# Controlling the Number of Metal Sites to Which a Di(tertiary phosphine) Coordinates in Group 6 Metal Carbonyls[1]

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**Abstract:** Reactions of $(OC)_5WPPh_2CH{=}CH_2$ with $PPh_2H$ under free-radical or base-catalyzed conditions yield $(OC)_5WPPh_2CH_2CH_2PPh_2$. The reaction of $(OC)_5WPPh_2H$ with $PPh_2CH{=}CH_2$ under free-radical conditions also gives this product, but in the presence of base only the chelated product, $(OC)_4W(PPh_2CH_2CH_2PPh_2)$, is formed. The chelation occurs because the intermediate $(OC)_5WPPh_2^-$ loses CO easily in the presence of $PPh_2CH{=}CH_2$ to form $(OC)_4W(PPh_2CH{=}CH_2)(Ph_2P)^-$, which subsequently undergoes cyclization. Reactions of *trans*-$(OC)_4M(PPh_2CH{=}CH_2)_2$ (M = Cr, Mo, W) with 2 mol of $PPh_2H$, under base-catalyzed conditions, yield *trans*-$(OC)_4M(PPh_2CH_2CH_2PPh_2)_2$, complexes in which two $PPh_2CH_2CH_2PPh_2$ molecules are coordinated as monodentate ligands. When these reactions are carried out under free-radical conditions, isomerization and cyclization result to give $(OC)_4M[PPh_2CH_2CH_2CH(PPh_2)CH_2PPh_2]$. The tridentate molecule is present as a bidentate ligand and forms a six-membered ring. The reaction of *cis*-$(OC)_4W(PPh_2H)_2$ with $Ph_2PCH{=}CH_2$ in the presence of base yields $(OC)_4W(PPh_2CH_2CH_2PPh_2)$ while in the presence of a free radical it gives *trans*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$. The isomerization which occurs in the latter reaction appears to proceed intramolecularly. All complexes are characterized by $^{31}P$ NMR. The reactions provide a method of synthesizing complexes in which di- and tri(tertiary phosphines) are not fully coordinated.

The inertness to substitution of group 6 metal carbonyls suggests the possibility of synthesizing many complexes of these metals in which $Ph_2PCH_2CH_2PPh_2$ serves as a monodentate ligand. Complexes of this type are somewhat rare principally because conditions normally employed for complexation favor the formation of chelated products. In this work we have explored catalytic methods of preparing $(OC)_5WPPh_2CH_2CH_2PPh_2$ and $(OC)_4M(PPh_2CH_2CH_2PPh_2)_2$ (M = Cr, Mo, W) by addition of $PPh_2H$ to coordinated diphenylvinylphosphine and by addition of coordinated diphenylphosphine to $PPh_2CH{=}CH_2$.

## Results and Discussion

The reaction of $(OC)_5WPPh_2CH{=}CH_2$ with $PPh_2H$ in THF in the presence of potassium *tert*-butoxide leads to the formation of $(OC)_5WPPh_2CH_2CH_2PPh_2$ in good yield. The mechanism for this reaction undoubtedly parallels that proposed previously for the base-catalyzed addition of secondary phosphines to vinylphosphines.[3,4] It is clear that the carbonyl groups of the complex are less susceptible to attack by the nucleophile $Ph_2P^-$ than is the vinyl group of the coordinated phosphine.[5]

The addition reaction was found to be equally productive when the base catalyst was replaced by the free-radical catalyst, 2,2′-azobisisobutyronitrile (AIBN), which is consistent with the mechanism proposed for the free-radical addition of secondary phosphines to vinylphosphines.[6]

To determine if the reaction proceeds equally well when $Ph_2PH$ is coordinated we examined the free radical catalyzed addition of $(OC)_5WPPh_2H$ to $PPh_2CH{=}CH_2$. The reaction proceeds very rapidly at 80 °C as evidenced by immediate solidification of the reaction mixture.

