Synthetic, Structural, and Mechanistic Studies of the C–H Bond Activation of Phenols by $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$

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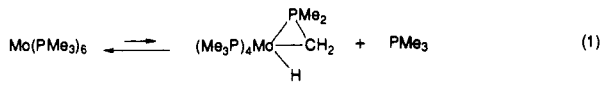
Abstract: Hexakis(trimethylphosphine)tungsten(0), $W(PMe_3)_6$, has been synthesized by the reduction of WCl_6 with Na(K) alloy using PMe_3 as a reactive solvent and structurally characterized by X-ray diffraction techniques. Facile dissociation of one of the PMe_3 ligands of $W(PMe_3)_6$ produces the metalated complex $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, with which it is in equilibrium. $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ react with phenols to give 4- and 5-membered oxametallacycle derivatives as a result of competitive sp^2 vs sp^3 C–H bond activation. 2-Alkylphenols 2-RC_6H_4OH (R = H, Et, Pr^i, Bu^t, Ph) give specifically the 4-membered oxametallacycle derivatives $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_3R\}$, whereas 2-methylphenol gives specifically the 5-membered oxametallacycle derivative $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_4(CH_2)\}$. 2,6-Dimethylphenol and 2,4,6-trimethylphenol also react to give 5-membered oxametallacycles, $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_3Me(CH_2)\}$ and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$, respectively. Mechanistic studies suggest that the formation of a 5-membered rather than a 4-membered oxametallacycle in the reaction with 2-methylphenol is a result of thermodynamic control. All the oxametallacycles react rapidly with hydrogen to result in an equilibrium with the aryloxide derivatives $W(PMe_3)_4H_3(OAr)$. For most of the derivatives, the equilibrium is shifted strongly in favor of the alkoxide derivative; however, for the complexes $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_3Me(CH_2)\}$ and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$, the oxametallacycles are the most stable form. $W(PMe_3)_6$ is cubic, $Im\bar{3}m$ (No. 229), a = 11.303 (2) Å, V = 1444.1 (6) Å^3, Z = 2. $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ is monoclinic, $P2_1/n$ (No. 14), a = 9.713 (2) Å, b = 16.008 (5) Å, c = 16.283 (2) Å, β = 93.51 (1)°, V = 2527.1 (9) Å^3, Z = 4. $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$ is monoclinic, $P2_1/n$ (No. 14), a = 9.898 (3) Å, b = 28.065 (9) Å, c = 10.663 (3) Å, β = 104.33 (2)°, V = 2870 (1) Å^3, Z = 4.

Introduction

The series of zerovalent homoleptic trimethylphosphine complexes, $M(PMe_3)_n$, exists for several of the transition metals, including Mo, Fe, Os, Co, Ni, Pd, and Pt.[1] The combination of strong σ-donor and weak π-acceptor properties of the trimethylphosphine ligand results in the metal centers of these complexes being classified as "electron rich", as exemplified by the susceptibility of such complexes toward oxidative–addition reactions. Here we report the synthesis and structure of another member of this series, the homoleptic hexakis(trimethylphosphine)tungsten(0) complex $W(PMe_3)_6$, the kinetics and thermodynamics of its conversion to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, and the C–H bond activation reactions of these complexes with phenols to give 4- and 5-membered oxametallacycles.[2]

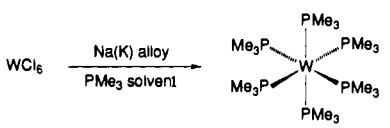
Results and Discussion

The synthesis, structure, and reactivity of the homoleptic hexakis(trimethylphosphine)molybdenum complex $Mo(PMe_3)_6$ has been previously reported.[1a,b] NMR studies demonstrated that $Mo(PMe_3)_6$ was in equilibrium with low concentrations of the complex $Mo(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and PMe_3 (eq 1). In



(1)

contrast, attempts to prepare the analogous tungsten complex $W(PMe_3)_6$ by both (i) the co-condensation of tungsten atoms with PMe_3[3] and (ii) the reduction of WCl_6 with alkali-metal reducing agents using PMe_3 as a reactive solvent[4] resulted in the isolation of the cyclometalated product $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ in each case. Furthermore, the ^1H NMR spectrum of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ in the presence of excess PMe_3 was reported to provide no evidence for the formation of $W(PMe_3)_6$.[4] However, evidence that $W(PMe_3)_6$ may exist has been recently provided by the observation that reduction of $W(N\text{-}2,6\text{-}Pr^i_2C_6H_3)Cl_4$ with Na sand in PMe_3 solvent gives $W(PMe_3)_6$, as a partially characterized product obtained in low yield, which converts to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and PMe_3 at room temperature.[5] Indeed, we have found that $W(PMe_3)_6$ may be isolated as a yellow crystalline solid in good yield (>50%) by the reduction of WCl_6 with Na(K) alloy using PMe_3 as a reactive solvent (eq 2), by a



