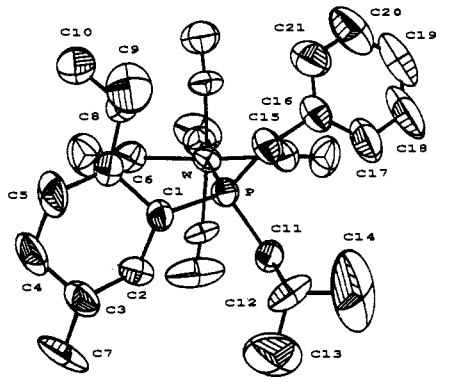
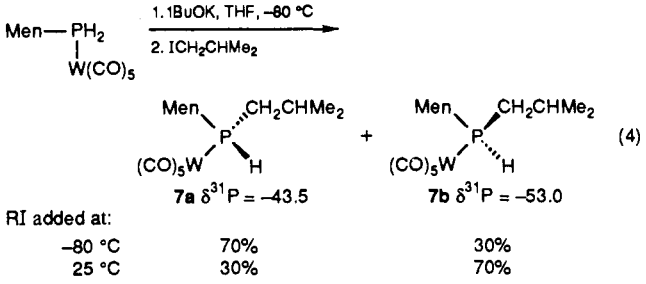


Figure 1. ORTEP drawing of one molecule of **8b** in the crystal with the atomic numbering scheme. The hydrogen atoms are omitted for clarity. The ellipsoids are scaled to enclose 50% of the electronic density. The phosphorus atom has the *S* configuration.

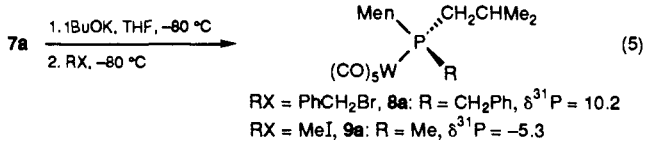
With L_2 = diphos, the diastereomeric excess (**7a** vs **7b**) was better than 90%. With L_2 = (−)chiraphos, only diastereomer **7a** was obtained. As a comparison, we prepared **7** by alkylation of **3**. Diastereomers **7a** and **7b** were obtained in various ratios, according to the alkylation temperature (eq 4):



RI added at:

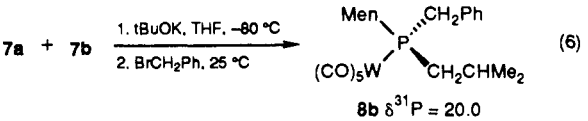
−80 °C	70%	30%
25 °C	30%	70%

The excellent induction observed during the hydrogenation of **6** prompted us to study the conversion of **7a** into usable optically active phosphorus species. Besides, it was interesting to establish on which face of **6** the hydrogenation takes place. For that purpose, we first investigated the metalation–alkylation of **7a**. A recent work has shown that complexed secondary phosphines can be alkylated at low temperature with retention of configuration at phosphorus.[6] Our observations were very similar to those of Wild and co-workers.[6] At −80 °C, alkylation of **7** proceeded with complete stereospecificity (eq 5):



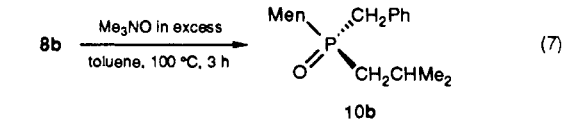
RX = $PhCH_2Br$, **8a**: R = CH_2Ph, $\delta^{31}P$ = 10.2
RX = MeI, **9a**: R = Me, $\delta^{31}P$ = −5.3

As an additional confirmation, a 60:40 mixture of diastereomers **7a** and **7b** was methylated at −80 °C to give a 60:40 mixture of diastereomers **9a** and **9b**. At room temperature, the picture completely changed. Regardless of which mixture of **7a** and **7b** was used, the benzylation always led to the preferential formation of **8b** with a diastereomeric excess of 80% (eq 6):

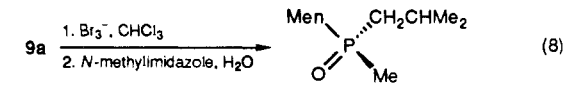


8b $\delta^{31}P$ = 20.0

Pure **8b** was obtained by crystallization of the mixture, and its stereochemistry was studied by X-ray diffraction (Figure 1). The configuration of **8b** at phosphorus was thus established and, as a consequence, also that for **7a**, **7b**, **8a**, **9a**, and **9b**. Both **8b** and **9a** were converted into the corresponding oxides via decomplexation techniques that have been shown to proceed with full retention of the stereochemistry at phosphorus[7] (eqs 7 and 8):



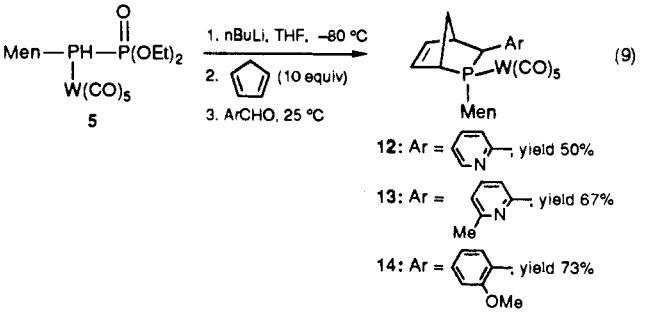
10b



11a

Even though each step of the sequence leading to **10b** and **11a** from **6** proceeds with high yield, the overall scheme is too complicated to be useful. We thus decided to check whether the face selectivity observed during the catalytic hydrogenation of **6** was specific for the chosen reaction or if it could be generalized to other reactions of the P=C double bond. We selected the [4 + 2] cycloaddition with cyclopentadiene.

The generation of the phosphaalkene complex and its trapping by cyclopentadiene were simultaneously performed (eq 9):



12: Ar = ; yield 50%

13: Ar = ; yield 67%

14: Ar = ; yield 73%

In each case, only one isomer was obtained according to ^{31}P NMR analysis of the reaction mixture. The precise stereochemistry of **13** was established by X-ray analysis (Figure 2). The preference of the P-substituent for the endo position has already been observed during the cycloaddition of cyclopentadiene with free phosphaalkenes.[8] The cycloaddition selectively takes place on the same face of the transient phosphaalkene complexes as does the catalytic hydrogenation on **6**. The face selectivity is thus specifically induced by the structure of the L-menthyl phosphaalkene complexes, and the reaction involved plays no major role in it.

Using structural parameters derived from those previously obtained during the X-ray study of [^{t}BuP=CH^{i}Pr]W(CO)$_5$,[1] we

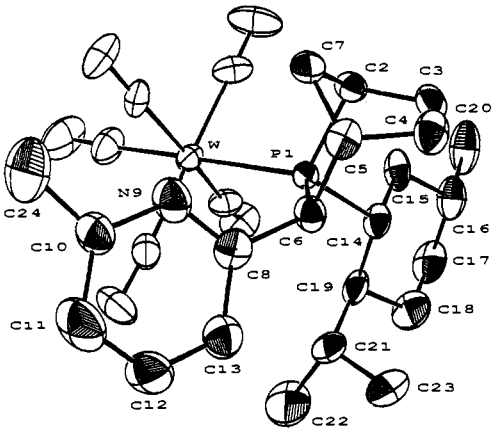


Figure 2. ORTEP drawing of one molecule of **13** in the crystal with the atomic numbering scheme. The hydrogen atoms are omitted for clarity. The ellipsoids are scaled to enclose 50% of the electronic density.