To our surprise we discovered that $(OC)_5WPPh_2H$ does not react with $PPh_2CH{=}CH_2$ in the presence of potassium *tert*-butoxide to give $(OC)_5WPPh_2CH_2CH_2PPh_2$. From this reaction only chelated product, $(OC)_4W(PPh_2CH_2CH_2PPh_2)$, was isolated. A mechanism to account for this reaction cannot involve $(OC)_5WPPh_2CH_2CH_2PPh_2$ since chelation does not occur when this compound is heated in refluxing THF in the presence of potassium *tert*-butoxide. One might expect $(OC)_5WPPh_2^-$, which undoubtedly forms, to interact with $PPh_2CH{=}CH_2$ to form the anionic $(OC)_5WPPh_2CH_2\bar{C}HPPh_2$. However, we have evidence which suggests that this species is not an intermediate. It appears that, when $PPh_2^-$ is in the coordination sphere, it labilizes a carbonyl group. This is not without precedent since it is well-known that group 6 anionic complexes, $(OC)_5MX^-$ (X = halide), readily give up CO in the presence of tertiary phosphines.[7] Experimental evidence for the displacement of CO from $(OC)_5WPPh_2^-$ is provided by isolation of *cis*-$(OC)_4W(PPh_3)(Ph_2PH)$ from the reaction of $(OC)_5WPPh_2H$ with $PPh_3$ in the presence of base.[8] This complex, unlike its $PPh_2CH{=}CH_2$ analogue, reacts no further. We propose the mechanism in Scheme I to account for the observed chelation. Support for the cyclization step is found in the work of Treichel and Wong, who have shown that *cis*-$(OC)_4Cr(PPh_2CH{=}CH_2)(PPh_2H)$, synthesized by an alternate route, cyclizes in the presence of base.[9]

The reactions of $(OC)_5WPPh_2CH{=}CH_2$ with $PPh_2H$ and of $(OC)_5WPPh_2H$ with $PPh_2CH{=}CH_2$ in the presence of potassium *tert*-butoxide and AIBN are summarized in Table I.

For a complex to contain two $Ph_2PCH_2CH_2PPh_2$ monodentate ligands is rare. King and Saran have isolated $(\eta^5\text{-}C_5H_5)Mo(PPh_2CH_2CH_2PPh_2)_2[C{=}C(CN)_2]_2Cl$ from a substitution reaction.[10] However, most attempts to prepare

**Scheme I**

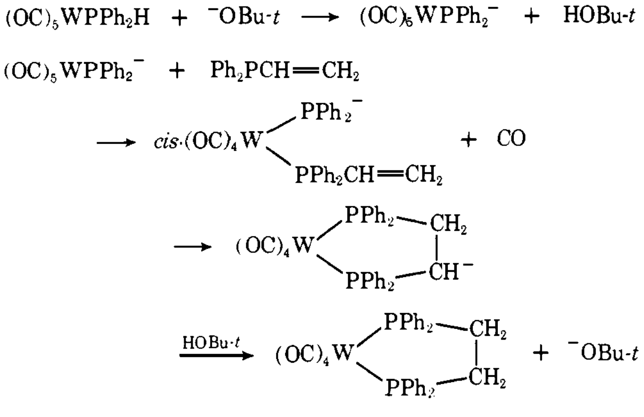

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**Table I.** Preparative Data for $(OC)_5WPPh_2CH_2CH_2PPh_2$

| reactants | | catalyst | yield, % |
|---|---|---|---|
| $(OC)_5WPPh_2CH{=}CH_2$ | $Ph_2PH$ | KOBu-*t* | 72 |
| $(OC)_5WPPh_2CH{=}CH_2$ | $Ph_2PH$ | AIBN | 82 |
| $(OC)_5WPPh_2H$ | $Ph_2PCH{=}CH_2$ | KOBu-*t* | 0 |
| $(OC)_5WPPh_2H$ | $Ph_2PCH{=}CH_2$ | AIBN | 75 |

complexes of this type by substitution lead predictably to chelation.

The addition of $PPh_2H$ to *trans*-$(OC)_4M(Ph_2PCH{=}CH_2)_2$ (M = W, Mo, Cr) to give *trans*-$(OC)_4M(PPh_2CH_2CH_2PPh_2)_2$ was easily accomplished with catalytic potassium *tert*-butoxide.[11] Our attempts to convert *cis*-$(OC)_4W(PPh_2H)_2$ into *cis*-$(OC)_4W(PPh_2CH_2CH_2Ph_2)_2$ were unsuccessful. The base-catalyzed reaction of *cis*-$(OC)_4W(PPh_2H)_2$ with $PPh_2CH{=}CH_2$ gave only the chelated product $(OC)_4W(PPh_2CH_2CH_2PPh_2)$. This can be explained by assuming that the $Ph_2P^-$ in the coordination sphere of $[(OC)_4W(PPh_2H)(Ph_2P)]^-$ labilizes the other ligands as was observed for $[(OC)_5WPPh_2]^-$. When the free-radical approach was applied to the same reaction, addition across the double bond took place but was accompanied by isomerization to give the trans derivative:

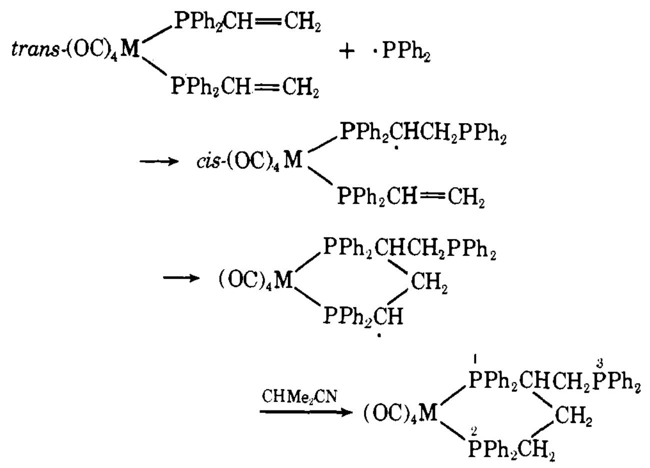
$$cis\text{-}(OC)_4W(PPh_2H)_2 + 2PPh_2CH{=}CH_2 \xrightarrow{AIBN} trans\text{-}(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$$

No evidence for chelated product was found. Some chelation would be expected if this isomerization proceeds by a dissociative mechanism unless dissociation followed by rearrangement and association is faster than dissociation followed by chelation. An intramolecular isomerization may be operative here, precedent for which is found in the case of *trans*-$(OC)_4W(CS)(^{13}CO)$, which has been shown to isomerize to cis intramolecularly.[12]

The $^{31}P$ NMR spectra of $(OC)_4M(PPh_2CH_2CH_2PPh_2)_2$ establish the presence of two $PPh_2CH_2CH_2PPh_2$ groups coordinated as monodentate ligands. The free phosphine is found upfield from 85% $H_3PO_4$ at about −12 ppm while the coordinated phosphorus is substantially downfield from the reference. The observed chemical shifts are consistent with those reported for other monoligate monometallic systems.[3,13,14] In the case of *trans*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$ coordination of one phosphorus for each ligand is confirmed by the presence of $^{183}W$ satellites.

The $^{31}P$ spectra are of special interest because they provide direct measurement of phosphorus–phosphorus coupling through a metal atom. The proton-decoupled phosphorus spectra may be classified as AA′XX′. Each spectrum has two doublets of separation $N(^3J_{PP} + {}^5J_{PP})$, one in the X and one in the A part, which represent half the total intensity. A pair of inner lines and a pair of outer lines in each part account for the other half of the intensity. The separation between an outer line and the first inner line is $^2J_{PP}$. While $^2J_{PP}$ has been determined for a variety of cis and trans isomers of group 6 complexes in which the phosphorus ligands are chemically equivalent, few if any of these studies involve ligands with phenyl substituents. Absolute values of $^2J_{PP}$ for the trans complexes of chromium, molybdenum, and tungsten are 26.0, 55.8, and 54.3 Hz, respectively. The much smaller $^2J_{PP}$ value for chromium is characteristic of other reported trans complexes as well. Spectral data for *cis*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$, which appeared as a minor impurity in a sample of impure *trans*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$, revealed a $^2J_{PP}$ value of 21.3 Hz. Other reported cis and trans pairs of tungsten complexes also show the trans isomer to have a larger $^2J_{PP}$ than the cis.[15]

**Scheme II**



I, M = W
II, M = Cr
III, M = Mo

The reaction of *trans*-$(OC)_4W(PPh_2CH{=}CH_2)_2$ with 2 mol of $Ph_2PH$ under free-radical conditions does not produce *trans*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$ but rather an air-sensitive cyclic product (I) (Scheme II). The absence of any product with $PPh_2H$ in the coordination sphere and the absence of chelated $PPh_2CH_2CH_2PPh_2$ suggests again that the isomerization proceeds by an intramolecular route.