(2)

similar procedure to that reported for the preparation of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$,[3,4] with the modification that extraction procedures are performed as quickly as possible (see Experimental Section). $W(PMe_3)_6$ is characterized by a singlet at δ 1.49 in the ^1H NMR spectrum and also a singlet at δ −41.5 with tungsten satellites ($^1J_{P\text{-}W}$ = 294 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum of $W(PMe_3)_6$ is a multiplet with the *approximate* appearance of a triplet of quintets in which $^1J_{C\text{-}P} \approx {}^3J_{C\text{-}P(trans)} \approx 2$ Hz and $^3J_{C\text{-}P(cis)} \approx 4$ Hz, thus supporting the presence of six PMe_3 ligands.

The molecular structure of $W(PMe_3)_6$ has been determined by X-ray diffraction methods, as shown in Figure 1, and is isomorphous with the molybdenum analogue. The immediate coordination sphere around tungsten (i.e., excluding methyl groups)

(1) (a) Brookhart, M.; Cox, K.; Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Hare, P. M.; Bashkin, J.; Derome, A. E.; Grebenik, P. D. *J. Chem. Soc., Dalton Trans.* **1985**, 423–433. (b) Cloke, F. G. N.; Cox, K. P.; Green, M. L. H.; Bashkin, J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 393–394. (c) Ermer, S. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *Organometallics* **1989**, *8*, 1377–1378. (d) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1975**, *108*, 944–955. (e) Klein, H.-F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 362–375. (f) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637–638. (g) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Chem. Ber.* **1977**, *110*, 2200–2212. (h) Timms, P. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 273–277. (i) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272–3273. (j) Ugo, R. *Coord. Chem. Rev.* **1968**, *3*, 319–344. (k) Malatesta, L.; Cenini, S. *Zerovalent Compounds of Metals*; Academic Press: New York, 1974.

(2) (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 5381–5383. (b) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 9632–9633.

(3) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227–2236.

(4) Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 2025–2035.

(5) Gibson, V. C.; Mitchell, J. P. Personal communication.

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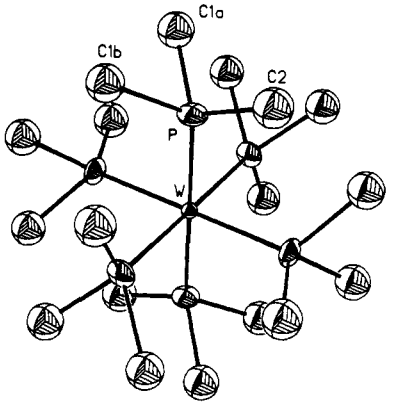


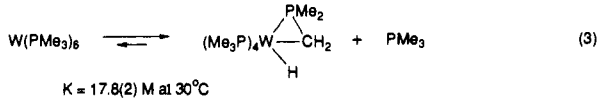
Figure 1. ORTEP drawing for $W(PMe_3)_6$.

Table I. Equilibrium Constants between $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (Equation 3)

T/°C	K/M	T/°C	K/M
30	17.8 (2)	60	84 (4)
40	30 (5)	70	101 (1)
50	60 (7)		

is rigorously octahedral (as imposed by crystallographic symmetry), with P–W–P bond angles of 90 and 180°. The W–P bond length [2.455 (5) Å] is very similar to, and indeed *slightly shorter* than, the corresponding Mo–P bond length [2.467 (2) Å] in $Mo(PMe_3)_6$.[1a] A similar trend has been reported for the complexes $M(Me_2PCH_2CH_2PMe_2)_3$ (M = Mo, W; M = Nb, Ta) and has been attributed to the lanthanide contraction.[6]

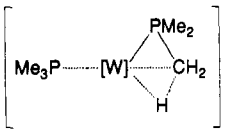
$W(PMe_3)_6$ may be stored under N_2 for prolonged periods in the solid state (>2 weeks at room temperature and >1 year at −30 °C). However, solutions of $W(PMe_3)_6$ are unstable at room temperature and are converted rapidly to an *equilibrium* mixture with $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and PMe_3 (eq 3). At the



concentration levels of PMe_3 that are generated by the dissociation (typically ~ 5–10 mM), the reaction is effectively irreversible and proceeds to completion with a half-life of ca. 2 h at room temperature, which accounts for the previous difficulty in isolating $W(PMe_3)_6$.[3,4] However, in the presence of a large excess of added PMe_3, the equilibrium is shifted toward $W(PMe_3)_6$ so that both $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ may be observed by ^1H NMR spectroscopy,[7] thereby allowing determination of the equilibrium constant, K(30 °C) = 17.8 (2) M. Furthermore, pure $W(PMe_3)_6$ may be obtained from solutions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ in PMe_3 solvent, since the lower solubility of $W(PMe_3)_6$ results in crystallization from the solution as the equilibrium is established. Indeed, this method was used for obtaining single crystals for the X-ray diffraction study.