(6) Crisp, G. T.; Salem, G.; Wild, S. B.; Stephens, F. S. *Organometallics* **1989**, *8*, 2360.

(7) Deschamps, E.; Ricard, L.; Mathey, F. *Heteroatom. Chem.* **1991**, *2*, 377.

(8) Appel, R.; Menzel, J.; Knoch, F. *Chem. Ber.* **1985**, *118*, 4068. Appel, R.; Casser, C. *Chem. Ber.* **1985**, *118*, 3419.

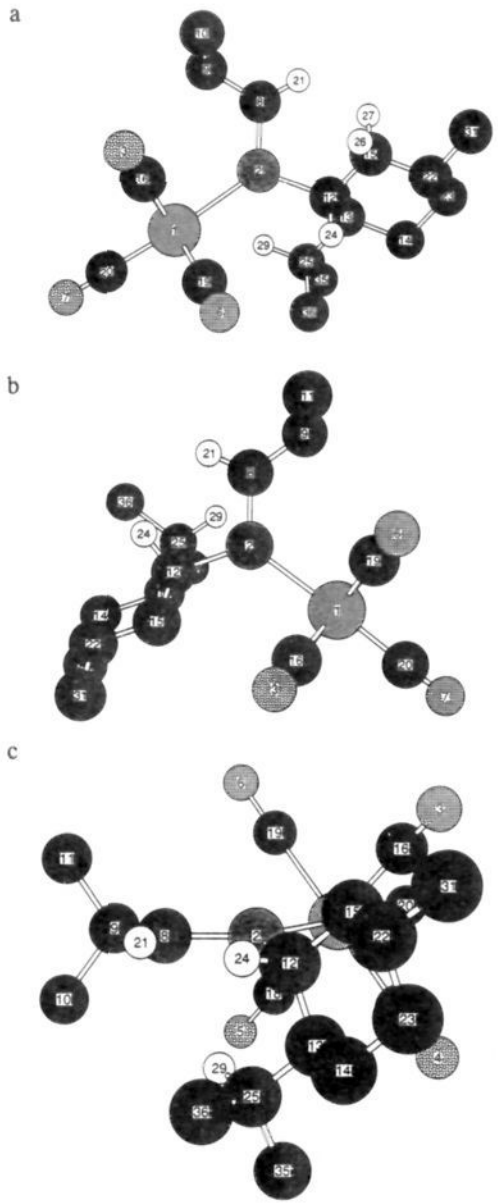
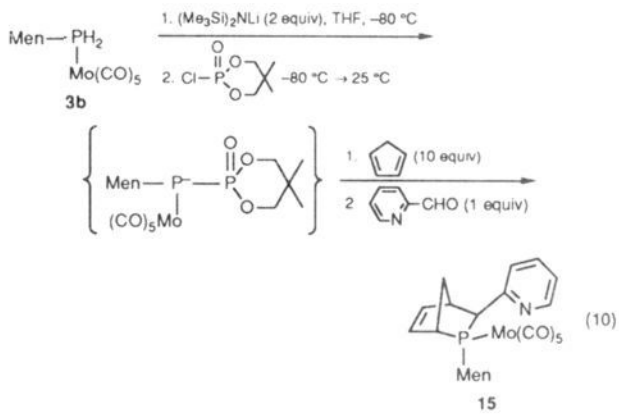


Figure 3. Chem 3D representations of one molecule of **6**. Numbering scheme: W = 1, P = 2, sp^2C = 8, C(menthyl) = 12. (a) Conformation with a C(8)–P–C(12)–C(13) dihedral angle of −102°; main distances are W–P = 2.49 Å, P–C(8) = 1.65 Å, P–C(12) = 1.83 Å. A strong interaction exists between C(18) and C(25): C(18)···C(25) = 2.54 Å. (b) Conformation with a C(8)–P–C(12)–C(13) dihedral angle of 103°. (c) Conformation with a C(8)–P–C(12)–C(13) dihedral angle of 103°, viewed from the menthyl side of the double bond.

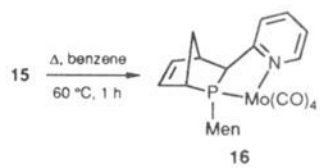
built a molecular model of **6** and studied the various conformations resulting from a rotation around the P–menthyl bond. For some conformations, a significant steric crowding results from through-space interactions between the isopropyl substituent of the menthyl group and both the $W(CO)_5$ complexing group and the phosphavinylic C–H bond. A priori, some $\sigma(C_{12}–C_{13}),\pi(P{=}C)$ overlap (hyperconjugation) may favor the conformations with a $C_8–P_2–C_{12}–C_{13}$ angle of ±100° against other conformations with intermediate dihedral angles. Such conformations are represented in Figure 3. The lowest crowding is observed for dihedral angles around +100° (Figure 3b,c). In this +100 conformation, it is quite clear that the *si* face[9] of the phosphaalkene is free for the incoming reagent (Figure 3c). Compounds **7a** and **12–14** all result from a selective attack of **6** on this face.

The last question needing an answer concerned the possible use of this kind of chemistry to prepare new optically active phosphines via a simplified procedure. For that purpose, we replaced tungsten with molybdenum in the complexing group in order to facilitate the final decomplexation step. Our approach is depicted in eq 10.



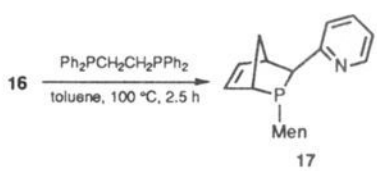
(10)

The crystalline cyclic chlorophosphate[10] used for the preparation of the phospha-Wittig reagent is easier to handle than $ClP(O)(OEt)_2$. Besides, the elimination of the corresponding cyclic phosphate ion in the phospha-Wittig reaction is a priori favored by the cyclic structure. Complex **15** thus obtained is unstable and readily loses one CO to give the stable chelate **16** (eq 11) (more than 90% de).



(11)

As in the tungsten case, the molybdenum complexes **15** and **16** were obtained as pure diastereomers. The overall yield of **16** from $[MenPH_2]Mo(CO)_5$ was 27%. Improvements are still possible. The decomplexation of **16** was performed by heating with diphos[11] (eq 12).



(12)

The phosphine **17** was obtained almost quantitatively as a pure diastereomer. Retention of stereochemistry during the decomplexation is very likely but was not established.

It is clear from this example that additions or cycloadditions onto prochiral phosphaalkene complexes represent an effective new route to optically active P^{III} species.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 SY spectrometer or a Bruker AM 400 spectrometer. ^{31}P NMR spectra were recorded on a Bruker WP 80 SY spectrometer operating at 32.44 MHz. Chemical shifts are expressed in parts per million downfield from internal TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants are expressed in hertz. Mass spectra were obtained at 70 eV with a Shimadzu GC–MS QP 1000 instrument by the direct-inlet method. Infrared spectra were recorded with a Perkin-Elmer Model 297 spectrometer. Elemental analyses were performed by the "Service d'analyse du CNRS", Gif sur Yvette, France. Silica gel (70–230 mesh)

(9) Diastereotopic faces of **6** can be named by an extension of the *re/si* system used for trigonal molecules: Hanson, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 2731. The unsaturated carbon atom was chosen as the prochiral center.