The structure of I was established with $^{31}P$ NMR. The complex contains three chemically nonequivalent phosphorus atoms and the proton-decoupled $^{31}P$ spectrum represents an AMX spin system with three phosphorus-phosphorus coupling constants, $^2J_{PP}$, $^3J_{PP}$, and $^5J_{PP}$. The chemical shift at −20 ppm can easily be assigned to phosphorus atom 3, which is not coordinated to the metal. The observed chemical shift is very close to the calculated value of −21 ppm which is obtained from the sum of the respective group contributions for the two phenyl groups (−6 ppm) and an "isobutyl" group (−15 ppm).[16] The chemical shifts +17.7 and +4.0 ppm can be assigned to phosphorus atoms 1 and 2, respectively. Grim and co-workers have shown that the chemical shifts of coordinated phosphorus atoms are much farther downfield for five-membered rings than for six-membered rings. For $(OC)_4W(PPh_2CH_2CH_2PPh_2)$ a chemical shift of +40 ppm was recorded, whereas for $(OC)_4W(PPh_2CH_2CH_2CH_2PPh_2)$ a value of 0 ppm was found. The structure around the phosphorus atom 2 in I resembles the structure around each phosphorus atom in Grim's six-membered ring and supports our assignment. Tungsten-phosphorus coupling constants for I were found to be 221.1 ($J_{WP1}$) and 226.5 ($J_{WP2}$) Hz. These values do not clearly distinguish between the two possible ring structures since reported coupling constants for the five- and six-membered rings are 231 and 222 Hz, respectively.[17] The most convincing evidence in support of the six-membered ring is provided by the value of $^2J_{PP}$ (21.5 Hz). It has been proposed that the observed phosphorus-phosphorus coupling constant for a chelated complex will be the sum of two contributions—coupling through the ligand backbone and coupling through the metal.[18] Based on data from a number of tungsten complexes, $^2J_{PP}$ values of 22 Hz for six-membered rings and 4 Hz for five-membered rings have been assigned. For six-membered rings it is assumed that coupling through the backbone is zero so the full 22 Hz is attributed to coupling through the metal. The argument appears valid in light of the fact that $^2J_{PP}$ was found to be 21.3 Hz in *cis*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$ (no possible backbone contribution) and 21.5 Hz in our six-membered ring system. Furthermore, ${}^2J_{PP}$ values for the cyclic chromium and molybdenum complexes II and III are 39 and 28 Hz, respectively, which is consistent with the values of 41 and 28 Hz predicted for six-membered rings. Predicted values for five-membered rings for chromium and molybdenum complexes are 12 and 5 Hz, respectively. Constants for the long-range coupling between phosphorus atoms 2 and 3 are 3.6, 3.7, and 4.9 Hz for the tungsten, molybdenum, and chromium complexes, respectively. Phosphorus-phosphorus coupling over five bonds in systems in which multiple bonding is not present is generally not observed.[19]

Air oxidation of I yields the expected phosphine oxide. The ${}^{31}P$ chemical shift for phosphorus atom 3, which appeared at −20.1 ppm for I, appears for the oxide at +32.2 ppm, consistent with chemical shifts for reported phosphine oxides.[20] As would be expected, the chemical shifts and coupling constants associated with the two coordinated phosphorus atoms change little upon oxide formation.

The reaction of *trans*-$(OC)_4Cr(PPh_2CH{=}CH_2)_2$ with $PPh_2H$ in the presence of AIBN gave a 2:1 mixture of II and *trans*-$(OC)_4Cr(PPh_2CH_2CH_2PPh_2)_2$ as shown by ${}^{31}P$ NMR. The reaction of *trans*-$(OC)_4Mo(Ph_2PCH{=}CH_2)_2$ with $PPh_2H$ in the presence of AIBN gave III, $(OC)_4Mo(PPh_2CH_2CH_2PPh_2)$, and free $Ph_2PCH_2CH_2PPh_2$ in approximately equal proportions. It appears that *trans*-$(OC)_4Mo(PPh_2CH_2CH_2PPh_2)_2$ is unstable under the reaction conditions with respect to diphos expulsion and chelation.

Chemical investigations of polydentate phosphorus ligands quite naturally have been focused on their chelating properties. There are, however, interesting synthetic possibilities for complexes in which a ligand is not fully coordinated. For example, the availability of these complexes as starting materials greatly enhances the ease with which two or more different metal atoms can be introduced into a single coordination compound.[20,21] Further, complexes in which a ligand is not fully coordinated contain a reactive phosphorus site upon which organic reactions can be carried out.[22]

## Experimental Section

**Physical Measurements.** ${}^{31}P$ NMR spectra were recorded at 40.5 MHz and ${}^{13}C$ spectra at 25.2 MHz on a Varian XL-100 NMR spectrometer equipped with Fourier transform and a pulsed deuterium lock. The ${}^{13}C-{}^{1}H$ and ${}^{31}P-{}^{1}H$ couplings were eliminated using broad-band ${}^{1}H$ noise-modulated decoupling. Phosphoric acid (85%) in a 1.0-mm capillary was used as an external reference for the ${}^{31}P$ NMR spectra, and $Me_4Si$ was used as the internal reference for the ${}^{13}C$ NMR spectra. $CDCl_3$ was used for solvent and lock. ${}^{31}P$ NMR chemical shifts are reported with positive values downfield from the reference.