The temperature dependence of K in benzene solutions over the range 30–70 °C (Table I) has allowed $\Delta H°$ and $\Delta S°$ for the above equilibrium to be determined. The values of $\Delta H° = 9.3$ (8) kcal mol^{-1} and $\Delta S° = 37$ (2) eu demonstrate that formation of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ is driven entropically by dissociation of PMe_3, and not enthalpically.[8]

The mechanism proposed for the formation of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ involves rate-determining dissociation of PMe_3 from $W(PMe_3)_6$ to give the 16-electron intermediate $[W(PMe_3)_5]$,



[W] = $W(PMe_3)_4$

Figure 2. Intermediate or transition state for a mechanism involving concerted PMe_3 dissociation and C–H bond activation.

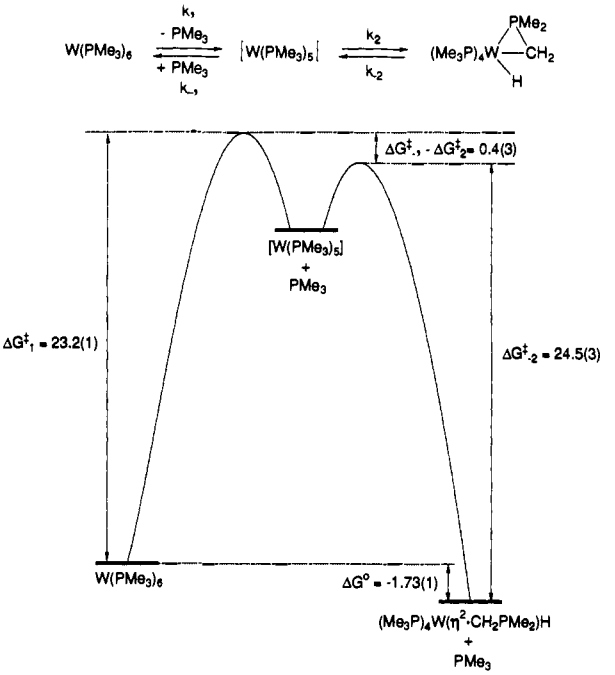
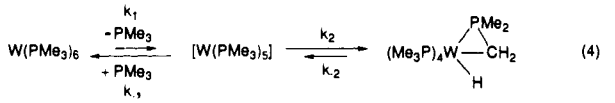


Figure 3. Energy surface connecting $W(PMe_3)_6$ to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and PMe_3. Energy values in kcal mol^{-1}; T = 30 °C; standard states of the components are 1 M.

Table II. First-Order Rate Constants for Dissociation of PMe_3 from $W(PMe_3)_6$

T/°C	k_1/s^{-1}	T/°C	k_1/s^{-1}
30	1.2 (1) × 10^{-4}	50	2.1 (1) × 10^{-3}
40	5.5 (3) × 10^{-4}	60	8.3 (4) × 10^{-3}

followed by rapid metalation of a C–H bond of one of the PMe_3 ligands (eq 4). An alternative mechanism in which PMe_3 dis-



sociation is accompanied by *concerted* C–H bond metalation via the intermediate or transition state illustrated in Figure 2, as opposed to the 16-electron intermediate $[W(PMe_3)_5]$, may also be considered. However, this mechanism is discounted by the lack of an observable kinetic isotope effect for the formation of d_n-$W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ from deuterium-enriched samples of $W(PMe_3)_6$.[9] If intramolecular C–H bond metalation was involved in the rate-determining step, a significant isotope effect would be expected. Furthermore, the rate of conversion of $W(PMe_3)_6$ to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ is inhibited by addition of excess PMe_3, consistent with a stepwise process involving initial disso-

(6) d(Mo–P) = 2.421 (3) Å, d(W–P) = 2.414 (6) Å; d(Nb–P) = 2.526 (3) Å, d(Ta–P) = 2.500 (6) Å. Cloke, F. G. N.; Fyne, P. J.; Gibson, V. C.; Green, M. L. H.; Ledoux, M. J.; Perutz, R. N.; Dix, A.; Gourdon, A.; Prout, K. *J. Organomet. Chem.* **1984**, *277*, 61–73.

(7) Presumably insufficient PMe_3 was added to allow detection of $W(PMe_3)_6$ in the previously reported study (ref 4).

(8) Standard states of the components are 1 M.