(10) Patois, C.; Ricard, L.; Savignac, P. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1577.

(11) Le Goff, P. Ph.D. Thesis, Ecole Polytechnique, 1990.

was used for chromatographic separations. All commercially available reagents were used as received from the suppliers. All reactions were performed under nitrogen atmosphere. Tetrahydrofuran (THF) was distilled over sodium/benzophenone. Diethyl ether was distilled over $LiAlH_4$. All other solvents used for preparation were reagent grade and used without further purification.

(L-Menthylphosphine)pentacarbonyltungsten and -molybdenum Complexes 3a and 3b. (a) L-Menthyldichlorophosphine was prepared by adding the corresponding Grignard reagent to a solution of PCl_3 in THF at 0 °C[12]: yield 62%; bp 110 °C (0.2 Torr); $[\alpha]_D = -107.5°$ (C_6H_6, $c = 4$).

(b) To a stirred suspension of 50 mmol of $M(CO)_6$ (M = W, Mo) in 200 mL of CH_3CN was added 50 mmol of $Me_3NO{\cdot}2H_2O$ in small portions over 30 min at room temperature (M = W) or at 0 °C (M = Mo). The yellow solution was stirred for an additional 30 min at room temperature and then evaporated to dryness in vacuo. The residue was dissolved in dry benzene and the solution evaporated to dryness. The crude $M(CO)_5(CH_3CN)$ was dissolved in 50 mL of THF, 50 mmol of L-menthyldichlorophosphine was added, and the mixture was heated at 40 °C overnight. After evaporation of the solvent, addition of ether, and filtration, the $(MenPCl_2)M(CO)_5$ complexes were obtained: M = W ^{31}P NMR (THF) δ = 169.2 ppm; M = Mo ^{31}P NMR (toluene) δ = 209.4 ppm.

(c) To a stirred suspension of 50 mmol of $LiAlH_4$ (Aldrich pellets, 10 × 13 mm) in ether at 0 °C was added an ethereal solution of the crude $(MenPCl_2)M(CO)_5$ complex. The mixture was then hydrolyzed at 0 °C with water. After extraction with ether and evaporation, the residue was chromatographed on a silica gel column with hexane as eluent.

3a: yield 19.3 g (78%), colorless oil; $[\alpha]_D = -3.53°$ ($c = 4.5$, C_6H_6); ^{31}P NMR (C_6D_6) −96.6 (^1J(P–^{183}W) = 214.8, ^1J(P–H) = 330); ^{13}C NMR (C_6D_6) δ 14.9 (s, CH_3), 21.22 (s, CH_3), 22.40 (s, CH_3), 24.31 (d, J(P–C) = 11.2), 29.10 (d, J(P–C) = 5.8), 32.55 (d, ^1J(P–C) = 27.9, PCH), 33.18 (d, J(P–C) = 14.1), 34.85 (s), 40.05 (d, J(P–C) = 2.5), 45.45 (s), 196.22 (d, ^2J(P–C) = 6.6, CO_{cis}), 198.25 (d, ^2J(P–C) = 21.6, CO_{trans}; ^{1}H NMR (C_6D_6) δ 0.56 (d, ^3J(H–H) = 6.8, CH_3), 0.78 (d, ^3J(H–H) = 6.3, CH_3), 0.84 (d, ^3J(H–H) = 6.8, CH_3), 0.7–2.8 (m, 10 H), 3.87 (*AB*, ^1J(P–H) = 330.8, $^2J_{AB}$ = 7.76, ^3J(H–H) = 1.6, PH), 4.08 (*AB*, ^1J(P–H) = 328.8, ^3J(H–H) = 4.8, PH); mass spectrum, (^{184}W) m/z 496 (M, 46); IR (decalin) ν (CO) 2070 (m), 1940 (vs) cm^{-1}. Anal. Calcd for $C_{15}H_{21}O_5PW$: C, 36.31; H, 4.27. Found: C, 36.38; H, 4.12.

3b: yield 9.2 g (45%), colorless oil; $[\alpha]_D = -3.58°$ ($c = 2.01$, C_6H_6); ^{31}P NMR (C_6D_6) −77.8; ^{13}C NMR (C_6D_6) δ 14.90 (s), 21.22 (s), 22.38 (s), 24.39 (d, J(P–C) = 10.8), 29.08 (d, J(P–C) = 5.9), 32.05 (d, ^1J(P–C) = 24.5, PCH), 33.26 (d, J(P–C) = 14.0), 34.84 (s), 40.70 (d, J(P–C) = 4.2), 45.46 (s), 205.76 (d, ^2J(P–C) = 8.9, CO_{cis}), 209.11 (d, ^2J(P–C) = 22.5, CO_{trans}; ^{1}H NMR (C_6D_6) δ 0.50 (d, ^3J(H–H) = 6.8, CH_3), 0.75 (d, ^3J(H–H) = 6.0, CH_3), 0.83 (d, ^3J(H–H) = 6.8, CH_3), 0.6–1.7 (m), 3.45 (*AB*, $^2J_{AB}$ = 8.2, ^1J(H–P) = 317.7, ^3J(H–H) = 2.0, PH), 3.72 (*AB*, ^1J(H–P) = 315.6, ^3J(H–H) = 4.8, PH); mass spectrum (^{96}Mo) 408 M, 16).

[L-Menthyl(diethoxyphosphoryl)phosphine]pentacarbonyltungsten (5). nBuLi (6.3 mL, 1.6 M solution in hexane) was added at −78 °C to a solution of (L-menthylphosphine)$W(CO)_5$ (**3a**) (5g, 10 mmol) in 10 mL of THF. After a few minutes, diethyl chlorophosphite (1.5 mL, 10 mmol) was added. After about 10 min at −78 °C, oxidation of complex **4** was performed by adding a solution of *m*-chloroperbenzoic acid (2.8 g, 80% acid, previously dried over $MgSO_4$) in THF at −78 °C. The reaction mixture was then warmed to room temperature and hydrolyzed with 6 mL of an aqueous solution of $NaHSO_3$. The THF was removed, and the resulting oil was dissolved in ether and washed with a 5% solution of Na_2CO_3 and then with water. The final product was purified by column chromatography using hexane/CH_2Cl_2 (50:50) as eluent. **5**: yield 5.3 g (84%), colorless oil, mixture of two isomers in a 75:25 ratio; ^{31}P NMR (C_6D_6) **5a** δ −65.7 (*AX*, ^1J(P–P) = 73.2, ^1J(P–^{183}W) = 295.4, ^1J(H–P) = 320), 23.0 (A*X*), **5b** δ −55.9 (*AX*, ^1J(P–P) = 58.6, ^1J(H–P) = 320), 21.1 (A*X*); ^{1}H NMR (C_6D_6) **5a** δ 0.68 (d, ^3J(H–H) = 6.8, CH_3), 0.84 (d, ^3J(H–H) = 6.3, CH_3), 0.88 (d, ^3J(H–H) = 6.9, CH_3), 1.04 (t, ^3J(H–H) = 7.0, CH_2CH_3), 1.06 (t, ^3J(H–H) = 7.0, 3 H, CH_2CH_3), 1.2–2.7 (m, 10 H), 3.9 (m, 4 H, OCH_2CH_3), 5.16 (ddd, ^1J(H–P) = 320, ^2J(H–P) ≈ ^3J(H–H) = 2.6, PH).