Infrared spectra in the carbonyl region were recorded with a Perkin-Elmer 337 infrared spectrometer and expanded with an E-H Sargent recorder. The data, obtained from chloroform solutions, are considered accurate to $\pm 2$ cm$^{-1}$.

Microanalyses and molecular weights were performed by Galbraith Laboratories, Knoxville, Tenn.

**Materials.** Diphenylvinylphosphine, diphenylphosphine, and the metal carbonyls were purchased from Pressure Chemical Co. and used without further purification. All reactions were carried out under a nitrogen atmosphere.

$(OC)_5WPPh_2CH{=}CH_2$ (79%) and $(OC)_5WPPh_2H$ (61%) were prepared by the indirect method of Strohmeier.[23]

$(OC)_5WPPh_2CH{=}CH_2$: mp 64–65 °C; IR 1984 ($B_1$), 2073 ($A_1{}^{(2)}$), and 1940 ($E + A_1{}^{(1)}$) cm$^{-1}$; ${}^{31}P$ NMR $\delta$ 11.4 ($J_{WP} = 239.4$ Hz).

Anal. Calcd for $C_{19}H_{13}O_5PW$: C, 42.57; H, 2.44; P, 5.78. Found: C, 42.69; H, 2.38; P, 5.69.

$(OC)_5WPPh_2H$: mp 91–93 °C (lit.[24] mp 90–92 °C); IR 1985 ($B_1$), 2077 ($A_1{}^{(2)}$), and 1947 ($E + A_1{}^{(1)}$) cm$^{-1}$; ${}^{31}P$ NMR $\delta$ −13.7 ($J_{WP}$ = 229.6, $J_{PH}$ = 344.9 Hz).

*trans*-$(OC)_4M(PPh_2CH{=}CH_2)_2$ (M = Cr, Mo, W) and *cis*-$(OC)_4W(PPh_2H)_2$ were prepared from the hexacarbonyls and the appropriate phosphine in diglyme by methods described previously.[25]

*trans*-$(OC)_4Cr(PPh_2CH{=}CH_2)_2$ (42%): mp 145–147 °C dec; IR 1891 ($E_u$), 1944 ($B_{1g}$), and 2011 ($A_{1g}$) cm$^{-1}$; ${}^{31}P$ NMR $\delta$ 64.2.

Anal. Calcd for $C_{32}H_{26}O_4PCr$: C, 65.31; H, 4.45; P, 10.53. Found: C, 65.14; H, 4.47; P, 9.88.

*trans*-$(OC)_4Mo(PPh_2CH{=}CH_2)_2$ (46%): mp 148–150 °C; IR 1897 ($E_u$), 1958 ($B_{1g}$), and 2026 ($A_{1g}$) cm$^{-1}$; ${}^{31}P$ NMR $\delta$ 41.8.

Anal. Calcd for $C_{32}H_{26}O_4PMo$: C, 60.77; H, 4.14; P, 9.79. Found: C, 60.68; H, 4.18; P, 9.88.

*trans*-$(OC)_4W(PPh_2CH{=}CH_2)_2$ (57%): mp 147–149 °C; IR 1890 ($E_u$), 1946 ($B_{1g}$), and 2021 ($A_{1g}$) cm$^{-1}$; ${}^{31}P$ NMR $\delta$ 17.9 ($J_{WP}$ = 281.1 Hz).

Anal. Calcd for $C_{32}H_{26}O_4PW$: C, 53.56; H, 3.64; P, 8.60. Found: C, 53.53; H, 3.78; P, 8.75.

*cis*-$(OC)_4W(PPh_2H)_2$ (38%): mp 88–90 °C; 2020 ($A_1{}^{(2)}$), 1917 ($A_1{}^{(1)}$), and 1903 ($B_1 + B_2$) cm$^{-1}$; ${}^{31}P$ NMR $\delta$ −2.8 ($J_{WP}$ = 224.1, $J_{PH}$ = 342 Hz).