(9) Samples of d_n-$W(PMe_3)_6$ were prepared by stirring $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ in $P(CD_3)_3$ for 4 days at room temperature. The composition of the d_n-$W(PMe_3)_6$ obtained was approximately $W[P(CD_3)_3]_4[P(CH_3)_3]_2$, as estimated from the ratio of $P(CD_3)_3$ [δ −65.1 ppm] and $P(CH_3)_3$ [δ −62.1 ppm] which dissociates, as observed by $^{31}P\{^1H\}$ NMR spectroscopy. At 30 °C, the observed rate constants for dissociation of trimethylphosphine from both $W(PMe_3)_6$ and $W[P(CD_3)_3]_4[P(CH_3)_3]_2$ are 1.2 (1) × 10^{-4} s^{-1}, as measured by ^{31}P NMR spectroscopy.

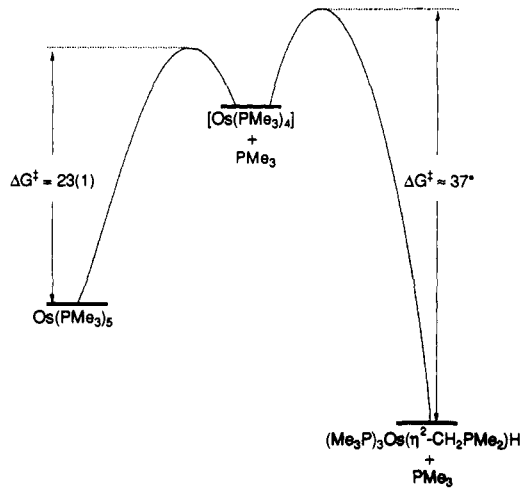


Figure 4. Energy surface connecting $Os(PMe_3)_5$ to $Os(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H$. Energy values in kcal mol^{-1}; T = 30 °C, except * at 155 °C.

ciation of PMe_3. At the low concentration levels of PMe_3 (~5–10 mM) that are generated during the course of the reaction in the absence of added PMe_3, the ratio $k_{-1}[PMe_3]/k_2$ is sufficiently small (~10^{-2}–10^{-3}) so that intramolecular C–H bond activation within $[W(PMe_3)_5]$ is greatly favored over coordination of PMe_3. Under these conditions, the rate-determining step is specifically dissociation of PMe_3 from $W(PMe_3)_6$, for which measurement of the kinetics over the temperature range 30–60 °C has allowed the activation parameters $\Delta H_1^{\ddagger}$ = 27.6 (6) kcal mol^{-1} and $\Delta S_1^{\ddagger}$ = 14 (3) eu to be determined (Table II). Measurement of the rate of the reaction as a function of PMe_3 concentration allows the ratio of k_{-1} and k_2, i.e., the competition between coordination of PMe_3 vs intramolecular oxidative-addition of the C–H bond to the 16-electron species $[W(PMe_3)_5]$, to be determined.[10] A knowledge of the equilibrium constant for the reaction also allows determination of k_{-2}, the rate constant for reductive-elimination of the metallacycle–hydride unit, $[W(\eta^2\text{-}CH_2PMe_2)H]$. At 30 °C these rate constants have the values k_1 = 1.2 (1) × 10^{-4} s^{-1} ($\Delta G^{\ddagger}_1$ = 23.2 (1) kcal mol^{-1}), k_{-2} = 1.3 (5) × 10^{-5} s^{-1} ($\Delta G^{\ddagger}_{-2}$ = 24.5 (3) kcal mol^{-1}), and k_{-1}/k_2 = 0.5 (2) M^{-1} ($\Delta G^{\ddagger}_{-1} - \Delta G^{\ddagger}_2$ = 0.4 (3) kcal mol^{-1}), as illustrated in Figure 3.

It is interesting to compare the energy profile for the $W(PMe_3)_6$ system with that for the related osmium system, $Os(PMe_3)_5$. Although the barrier for PMe_3 dissociation from $W(PMe_3)_6$ ($\Delta G^{\ddagger}_{30°C}$ = 23.2 (1) kcal mol^{-1}) to form the 16-electron intermediate $[W(PMe_3)_5]$ is comparable to that observed for PMe_3 dissociation from $Os(PMe_3)_5$ ($\Delta G^{\ddagger}_{30°C}$ = 23 (1) kcal mol^{-1}),[1c,11,12] the barrier for formation of these 16-electron intermediates $[M(PMe_3)_{n-1}]$ (M = W, n = 6; M = Os, n = 5) by reductive elimination of the C–H bond of the cyclometalated derivatives $[M(PMe_3)_{n-2}(\eta^2\text{-}CH_2PMe_2)H]$ is significantly greater for Os than for W, as illustrated in Figure 4.[13] Thus, whereas both $W(PMe_3)_6$ and $Os(PMe_3)_5$ act as efficient sources of the 16-electron intermediate $[M(PMe_3)_{n-1}]$ by PMe_3 dissociation, for the cyclometalated derivatives $[M(PMe_3)_{n-2}(\eta^2\text{-}CH_2PMe_2)H]$ only the tungsten complex is capable of generating $[M(PMe_3)_{n-1}]$ under mild conditions. Reductive elimination is therefore greatly favored for $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ over $Os(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H$, an observation which may represent a ground-state stabilization effect since the Os complex formally contains an octahedral d^6 metal center, a particularly favorable situation.