(L-Menthylisobutylidenephosphine)pentacarbonyltungsten (6). A solution of the phosphorylphosphine complex **5** (6.4 g, 10 mmol) in THF (20 mL) was cooled to −78 °C. nBuLi (6.3 mL, 1.6 M solution in hexane) was then added. The reaction mixture was warmed to room temperature, and isobutyraldehyde (1.3 mL, 13 mmol) was added. After 15 min, ether (80 mL) was added and the solution was filtered through a short Celite column. After evaporation, the crude product was purified by chromatography on silica gel with hexane as eluent. **6**: yield 4.6 g (83%), yellow oil; ^{31}P NMR (C_6D_6) δ 213.77 (^1J(P–^{183}W) = 244); ^{13}C NMR (C_6D_6) δ 14.86 (s, CH_3), 21.36 (s, CH_3), 22.52 (s, CH_3), 23.91 (d, ^3J(C–P) = 16.8, $CHMe_2$), 24.05 (d, ^3J(C–P) = 16.9, $CHMe_2$), 24.45 (d, J(C–P) = 10.3), 30.77 (d, J(C–P) = 4.8), 33.34 (d, J(C–P) = 11.2), 34.07 (d, J(C–P) = 4.3), 34.78 (s), 41.15 (s), 44.48 (s), 52.13 (d, ^1J(C–P) = 8.6, PCH), 181.43 (d, ^1J(C–P) = 38.5, P=C), 195.52 (d, ^2J(C–P) = 9.2, CO_{cis}), 198.54 (d, ^2J(C–P) = 27.0, CO_{trans}); ^{1}H NMR (C_6D_6) δ 0.66 (d, ^3J(H–H) = 6.8, CH_3), 0.81 (d, ^3J(H–H) = 5.9, CH_3), 0.90 (d, ^3J(H–H) = 6.8, CH_3), 0.97 (d, ^3J(H–H) = 6.5, ^4J(H–P) = 1.4, CH_3), 1.00 (d, ^3J(H–H) = 6.5, ^4J(H–P) = 1.4, CH_3), 1.1–1.7 (m), 1.90 (m, 1 H), 2.14 (m, 1 H), 2.98 (m, ^3J(H–P) = 27.3, 1 H, =*CCH*), 7.61 (dd, ^3J(H–H) = 11.6, ^2J(H–P) = 17.7, 1 H, =*CH*); mass spectrum (^{184}W), m/z 550 (M, 23); IR (decalin) ν (CO) 2070 (m), 1940 (vs) cm^{-1}. Anal. Calcd for $C_{19}H_{27}O_5PW$: C, 41.47; H, 4.95. Found: C, 41.69; H, 5.15.

Hydrogenation of Complex 6. Hydrogenation was performed in a constant-volume apparatus (100 mL). The phosphaalkene complex **6** (3 g, 5.5 mmol) was added to a solution containing 0.27 mmol (126 mg) of $Rh(COD)_2PF_6$[13] and 0.27 mmol (110 mg) of diphos in 12 mL of CH_2Cl_2. The reaction mixture was introduced into the hydrogenation flask under inert atmosphere. The flask was then successively evacuated and filled with hydrogen. The total pressure was 8 bars. The reaction mixture was stirred at room temperature for 17 h. After evaporation of the solvent, the final product was purified by chromatography with hexane as eluent. **7**: yield 2.9 g (95%), mixture of **7a** and **7b** (**7a**:**7b** ≈ 95:5), colorless oil.

7a: ^{31}P NMR (C_6D_6) δ −43.70 (^1J(P–^{183}W) 222.2, ^1J(P–H) = 322); ^{13}C NMR (C_6D_6) δ 15.25 (s, CH_3), 21.41 (s, CH_3), 22.55 (s, CH_3), 22.83 (d, ^3J(P–C) = 4.6, CH_3), 24.00 (d, J(P–C) = 9.5), 24.75 (d, J(P–C) = 10.1), 26.95 (s), 29.17 (d, J(P–C) = 2.6), 33.59 (d, J(P–C) = 12.8), 34.45 (d, ^1J(P–C) = 22.0), 34.94 (s), 39.09 (s), 39.14 (d, ^1J(P–C) = 23.7), 45.15 (s), 197.30 (d, ^2J(P–C) = 6.8, CO_{cis}), 198.90 (d, ^2J(P–C) = 20.4, CO_{trans}); ^{1}H NMR (C_6D_6) δ 0.61 (d, ^3J(H–H) = 6.9, CH_3), 0.78 (d, ^3J(H–H) = 6.3, CH_3), 0.84 (d, ^3J(H–H) = 6.5, CH_3), 0.86 (d, ^3J(H–H) = 5.5), 0.89 (d, ^3J(H–H) = 6.7, CH_3), 0.7–1.05 (m), 1.10–1.90 (m), 4.87 (ddd, ^1J(P–H) = 325.4, ^3J(H–H) = 8.6, ^3J(H–H) = 5.1, 1 H, PH); mass spectrum (^{184}W), m/z 552 (M, 23); IR (decalin) ν (CO) 2060 (m), 1930 (vs) cm^{-1}. Anal. Calcd for $C_{19}H_{29}O_5PW$: C, 41.34; H, 5.25. Found: C, 41.59; H, 5.19.

7b: minor isomer, observed in the reaction mixture by ^{31}P NMR (C_6D_6) δ −52.9. The main ^{1}H NMR data were obtained from the **7a**/**7b** mixture (ratio 30:70) produced by direct alkylation of complex **3a** at room temperature (eq 4): ^{1}H NMR (400 MHz) (C_6D_6) δ 0.61 (d, ^3J(H–H) = 6.8, CH_3), 0.71 (d, ^3J(H–H) = 6.1, CH_3), 0.77 (d, ^3J(H–H) = 6.2, CH_3), 0.83 (d, ^3J(H–H) = 6.1, CH_3), 0.91 (d, ^3J(H–H) = 6.8, CH_3), 4.92 (dm, ^1J(P–H) = 324.9, ^3J(H–H) ≈ ^3J(H–H′) = 7, ^3J(H–H) = 2.3, PH).

Stereospecific Alkylation of 7a. tBuOK (1 mL, 1 M solution in THF) was added at −78 °C to a solution of complex **7a** (0.55 g, 1 mmol) in THF (5 mL). After a few minutes, 1.1 mmol of benzyl bromide (or iodomethane) was added at −78 °C. After 5 min, the reaction mixture was warmed to room temperature, and the final product was purified by chromatography with hexane as eluent.