**Reactions of $(OC)_5WPh_2CH{=}CH_2$ with $PPh_2H$. A. Base Catalyzed.** A solution of $(OC)_5WPPh_2CH{=}CH_2$ (0.006 mol) in THF (40 mL) was added dropwise to a refluxing solution of $PPh_2H$ (0.007 mol) and potassium *tert*-butoxide (0.2 g) in THF (100 mL) over a 1-h period. After an additional 30 min of reflux, the solution was cooled and the solvent was removed with a rotary evaporator. The oily residue was dissolved in $CH_2Cl_2$ (10 mL) and $H_2O$ (10 mL). Addition of 20 mL of $CH_3OH$ to the organic layer gave, after 12 h at 5 °C, white crystals of $(OC)_5WPPh_2CH_2CH_2PPh_2$. The product (72%) was recrystallized from $CH_2Cl_2$ (5 mL) and $CH_3OH$ (15 mL).

**B. Free Radical Catalyzed.** A mixture of $(OC)_5WPPh_2CH{=}CH_2$ (0.006 mol), $PPh_2H$ (0.007 mol), and AIBN (0.1 g) was heated without solvent at 65 °C for 12 h. Excess $PPh_2H$ was removed by heating under vacuum for 2 h. The oily product was crystallized as described above (82%), mp 122 °C (lit.[13] mp 116–117 °C). Identification was by ${}^{31}P$ NMR.[13]

**Reactions of $(OC)_5WPPh_2H$ with $PPh_2CH{=}CH_2$. A. Base Catalyzed.** Diphenylvinylphosphine (0.002 mol) in THF (25 mL) was added to a refluxing solution of $(OC)_5WPPh_2H$ (0.002 mol) and potassium *tert*-butoxide (0.2 g) in THF (50 mL) over a 1-h period. After removal of solvent, the crude product was crystallized from $CH_2Cl_2$ (10 mL) and $CH_3OH$ (20 mL). The chelated product, $(OC)_4W(PPh_2CH_2CH_2PPh_2)$ (52%), was identified by ${}^{31}P$ NMR.[17]

**B. Free Radical Catalyzed.** A mixture of $(OC)_5WPPh_2H$ (0.004 mol), $PPh_2CH{=}CH_2$ (0.005 mol), and Albn )0.1 g) was heated to 75 °C, whereupon immediate solidification of the reaction mixture occurred. Recrystallization as described above gave $(OC)_5WPPh_2CH_2Ch_2PPh_2$ (75%).

**Reaction of $(OC)_5WPPh_2H$ with $PPh_3$. Base Catalyzed.** Care was taken to follow a procedure identical with that for the reaction of $(OC)_5WPPh_2H$ with $PPh_2CH{=}CH_2$. White crystals of *cis*-$(OC)_4W(PPh_3)(PPh_2H)$ (58%) were obtained: mp 166 °C dec; IR 2024 ($A_1{}^{(2)}$), 1920 ($A_1{}^{(1)}$), 1903 ($B_1$), and 1889 ($B_2$) cm$^{-1}$; ${}^{31}P$ NMR $\delta$ 3.1 (d, $J_{PP}$ = 17.0, $J_{WP}$ = 229.6 Hz, $PPh_2H$), 24.0 (d, $J_{PP}$ = 17.0, $J_{WP}$ = 230.9 Hz, $PPh_3$).

Anal. Calcd for $C_{34}H_{26}O_4P_2W$: C, 54.86; H, 3.52; P, 8.32. Found: C, 54.82; H, 3.70; P, 8.19.

**Reactions of *trans*-$(OC)_4M(PPh_2CH{=}CH_2)_2$ (M = W, Mo, Cr) with $PPh_2H$. A. Base Catalyzed.** To refluxing $PPh_2H$ (0.008 mol) and AIBN (0.2 g) in THF (100 mL), *trans*-$(OC)_4M(PPh_2CH{=}CH_2)_2$ (0.004 mol) was added dropwise over a 1-h period. After an additional 30 min of reflux the solution was cooled, filtered, and reduced to an oily mass with a rotary evaporator. The impure product was treated with $CH_2Cl_2$ (15 mL) and $H_2O$ (20 mL). Addition of $CH_3OH$ (20 mL) to the organic layer gave, after cooling at 5 °C for 12 h, *trans*-$(OC)_4M(PPh_2CH_2CH_2PPh_2)_2$.

*trans*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$ (56%): mp 151–152 °C; IR 1888 ($E_u$), 1945 ($B_{1g}$), and 2020 ($A_{1g}$) cm$^{-1}$; ${}^{31}P$ NMR $\delta_{WP}$ 18.8 (m, AA′XX′ pattern, ${}^2J_{PP}$ = 54.3, ${}^3J_{PP} + {}^5J_{PP}$ = 37.6, $J_{WP}$ = 279.4 Hz), $\delta_P$ −12.1 (m, AA′XX′ pattern, ${}^2J_{PP}$ = 54.3, ${}^3J_{PP} + {}^5J_{PP}$ = 37.6 Hz).