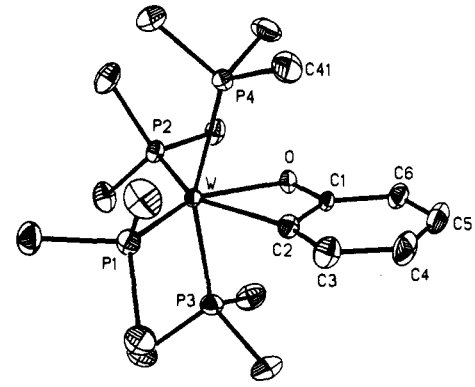


Figure 5. ORTEP drawing for $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$. The hydride ligands were not located but are presumed to lie in the plane defined by P(3)–W–P(4) such that the overall condition geometry is dodecahedral.

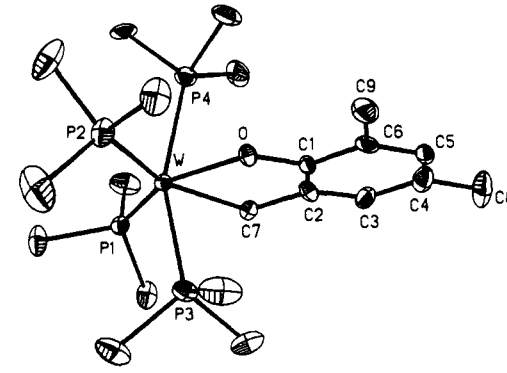


Figure 6. ORTEP drawing for $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$. The hydride ligands were not located but are presumed to lie in the plane defined by P(3)–W–P(4) such that the overall coordination geometry is dodecahedral.

C–H Bond Activation of Phenols: Formation of Four- and Five-Membered Oxametallacycles. The electron-rich nature of the complexes $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ suggests that these complexes may be candidates for C–H bond activation reactions.[14] Indeed, we have observed that reactions with phenols result in the formation of 4- and 5-membered oxametallacycles as a result of selective C–H bond activation as summarized in Scheme I. Identical products were also obtained from the analogous reactions with $W(PMe_3)_6$, although the reactions were noticeably faster and cleaner for $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, the preferred starting material. A simplified mechanism to rationalize the formation of the oxametallacycle derivatives involves cyclometalation of an aryloxy–hydride intermediate (eq 5). The

$$W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H \xrightarrow{HArOH} [W(PMe_3)_5H(OArH)] \xrightarrow{-PMe_3} W(PMe_3)_4H_2(OAr) \quad (5)$$

specific product isolated in each case is the result of cyclometalation of the aryloxy ligand at either the aryl ring or alkyl substituent. Thus, phenol reacts to form the 4-membered oxametallacycle $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ as a result of sp^2 C–H bond activation at one of the ortho positions. The presence of the 4-membered oxametallacycle ring in $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$

(10) In the presence of a large excess of PMe_3 (*pseudo*-first-order conditions), the reaction approaches equilibrium with an observed rate constant $k_{obs} = k_f + k_r[PMe_3]$, where $k_f = k_1k_2/\{k_{-1}[PMe_3] + k_2\}$ and $k_r = k_{-1}k_{-2}/\{k_{-1}[PMe_3] + k_2\}$ and $k_f/k_r = K$. In the initial stages of the reaction, $k_r \approx 0$ and $k_{obs} \approx k_f \approx k_1k_2/\{k_{-1}[PMe_3] + k_2\}$. A plot of $1/k_{obs}$ vs $[PMe_3]$ allows k_1 and the ratio k_{-1}/k_2 to be determined. k_{-2} can be determined from a knowledge of the equilibrium constant since $K = k_1k_2/k_{-1}k_{-2}$.

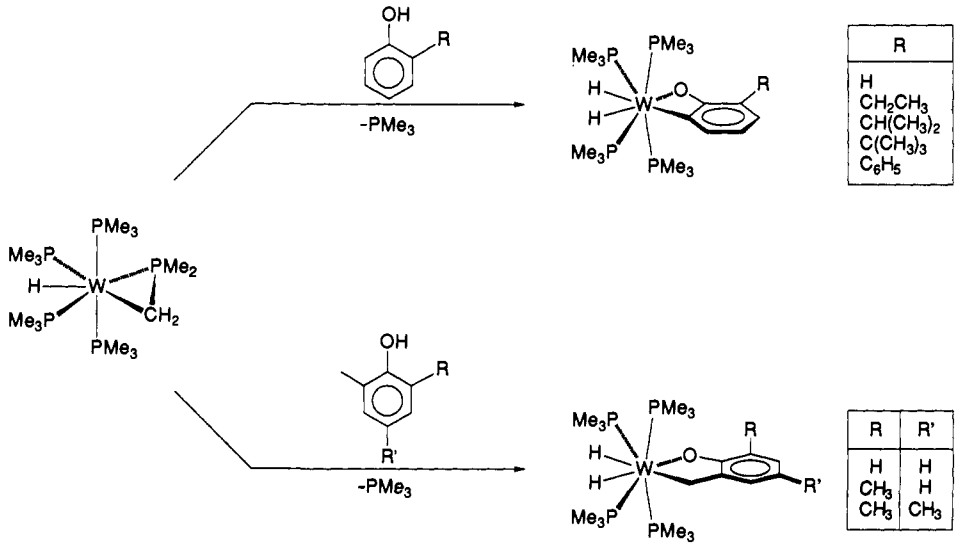
(11) Shinomoto, R. S.; Desrosiers, P. J.; Harper, G. P.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704–713.