8a: yield 0.4 g (77%), colorless oil; −24.75° ($c = 1.14$, $CHCl_3$); ^{31}P NMR (C_6D_6) δ 10.2 (^1J(P–^{183}W) = 234); ^{13}C NMR (C_6D_6) δ 16.02 (s, CH_3), 21.83 (s, CH_3), 22.70 (s, CH_3), 25.44–25.66 (unresolved m, 3C), 26.11 (s), 28.89 (d, ^2J(P–C) = 2.7, PCH_2CH), 33.39 (d, J(P–C) = 10.5), 34.92 (s), 37.14 (d, ^1J(P–C) = 18.8), 37.76 (s), 38.83 (d, ^1J(P–C) = 19.4), 41.30 (d, ^1J(P–C) = 17.2), 47.35 (s), 135.64 (d, ^2J(P–C) = 8.7), 198.44 (d, ^2J(P–C) = 6.7, CO_{cis}); ^{1}H NMR (400 MHz) (C_6D_6) δ 0.52 (d, ^3J(H–H) = 6.7, CH_3), 0.65 (d, ^3J(H–H) = 6.4, CH_3), 0.85 (m, 4 H), 0.86 (d, ^3J(H–H) = 5.9, CH_3), 0.96 (d, ^3J(H–H) = 6.6, CH_3), 1.07 (d, ^3J(H–H) = 6.3, CH_3), 1.25 (m, 4 H), 1.50–1.85 (m), 1.95–2.01 (m, 2 H), 3.18 (dd, *AB*, ^2J(AB) = 15.4, ^2J(P–H) = 1.7, PCH_2), 3.43 (dd, A*B*, ^2J(P–H) = 6.0, PCH_2).

9a: yield 0.42 g (75%), colorless oil; ^{31}P NMR (C_6D_6) −5.3 (^1J(P–^{183}W) = 232); ^{13}C NMR (C_6D_6) δ 16.13 (s, CH_3), 17.85 (d, ^1J(P–C) = 26.5, PCH_3), 21.71 (s, CH_3), 22.72 (s, CH_3), 25.12 (d, J(P–C) = 11.4), 25.7 (m, unresolved, 3C), 29.08 (d, ^2J(P–C) = 3.7), 33.58 (d, J(P–C) = 10.6), 34.66 (s), 36.81 (s), 41.84 (d, ^1J(P–C) = 20.3), 43.36 (d, ^1J(P–C) = 21.4), 47.02 (d, J(P–C) = 4.5), 198.30 (d, ^2J(P–C) = 6.7, CO_{cis}); 198.90 (d, ^2J(P–C) = 19.3, CO_{trans}); ^{1}H NMR (C_6D_6) δ 0.65 (d, ^3J(H–H) = 6.7, CH_3), 0.82 (d, ^3J(H–H) = 6.2, CH_3), 0.85 (d, ^3J(H–H) = 6.3, CH_3), 0.92 (d, ^3J(H–H) = 6.2, CH_3), 0.98 (d, ^3J(H–H) = 6.7, CH_3), 1.28 (d, ^2J(P–H) = 6.4, PCH_3), 1.10–2.05 (m); mass spectrum (^{184}W), m/z 566 (M, 17). Anal. Calcd for $C_{20}H_{31}O_5PW$: C, 42.44; H, 5.48. Found: C, 43.24; H, 5.67.

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Benzylation of 7 at Room Temperature. tBuOK (1 mL, 1 M solution in THF) was added at −78 °C to a solution of complex **7** (0.55 g, 1 mmol mixture **7a**/**7b**) in THF (5 mL). The reaction mixture was warmed to room temperature, and 1 mmol of benzyl bromide was then added. A ^{31}P NMR spectrum of the mixture showed a 90:10 ratio of the final products **8b** and **8a**. The major isomer **8b** was purified by column chromatography with hexane as eluent, followed by crystallization from pentane. A small sample of pure **8b** was recrystallized from pentane to obtain X-ray-suitable single crystals. **8b**/**8a**: yield 0.51 g (80%).

8b: colorless solid, mp 125 °C (hexane); $[\alpha]_D = -19.15°$ (c = 1.41, $CHCl_3$); ^{31}P NMR (C_6D_6) δ 18.16 ($^1J(P-^{183}W)$ = 236); ^{13}C NMR (C_6D_6) δ 16.06 (s, CH_3), 21.86 (s, CH_3), 22.65 (s, CH_3), 24.40 (s), 25.56, 25.68, 25.79, 26.11 (d, $^2J(P-C)$ = 8.1, 39.22 (s), 33.38 (d, $J(P-C)$ = 10.8), 34.92 (s), 35.77 (d, $^1J(P-C)$ = 17.4), 38.08 (s), 38.76 (d, $^1J(P-C)$ = 20.2), 41.18 (d, $^1J(P-C)$ = 15.2), 47.46 (d, $J(P-C)$ = 2.2), 129.10 (s), 130.81 (s), 130.88 (s), 135.71 (s, PCH_2C_{aryl}), 198.00 (d, $^2J(P-C)$ = 6.5, CO_{cis}), 198.61 (d, $^2J(P-C)$ = 21.2, CO_{trans}); ^1H NMR (400 MHz) (C_6D_6) δ 0.68 (d, $^3J(H-H)$ = 6.8, CH_3), 0.81 (d, $^3J(H-H)$ = 6.5, CH_3), 0.83 (d, $^3J(H-H)$ = 7.6, CH_3), 0.85 (d, $^3J(H-H)$ = 6.3, CH_3), 0.8–1.0 (m), 1.05 (d, $^3J(H-H)$ = 6.7, CH_3), 1.18 (m, 1 H), 1.22 (m, 1 H), 1.60–2.00 (m, 8 H), 2.19 (m, $^3J(H-H)$ = 6.8, 1 H), 3.27 (dd, *AB*, $^2J(AB)$ = 14.2, $^2J(P-H)$ = 4.0, PCH_2), 3.43 (dd, A*B*, $^2J(P-H)$ = 14.1, PCH_2), 7.08–7.18 (m, 5 H); mass spectrum (^{184}W), m/z 642 (M, 17); IR (toluene) ν (CO) 2060 (m), 1930 (vs) cm^{-1}. Anal. Calcd for $C_{26}H_{35}O_5PW$: C, 48.60; H, 5.45. Found: C, 48.57; H, 5.48.

Decomplexation of the $W(CO)_5$ Complexes 8b and 9a. (a) The tungsten complex **8b** (0.50 g) was heated with an excess of trimethylamine *N*-oxide dihydrate (9:1 ratio) in toluene (5 mL) at 100 °C for 3 h. Filtration of the solid phase, drying with $MgSO_4$, and evaporation of the solvent gave the pure oxide **10b**: yield 77%, colorless solid; ^{31}P NMR (C_6D_6) δ 42.4; ^{13}C NMR (C_6D_6) δ 16.07 (s), 21.77 (s), 22.92 (s), 23.99 (d, $J(P-C)$ = 4.0), 24.92, 25.06, 25.19, 25.41, 28.23 (s), 33.13 (d, $J(P-C)$ = 12.9), 34.61 (d, $^1J(P-C)$ = 60.1), 34.97 (s), 36.53 (d, $^1J(P-C)$ = 58.0), 36.82 (s), 40.08 (d, $^1J(P-C)$ = 62.5), 44.41 (s); ^1H NMR (400 MHz) (C_6D_6) δ 0.57 (dq, J = 5.0, 11.8, 1 H), 0.65 (dq, J = 2.6, 12.2, 1 H), 0.82 (d, $^3J(H-H)$ = 6.4, $CHCH_3$), 0.88 (d, $^3J(H-H)$ = 6.7, 3 H, $CHCHMe_2$), 0.90 (d, $^3J(H-H)$ = 7.1, 3 H, $CHCHMe_2$), 0.96 (d, $^3J(H-H)$ = 6.8, 3 H, PCH_2CHMe_2), 1.10 (d, $^3J(H-H)$ = 6.6, 3 H, PCH_2CHMe_2), 1.23 (m, *AB*, $J(AB)$ = 14.9, J = 6.3, 7.7, 1 H, PCH_2CH), 1.39 (m, 1 H, Me_2CHCH), 1.47–1.7 (m, 5 H), 2.08 (m, 1 H, PCH_2CHMe_2), 2.64 (dd, *AB*, $^2J(AB)$ = 14.5, $^2J(H-P)$ = 9.7, 1 H, PCH_2Ph), 2.91 (dd, A*B*, $^2J(H-P)$ = 14.5, 1 H, PCH_2Ph), 3.07 (m, $^3J(H-H)$ = 6.8, $^3J(H-H)$ = 2.6, 1 H, $CHCHMe_2$), 7.0–7.5 (m, 5 H, Ph); mass spectrum, m/z 334 (M, 100). Anal. Calcd for $C_{21}H_{35}OP$: C, 75.45; H, 10.50. Found: C, 75.39; H, 10.48.