Anal. Calcd for $C_{56}H_{48}P_4O_4W$: C, 61.55; H, 4.43; P, 11.34. Found: C, 61.70; H, 4.30; P, 11.11.

*cis*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$ was observed as a minor product in the ${}^{31}P$ NMR spectrum of impure *trans*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$: ${}^{31}P$ NMR $\delta_{WP}$ 12.7 (m, AA′XX′ pattern,

$^{2}J_{PP} = 21.3$, $^{3}J_{PP} + {}^{5}J_{PP} = 36.7$ Hz, $J_{WP}$ unobserved), $\delta_P$ −12.6 (m, AA′XX′ pattern, $^{2}J_{PP} = 21.3$, $^{3}J_{PP} + {}^{5}J_{PP} = 36.7$ Hz).

*trans*-$(OC)_4Mo(PPh_2CH_2CH_2PPh_2)_2$ (28%): mp 134–136 °C; IR 1900 ($E_u$), 1945 ($B_{1g}$), and 2020 ($A_{1g}$) cm$^{-1}$; $^{31}P$ NMR $\delta_{MoP}$ 43.1 (m, AA′XX′ pattern, $^{2}J_{PP} = 45.7$, $^{3}J_{PP} + {}^{5}J_{PP} = 36.6$ Hz), $\delta_P$ −12.6 (m, AA′XX′ pattern, $^{2}J_{PP} = 45.7$, $^{3}J_{PP} + {}^{5}J_{PP} = 36.6$ Hz).

Anal. Calcd for $C_{56}H_{48}P_4O_4Mo$: C, 66.94; H, 4.81; P, 12.33. Found: C, 66.69; H, 4.60; P, 12.01.

*trans*-$(OC)_4Cr(PPh_2CH_2CH_2PPh_2)_2$ (46%): mp 147–149 °C; IR 1886 ($E_u$), 1942 ($B_{1g}$), and 2009 ($A_{1g}$) cm$^{-1}$; $^{31}P$ NMR $\delta_{CrP}$ 66.0 (m, AA′XX′ pattern, $^{2}J_{PP} = 26.0$, $^{3}J_{PP} + {}^{5}J_{PP} = 35.3$ Hz), $\delta_P$ −12.0 (m, AA′XX′ pattern, $^{2}J_{PP} = 26.0$, $^{3}J_{PP} + {}^{5}J_{PP} = 35.3$ Hz).

Anal. Calcd for $C_{56}H_{48}P_4O_4Cr$: C, 70.00; H, 5.03; P, 12.89. Found: C, 69.72; H, 4.88; P, 12.41.

**B. Free Radical Catalyzed.** A mixture of *trans*-$(OC)_4M(PPh_2CH{=}CH_2)_2$ (0.0025 mol), $PPh_2H$ (0.005 mol), and AIBN (0.1 g) was heated to 75 °C for 24 h. Unreacted $PPh_2H$ was removed under high vacuum at 65 °C for 2 h.

$(OC)_4W[P^2Ph_2CH_2CH_2CH(P^1Ph_2)CH_2P^3Ph_2]$(I, 65%) was obtained by eluting the crude product with 4:1 petroleum ether (35–60 °C)/ethyl acetate from a silica gel column and recrystallizing from 1:1 $CH_2Cl_2/CH_3OH$: mp 121–123 °C; mol wt ($CHCl_3$) 884, calcd 907; IR 2013 ($A_1^{(2)}$), 1918 ($A_1^{(1)}$), and 1888 ($B_1 + B_2$) cm$^{-1}$; $^{31}P$ NMR $\delta_{P^1}$ 17.1 (dd, $^{2}J_{PP} = 21.5$, $^{3}J_{PP} = 9.6$, $J_{WP} = 221.1$ Hz), $\delta_{P^2}$ 4.0 (dd, $^{2}J_{PP} = 21.5$, $^{5}J_{PP} = 3.6$, $J_{WP} = 226.5$ Hz), $\delta_{P^3}$ −20.1 (dd, $^{3}J_{PP} = 9.6$, $^{5}J_{PP} = 3.6$ Hz); $^{13}C$ NMR $\delta$ 34.8 (dd, $J_{PC} = 17.0$, 13.3 Hz), 30.8 (dd, $J_{PC} = 16.2$, 4.5 Hz), 31.2 (d, $J_{PC} = 23.5$ Hz), 25.9 (dd, $J_{PC} = 13.8$, 6.1 Hz).