(12) Flood, T. C. Personal communication.

(13) Although the barriers for reductive elimination ($\Delta G^{\ddagger}_{30°C}$ = 24.5 (3) kcal mol^{-1} for $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$; $\Delta G^{\ddagger}_{155°C} \approx 37$ kcal mol^{-1} for $Os(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H$) cannot be compared quantitatively since the experiments were carried out at different temperatures, the relative ease of the two processes is clearly indicated.

(14) (a) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403–424. (b) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91–100. (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269. (d) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. A.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13–23. (e) O'Hare, D.; Green, M. L. H. *Pure Appl. Chem.* **1985**, *57*, 1897–1910. (f) Shilov, A. E.; Shul'pin, G. B. *Russ. Chem. Rev.* **1990**, *59*, 853–867.

Scheme I. Formation of Four- and Five-Membered Oxametallacycles from the Reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with Phenols



has been confirmed by an X-ray diffraction study (Figure 5).[15] Four-membered oxametallacycles[16] derived from ortho metalation of aryloxy ligands are surprisingly uncommon[17] compared with 5- and 6-membered derivatives.[18] The reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with 2,6-dimethylphenol, in which ortho C–H bonds are absent, results in the formation of the 5-membered oxametallacycle $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_3Me(CH_2)\}$ derived from sp^3 C–H bond activation at one of the methyl groups. Similarly, 2,4,6-trimethylphenol gives the 5-membered oxametallacycle $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$, which has been structurally characterized by X-ray diffraction (Figure 6).[15]

The above reactions clearly indicate the ability of the tungsten centers in $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ to activate both sp^2 and sp^3 C–H bonds. More interesting situations arise in the reactions of monosubstituted phenols, $2\text{-}RC_6H_4OH$ (R = Me, Et, Pr^i, Bu^t, Ph), in which a variety of potential C–H bond activation reactions are now possible, leading to the formation of either 4-, 5-, or 6-membered oxametallacycles. Thus, we have observed that the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with 2-methylphenol gives the 5-membered oxametallacycle $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_4(CH_2)\}$ as a result of selective sp^3 C–H bond activation of the methyl substituent, in preference to the 4-membered ortho-metalated alternative. However, in marked contrast, the corresponding reactions of the 2-ethyl-, 2-isopropyl-, 2-*tert*-butyl-, and 2-phenylphenol derivatives give *specifically* the 4-membered oxametallacycles as a result of selective C–H bond activation at the ortho position (see below for a discussion of kinetic vs thermodynamic control). The propensity for the formation of 4-membered metallacycles within this system is striking, especially given the marked tendency of *o*-alkyl groups of aryloxy ligands in other systems to undergo facile metalation, with the resulting formation of 5- or 6-membered oxametallacycles.[18,19]