(b) Pyridinium tribromide (1 mmol) was added to a solution of complex **9a** (1 mmol) in $CHCl_3$ (5 mL) at −40 °C. CO release was observed while the solid reagent dissolved. The reaction mixture was warmed to room temperature, *N*-methylimidazole (0.4 mL, 5 mmol) and water (1 mL) were added, and the mixture was heated at 45 °C for 15 min. The reaction mixture was directly filtered through a short Celite column, washed with water, and dried with $MgSO_4$. Oxide **11a** was purified by chromatography with hexane/$CHCl_3$ (50:50) as eluent. **11a**: yield 0.12 g (46%), colorless oil; ^{31}P NMR (C_6D_6) δ 42.85; ^{13}C NMR (C_6D_6) δ 12.57 (d, $^1J(P-C)$ = 61.9, PCH_3), 16.07 (s), 21.83 (s), 22.84 (s), 23.69 (d, $J(P-C)$ = 3.1), 24.82 (d, $J(P-C)$ = 7.5), 25.02 (s), 25.23 (d, $J(P-C)$ = 3.9), 28.31 (s), 33.20 (d, $J(P-C)$ = 12.7), 34.86 (s), 36.64 (s), 38.01 (d, $^1J(P-C)$ = 65.2), 41.32 (d, $^1J(P-C)$ = 65.0), 44.25 (s); ^1H NMR (400 MHz) (C_6D_6) δ 0.52 (dq, J = 6.0, 11.9, 1 H), 0.70 (m, J = 2.5, 11.9, 1 H), 0.81 (d, $^3J(H-H)$ 6.5, CH_3CH), 0.93 (d, $^3J(H-H)$ = 6.7, 3 H, $CHCHMe_2$), 0.95 (d, $^3J(H-H)$ = 6.5, 3 H, $CHCHMe_2$), 1.03 (d, $^3J(H-H)$ = 6.7, 3 H, CH_2CHMe_2), 1.04 (d, $^3J(H-H)$ = 6.8, 3 H, CH_2CHMe_2), 1.07 (d, $^2J(P-H)$ = 11.9, PCH_3), 1.1–1.2 (m), 1.3 (m, 1 H, $CHCHMe_2$), 1.41 (m, *AB*, $^2J(AB)$ = 14.8, J = 11.1, 6.1, PCH_2), 1.5–1.7 (m), 2.12 (m, 1H, CH_2CHMe_2), 2.87 (m, $^3J(H-H)$ 6.8, $^3J(H-H)$ = 2.6, $CHCHMe_2$); mass spectrum, m/z 258 (M, 45).

Cycloaddition of in Situ Generated Phosphaalkene–$W(CO)_5$ Complexes with Cyclopentadiene. A solution of [L-menthyl(diethoxyphosphoryl)-phosphine]pentacarbonyltungsten (**5**) (1 mmol) in THF (3 mL) was cooled to −78 °C. nBuLi (0.7 mL, 1.6 M solution in hexane) was then added. The reaction mixture was warmed to room temperature, and an excess of cyclopentadiene (1.0 mL, freshly distilled) was added. The appropriate aldehyde (1.1 mmol) was then added slowly at room temperature. The reaction was instantaneous. After evaporation and extraction with ether, the final product was purified by chromatography on a silica gel column with hexane/CH_2Cl_2 (95:5) as eluent.

12: yield 0.33 g (50%), colorless oil; ^{31}P NMR (C_6D_6) δ 41.0 ($^1J(P-^{183}W)$ = 235); ^{13}C NMR (C_6D_6) δ 16.28 (s, CH_3), 21.71 (s, CH_3), 22.76 (s, CH_3), 25.22 (d, $J(P-C)$ = 10.8), 28.97 (d, $J(P-C)$ = 3.8), 33.42 (d, $J(P-C)$ = 11.8), 34.72 (s), 37.95 (s), 43.84 (d, $J(P-C)$ = 17.0), 45.22 (d, $J(P-C)$ = 3.7), 45.69 (d, $J(P-C)$ = 15.0), 47.85 (d, $J(P-C)$ = 14.8), 50.48 (d, $J(P-C)$ = 20.7), 52.14 (s), 121.91 (s), 123.76 (d, $J(P-C)$ = 4.6), 135.00 (d, $J(P-C)$ = 10.3, CH=CH), 136.23 (s), 137.35 (d, $J(P-C)$ = 5.8, CH=CH), 149.80 (s), 160.57 (d, $^2J(P-C)$ = 4.9, C(Py)), 198.08 (d, $^2J(P-C)$ = 7.2, CO_{cis}), 198.91 (d, $^2J(P-C)$ = 23.7, CO_{trans}); ^1H NMR (C_6D_6) (400 MHz) δ 0.77 (d, $^3J(H-H)$ = 6.6, CH_3), 0.89 (d, $^3J(H-H)$ = 6.4, 3 H, CH_3), 0.96 (d, $^3J(H-H)$ = 6.7, 3 H, CH_3), 1.1–1.7 (m, 9 H), 1.91 (m, $^3J(H-H) \approx 6.6$, $CHMe_2$), 2.82 (m, 2 H), 3.02 (dd, J = 10.2, 7.2), 3.37 (d, $^2J(H-P)$ = 14.9, 1 H), 5.82 (s, 2 H, CH=CH), 6.68 (t, $^3J(H-H) \approx 6.0$, CH(β)), 6.84 (d, $^3J(H-H)$ = 7.8, CH(β')), 7.06 (t, $^3J(H-H) \approx 7.5$, CH(γ)), 8.49 (d, $^3J(H-H)$ = 4.0, CH(α)); mass spectrum, (^{184}W) m/z 623 (M − CO, 30); IR (toluene) ν (CO) 2070 (m), 1930 (vs) cm^{-1}. Anal. Calcd for $C_{26}H_{30}NO_5PW$: C, 47.94; H, 4.64. Found: C, 47.66; H, 4.59.