Anal. Calcd for $C_{44}H_{37}P_3O_4W$: C, 58.30; H, 4.11; P, 10.25. Found: C, 57.85; H, 4.02; P, 9.81.

Increasing the concentration of ethyl acetate to 50% in the eluting solvent allowed the collection of $(OC)_4W[P^2Ph_2CH_2CH_2CH(P^1Ph_2)CH_2P^3(O)Ph_2]$ (8%): mp 125–127 °C; IR 2016 ($A_1^{(2)}$), 1920 ($A_1^{(1)}$), and 1890 ($B_1 + B_2$) cm$^{-1}$; $^{31}P$ NMR $\delta_{P^1}$ 18.2 (dd, $^{2}J_{PP} = 21.8$, $^{3}J_{PP} = 30.2$, $J_{WP} = 223.5$ Hz), $\delta_{P^2}$ 2.3 (d, $^{2}J_{PP} = 21.8$, $J_{WP} = 225.6$ Hz), $\delta_{P^3}$ 32.2 (d, $^{3}J_{PP} = 30.2$ Hz); $^{13}C$ NMR $\delta$ 32.9 (dd, $J_{PC} = 16.1$, 4.3 Hz), 30.6 (d, $J_{PC} = 63.9$ Hz), 30.3 (d, $J_{PC} = 24.3$ Hz), 25.2 (d, $J = 4.40$ Hz).

Anal. Calcd for $C_{44}H_{37}P_3O_5W$: C, 57.29; H, 4.04; P, 10.07. Found: C, 56.95; H, 4.25; P, 9.60.

$(OC)_4Mo[P^2Ph_2CH_2CH_2CH(P^1Ph_2)CH_2P^3Ph_2]$ (III), *trans*-$(OC)_4Mo(PPh_2CH_2CH_2PPh_2)_2$, and $Ph_2PCH_2CH_2PPh_2$ were identified as present in approximately equal proportions by $^{31}P$ NMR: $^{31}P$ NMR (III) $\delta_{P^1}$ 38.6 (dd, $^{2}J_{PP} = 28.0$, $^{3}J_{PP} = 8.1$ Hz), $\delta_{P^2}$ 24.1 (dd, $^{2}J_{PP} = 28.0$, $^{5}J_{PP} = 3.70$ Hz), $\delta_{P^3}$ −19.9 (dd, $^{3}J_{PP} = 8.1$, $^{5}J_{PP} = 3.70$ Hz).

$(OC)_4Cr[P^2Ph_2CH_2CH_2CH(P^1Ph_2)CH_2P^3Ph_2]$ (II) and *trans*-$(OC)_4Cr(PPh_2CH_2CH_2PPh_2)_2$ (2:1 mixture) were identified by $^{31}P$ NMR. $^{31}P$ NMR (II) $\delta_{P^1}$ 59.4 (dd, $^{2}J_{PP} = 39.7$, $^{3}J_{PP} = 6.1$ Hz), $\delta_{P^2}$ 44.5 (dd, $^{2}J_{PP} = 39.7$, $^{5}J_{PP} = 4.90$ Hz) $\delta_{P^3}$ −20.0 (dd, $^{3}J_{PP} = 6.1$, $^{5}J_{PP} = 4.90$ Hz).

**Reactions of *cis*-$(OC)_4W(PPh_2H)_2$ with $PPh_2CH{=}CH_2$. A. Base Catalyzed.** A solution of *cis*-$(OC)_4W(PPh_2H)_2$ (0.0022 mol) in THF (20 mL) was added to $PPh_2CH{=}CH_2$ (0.005 mol) and potassium *tert*-butoxide (0.2 g) in THF (100 mL). After refluxing for 2 h, the solvent was removed and the impure product was dissolved in $CH_2Cl_2$ (15 mL) and $H_2O$ (10 mL). Addition of $CH_3OH$ (20 mL) to the organic layer gave $(OC)_4W(PPh_2CH_2CH_2PPh_2)$ (63%). Identification was as previously described.

**B. Free Radical Catalyzed.** A mixture of *cis*-$(OC)_4W(PPh_2H)_2$ (0.002 mol), $PPh_2CH{=}CH_2$ (0.004 mol), and AIBN (0.1 g) was heated at 75 °C for 24 h. Unreacted $PPh_2CH{=}CH_2$ was removed by high vacuum and *trans*-$(OC)_4W(PPh_2CH_2CH_2PPh_2)_2$ (43%) was purified and identified as previously described.

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