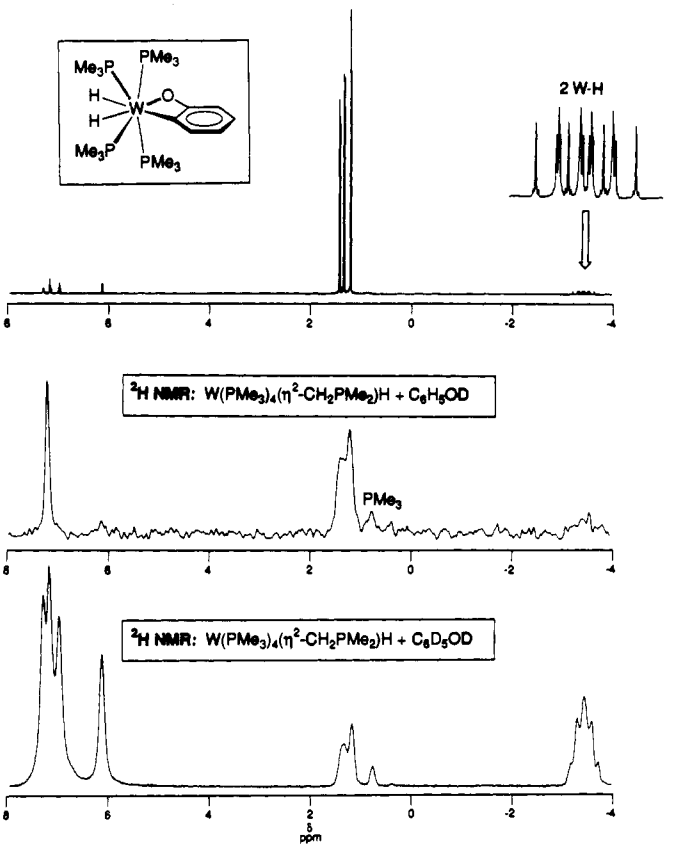


Figure 7. Upper trace: ^{1}H NMR spectrum of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ in C_6D_6. Middle trace: ^{2}H NMR spectrum in C_6H_6 for the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with C_6H_5OD. Lower trace: ^{2}H NMR spectrum in C_6H_6 for the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with C_6D_5OD (excess C_6D_5OD is present).

(15) Although the hydride ligands were not located, on the basis of steric grounds they are presumably located in the plane defined by P(3)–W–P(4), such that the overall coordination geometry is dodecahedral.

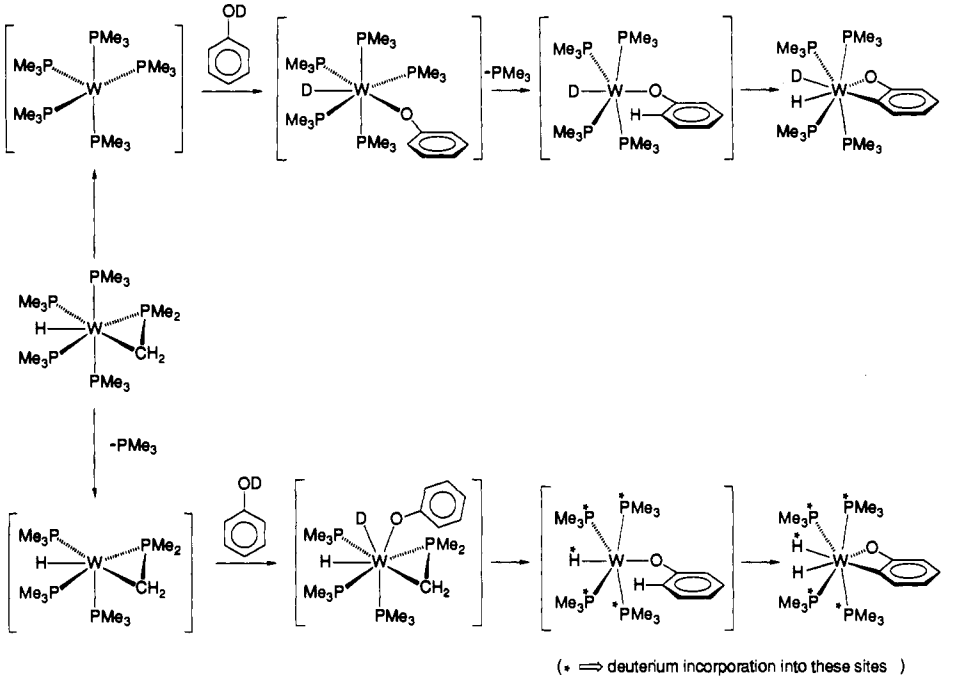
(16) Examples of 4-membered oxametallacycles include $(AsPh_3)_2Pt\{OC(CN)_2C(CN)_2\}$,[16a,b] $(PPh_3)_2Pt(CH_2OCH_2)$,[16c] $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir(OCMe_2CH_2)$,[16d] $(\eta^5\text{-}C_5H_5)_2Ti\{OC(CH_2)CH_2\}$,[16e] $[(\eta^5\text{-}C_5H_5)_2Zr(OC_6H_8)]_2$,[16f] $(\eta^5\text{-}C_5Me_5)_2Zr(OCPh{=}CPh)$,[16g] and $(PMe_3)_3Rh\{OC(Me)_2CH_2\}Br$.[16h] (a) Schlodder, R.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Am. Chem. Soc.* **1974**, *96*, 6893–6900. (b) Lenarda, M.; Ros, R.; Traverso, O.; Pitts, W. D.; Baddley, W. H.; Graziani, M. *Inorg. Chem.* **1977**, *16*, 3178–3182. (c) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 6466–6468. (d) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704–3706. (e) Ho, S. C.; Hentges, S.; Grubbs, R. H. *Organometallics* **1988**, *7*, 780–782. (f) Vaughan, G. A.; Hillhouse, G. L.; Lum, R. T.; Buchwald, S. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 7215–7217. (g) Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7994–8001. (h) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Am. Chem. Soc.* **1990**, *112*, 6411–6413.