13: yield 0.45 g (67%), colorless solid; mp 169 °C (hexane); $[\alpha]_D$ = −123.3° (c = 1.33, $CHCl_3$); ^{31}P NMR (C_6D_6) δ 41.8; ^{13}C NMR (C_6D_6) δ 16.34 (s, CH_3), 21.76 (s, CH_3), 22.78 (s, CH_3), 24.32 (s, CH_3-picoline), 25.34 (d, $J(P-C)$ = 10.9), 28.56 (s), 33.50 (d, $J(P-C)$ = 11.5), 34.81 (s), 38.15 (s), 43.96 (d, $J(P-C)$ = 17.0), 45.30 (s), 45.89 (d, $J(P-C)$ = 14.6), 48.09 (d, $J(P-C)$ = 14.9), 50.80 (d, $J(P-C)$ = 19.4), 51.41 (s), 120.48 (s), 121.50 (s), 134.91 (d, $J(P-C)$ = 10.4, CH=CH), 136.60 (s), 137.38 (d, $J(P-C)$ = 6.0, CH=CH), 158.74 (s, CCH_3), 160.22 (d, $J(P-C)$ = 4, C(Py)), 197.91 (d, $^2J(P-C)$ = 6.3, CO_{cis}), ^1H NMR (C_6D_6) (400 MHz) δ 0.82 (d, $^3J(H-H)$ = 6.6, CH_3), 0.90 (d, $^3J(H-H)$ = 6.4, 3 H, CH_3), 1.02 (d, $^3J(H-H)$ = 6.7, 3 H, CH_3), 1.0 (m), 1.1–1.8 (m, 7 H), 2.30 (m, $^3J(H-H) \approx 6.5$, $CHMe_2$), 2.41 (s, CH_3-picoline), 2.79 (dd, J = 10.0, 6.8, 1 H), 2.9 (m, 2 H), 3.35 (d, $^2J(H-P)$ = 14.6, 1 H), 5.80 (m, 2 H, CH=CH), 6.64 (d, $^3J(H-H)$ = 7.7, 1 H, CH(β)), 6.76 (d, $^3J(H-H)$ = 7.7, 1 H, CH(β')), 7.08 (t, CH(γ)); mass spectrum (^{184}W), m/z 637 (M − CO, 45); IR (toluene) ν (CO) 2060 (m), 1930 (vs) cm^{-1}. Anal. Calcd for $C_{27}H_{32}NO_5PW$: C, 48.74; H, 4.85. Found: C, 48.96; H, 4.81.

14: yield 0.50 g (73%), colorless solid; ^{31}P NMR (C_6D_6) δ 41.4 ($^1J(P-^{183}W)$ = 230); ^{13}C NMR (C_6D_6) δ 16.52 (s, CH_3), 21.98 (s, CH_3), 22.87 (s, CH_3), 25.32 (d, $J(P-C)$ = 11.1), 28.95 (s), 33.44 (d, $J(P-C)$ = 11.4), 34.41 (s), 38.56 (s), 41.74 (d, $J(P-C)$ = 20.6), 43.62 (d, $J(P-C)$ = 17.1), 44.69 (s), 46.89 (d, $J(P-C)$ = 13.8), 47.82 (d, $J(P-C)$ = 15.2), 53.97 (s), 54.97 (s), 110.76 (s), 120.88 (s), 130.61 (d, $J(P-C)$ = 4.1), 134.36 (d, $J(P-C)$ = 9.8, CH=CH), 138.11 (d, $J(P-C)$ = 5.7, CH=CH), 157.30 (d, $^3J(P-C)$ = 5.0), 198.68 (d, $^2J(P-C)$ = 7.2, CO_{cis}); ^1H NMR (C_6D_6) (400 MHz) δ 0.79 (d, $^3J(H-H)$ = 6.5, 3 H, CH_3), 0.89 (d, $^3J(H-H)$ = 6.8, 3 H, CH_3), 0.91 (d, $^3J(H-H)$ = 6.4, 3 H, CH_3), 0.99 (m, 2 H), 1.15 (m, 1 H), 1.40–1.85 (m, 8 H), 2.32 (dd, $^2J(H-H)$ = 10.8, $^3J(H-P)$ = 4.4, 1 H, CH_2(exo)), 2.67 (d, $^3J(P-H)$ = 9.7, PCH(Ar)CH), 3.27 (s, 3 H, OCH_3), 3.32 (d, $^2J(P-H)$ = 15.0, PCHCH=), 3.59 (dd, $^2J(P-H)$ = 10.2, $^3J(H-H)$ = 1.6, 1 H, PCHAr), 5.77 (m, 1 H, PCHCH=), 5.90 (m, 1 H, PCHCH=CH), 6.48 (d, $^3J(H-H)$ = 8.2, CH ortho), 6.98 (t, $^3J(H-H) \approx 7.9$, 1 H), 7.08 (t, $^3J(H-H) \approx 7.9$, 1 H), 7.78 (d, $^3J(H-H)$ = 7.7, CH meta); mass spectrum (^{184}W), m/z 679 (M − 1, 12); IR (toluene) ν (CO) 2060 (m), 1920 (vs) cm^{-1}. Anal. Calcd for $C_{28}H_{33}O_6PW$: C, 49.43; H, 4.92. Found: C, 49.38; H, 4.89.

One-Pot Synthesis of the Molybdenum Complex 16. A solution of (L-menthylphosphine)$Mo(CO)_5$ (**3b**) (8.2 g, 20 mmol) in THF (20 mL) was added at −78 °C to a solution containing 40 mmol of $(TMS)_2NLi$ in THF (4.2 mL of hexamethyldisilazane and 25 mL of nBuLi 1.6 M in hexane). After about 10 min, 2-chloro-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane (20 mmol in 20 mL THF) was added at −78 °C. The reaction mixture was warmed to room temperature, and an excess of cyclopentadiene (5 mL) and then slowly 20 mmol of 2-pyridinecarboxaldehyde were added. After evaporation, extraction with ether, and filtration, a solution of crude **15** was obtained (^{31}P NMR (THF) δ 60.24 ppm). Small amounts of the chelate complex **16** may be present at this stage of the reaction. Complex **15** was directly converted to the more stable complex **16** by heating at 60 °C for 1 h in benzene solution. The final product was purified by chromatography on a silica gel column with an hexane/benzene gradient as eluent.

16: yield 2.9 g (27%), brown solid; mp 164 °C dec; $[\alpha]_D$ = −79.3° (c = 1.28, $CHCl_3$); ^{31}P NMR ($CHCl_3$) δ 61.1; ^{13}C NMR ($CDCl_3$) δ 15.54 (s, CH_3), 20.71 (s, CH_3), 22.65 (s, CH_3), 24.07 (d, $J(P-C)$ = 11.0), 28.32 (d, $J(P-C)$ = 4.2), 33.25 (d, $J(P-C)$ 13.0), 34.38 (s), 37.68 (d, $J(P-C)$ = 7.3), 39.46 (d, $J(P-C)$ = 12.3), 41.28 (d, $J(P-C)$ = 13.3), 44.32, 44.38, 44.43, 44.62, 53.01 (d, $J(P-C)$ = 15.5), 55.01 (s), 121.87 (s), 125.32 (d, $J(P-C)$ = 8.0), 134.18 (d, $J(P-C)$ = 5.9), 135.83 (d, $J(P-C)$ = 9.6), 138.88 (s), 155.01 (d, $J(P-C)$ = 4.7), 165.89 (d, $J(P-C)$ = 14.1, C(py)), 209.67 (d, $^2J(P-C)$ = 9.0, CO), 210.26 (d, $^2J(P-C)$ = 9.1, CO), 215.71 (d, $^2J(P-C)$ = 32.4, CO trans to P), 222.20 (d, $^2J(P-C)$ = 7.3, CO); ^1H NMR ($CDCl_3$) (400 MHz) δ 0.66 (d, $^3J(H-H)$ = 6.7, CH_3), 0.82 (d, $^3J(H-H)$ = 6.7, CH_3), 0.88 (m, 2 H), 0.96 (d, $^3J(H-H)$ = 6.0, CH_3), 1.25–1.40 (m, 3 H), 1.47 (m, 1 H), 1.6–1.8 (m, 9 H), 3.10 (d, $J(P-H)$ = 7.8, 1 H), 3.37 (d, $J(P-H)$ = 5.7, 1 H), 3.50 (d, $J(P-H)$ = 14.7, 1 H), 6.31 (m, 1 H, =CH), 6.36 (m, 1 H, =CH), 7.03 (t,

^3J(H-H) ≈ 7.0, 1 H), 7.42 (d, ^3J(H-H) ≈ 7.8, 1 H), 7.70 (t, ^3J(H-H) = 7.6, 1 H), 9.00 (dd, ^3J(H-H) = 5.6, J = 1.3, 1 H); mass spectrum (^{96}Mo), m/z 535 (M, 19); IR (toluene) ν (CO) 2010 (m), 1890 (vs), 1855 (vs). Anal. Calcd for $C_{25}H_{30}NO_4PMo$: C, 56.10; H, 5.61. Found: C, 55.88; H, 5.62.

Decomplexation of the Mo(CO)$_4$ Complex 16. Complex **16** (1 mmol) and diphos (1 mmol) were heated at 100 °C for 2.5 h in toluene (5 mL) under argon. After evaporation and extraction with pentane, the phosphine **17** was purified by filtration through a short Celite column. **17**: yield 0.26 g (80%), colorless oil; ^{31}P NMR (C_6D_6) δ 9.06; ^{1}H NMR (C_6D_6) (400 MHz) δ 0.77 (d, ^3J(H-H) = 6.7, CH_3), 0.81 (d, ^3J(H-H) = 6.7, CH_3), 0.89 (d, ^3J(H-H) = 6.3, CH_3), 1.0-1.9 (m), 2.48 (t, J(H-H) ≈ J(H-P) = 8.9, 1 H), 2.86 (d, J = 3.07, 1 H), 3.09 (s, 1 H), 3.23 (d, J(H-P) = 25.3, 1 H), 6.0-6.1 (m, 2 H, CH=CH), 6.61 (t, ^3J(H-H) ≈ 6.1, 1 H), 7.10 (t, ^3J(H-H) ≈ 6.7, 1 H), 7.29 (d, ^3J(H-H) = 7.8, 1 H), 8.51 (d, ^3J(H-H) = 4.8, 1 H); mass spectrum, m/z 327 (M, 17), 188 (M - Men, 100).

X-ray Structure Determinations. Single crystals of both compounds were grown at 4 °C from hexane solutions. Data were collected at 20 ± 1 °C on an Enraf Nonius CAD4 diffractometer; Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator were used. The crystal structures were solved and refined using the Enraf Nonius supplied SDP package. Direct methods provided a suitable starting point, and the initial model was obtained from difference Fourier maps. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms.

Compound **8b**: $C_{26}H_{35}O_5PW$ crystallises in space group $P6_5$, a = 10.998 (1) Å, c = 40.064 (4) Å; V = 4195.47 (2.48) Å^3; Z = 6; d_{calcd} = 1.525 g/cm^3; μ = 43.0 cm^{-1}; F(000) = 1920. A total of 4175 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$ of which 2326 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 1849 for solution and refinement. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.037, R_w = 0.056, G.O.F. = 1.11. For the enantiomeric space group, these factors were respectively equal to 0.042, 0.062, and 1.22.

Compound **13**: $C_{27}H_{32}NO_5PW$ crystallises in space group $P2_1$, a = 11.352 (1) Å, b = 14.419 (1) Å; c = 17.007 (2) Å, β = 94.30 (1)°; V = 2775.95 (79) Å^3; Z = 4; d_{calcd} = 1.592 g/cm^3; μ = 43.4 cm^{-1}; F(000) = 1320. A total of 8356 unique reflections were recorded in the range $2° \le 2\theta \le 60.0°$; 5299 of these were considered as observed and used for structure solution and refinement. A non-Poisson weighting scheme was applied with a p factor equal to 0.06. The final agreement factors were R = 0.031, R_w = 0.039, G.O.F. = 1.00. For the enantiomeric structure, these factors were respectively equal to 0.048, 0.068, and 1.754.

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Supplementary Material Available: Tables of crystallographic data, positional and displacement parameters, and bond distances and angles (15 pages); tables of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

Can Polymerization Trap Intermediates in 1,3-Dipolar Cycloadditions?

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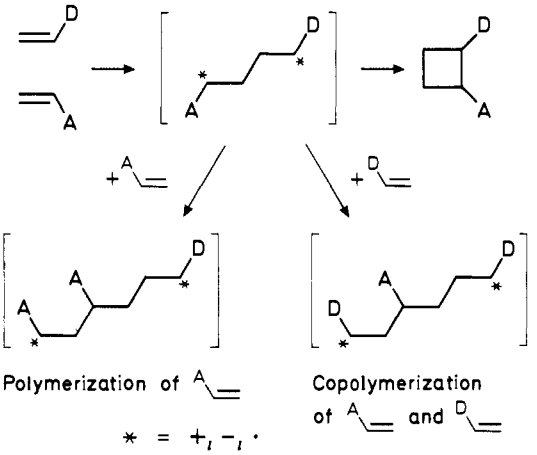
Abstract: 2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-methylide (TTCM) is a nucleophilic 1,3-dipole which is known to undergo two-step cycloadditions to very electron poor olefins. When this 1,3-dipole is generated from its precursor, the 1,3,4-thiadiazoline **7**, in acrylonitrile or acrylic esters at 45 °C, only cycloaddition and no polymerization is observed, suggesting a concerted cycloaddition. Small amounts of polymers were observed alongside the cycloadducts with nitroethylene, methacrylonitrile, and methacrylates. Most cycloadducts were produced as regioisomeric mixtures. The reaction of TTCM with benzylidenemalononitrile, a nonpolymerizable olefin, is nonconcerted and furnished in THF and 1 vol % methanol or 3 vol % water a 7-membered lactim methyl ether or lactam formed by interception of a ketene imine. The observed polymerizations are radical in nature and are proposed to be initiated by a minor contribution of a diradical intermediate to the cycloaddition reaction.

Introduction

The evidence for the concerted character of certain cycloadditions is necessarily *indirect* and centers on the exclusion of intermediates.[2] The experimental criteria for diradical or zwitterionic intermediates are based on the phenomena of *kinetic competition*.[3] The interception of a putative intermediate must be competitive in rate to its ring closure. Nonstereospecificity is observed when bond rotation in the intermediate successfully competes with the generally very rapid ring closure. Rate measurements can also speak in favor of or against concertedness. Sometimes substituent effects on the rate allow one to distinguish between early, i.e., reactant-like transition states, and late ones, which are structurally close to intermediates.[4] The dependence of rate on solvent polarity is informative about the amount of charge separation in the activation process.

Scheme I



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