(17) Some examples include $(PMe_3)_4Ru(\eta^2\text{-}OC_6H_3Me)$[17a,b] and $Ru(\eta^2\text{-}OC_6H_2MeX)(CO)(PPh_3)_2Cl$ (X = *p*-$MeC_6H_4NH^+{=}CH$).[17c] (a) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 3404–3418. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Organomet. Chem.* **1990**, *394*, 417–432. (c) Bag, N.; Choudhury, S. B.; Pramanik, A.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 5013–5014.

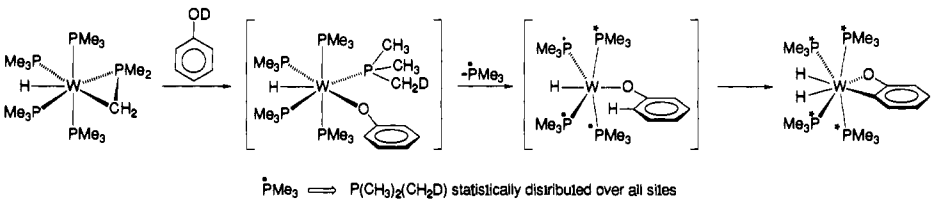
(18) (a) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153–159. (b) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177–200. (c) Yu, J. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1990**, *112*, 8171–8172.

(19) We also note that although *ortho* metalation of tertiary arylphosphine ligands giving 4-membered metallacycles is common, incorporation of an *o*-alkyl substituent may result in the formation of a 5-membered metallacycle. See for example: Gill, D. F.; Mann, B. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973**, 270–278.

Scheme II. Potential Mechanisms for Reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with Phenol



Scheme III. Proposed Mechanism for the Reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with C_6H_5OD



The determination of the mechanisms of the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with phenols is essential for understanding the selectivity of the aforementioned C–H bond activation reactions. Potential mechanisms for the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with phenols involve sequences comprising oxidative addition of the phenol O–H bond to a 16-electron intermediate, either zerovalent $[W(PMe_3)_5]$ generated by reductive elimination of the metallacycle–hydride unit or divalent $[W(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$ generated by dissociation of PMe_3, as shown in Scheme II. However, our mechanistic studies conclusively demonstrate that *neither* of these mechanistic possibilities operate and that the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with phenols *do not* occur via oxidative addition of the O–H bond to either of the 16-electron intermediates $[W(PMe_3)_5]$ or $[W(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$. Firstly, kinetic studies indicate that the reactions with phenols are significantly faster than the rates of formation of either $[W(PMe_3)_5]$ or $[W(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$[20] from $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ which can not, therefore, be intermediates. Secondly, a series of labeling studies demonstrate that *neither* of the two W–H ligands in the product are derived from the hydroxylic proton of the phenol. Thus, the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with C_6H_5OD gives $d_1\text{-}W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ in which the deuterium is located principally in the PMe_3 ligands and *not* at the tungsten center, as illustrated in the ^2H NMR spectrum shown in Figure 7. However, deuterium is incorporated into the tungsten-hydride positions when C_6D_5OD is used as the reagent, as also shown in Figure 7. Thus, the two W–H ligands in the product are derived from the original W–H ligand in $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and one of the ortho hydrogen atoms of the phenol, with the hydroxylic O–H hydrogen terminating in one of the trimethylphosphine ligands or dissociated PMe_3. Therefore, we propose that the first step of the mechanism for the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with phenols involves direct attack at the W–C bond of the metallacycle unit, either by protonation or by σ-bond metathesis[21] with the phenolic O–H bond. Dissociation of PMe_3, followed by C–H bond activation of the aryl group, gives the observed product, as illustrated in Scheme III for the specific reaction with C_6H_5OD. Hartwig, Bergman, and Andersen have also demonstrated that the reaction of 4-MeC_6H_4OH with the benzyne complex $Ru(PMe_3)_4(\eta^2\text{-}C_6H_4)$ does not occur via a sequence involving PMe_3 dissociation followed by oxidative addition of the O–H bond.[17a] However, they suggest direct protonation at the metal center and not the benzyne ligand. Direct protonation of the metal center can be excluded for our system by the above deuterium-labeling experiment.[22]

The final step of the proposed mechanism for the formation of the oxametallacycle involves intramolecular C–H bond activation of the aryloxy group within the 16-electron intermediate $[W(PMe_3)_4H(OC_6H_3R)]$ to give either the 4-membered or the 5-membered (or potentially 6-membered) derivative. The selectivity of the reaction is, therefore, a consequence of the relative kinetic and thermodynamic favorabilities of the possible C–H bond activation steps for the 16-electron intermediate $[W(PMe_3)_4H(OC_6H_3R)]$. Thus, one factor that is central to the issue of selectivity is concerned with whether the C–H bond activation

(20) Ligand exchange between $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and $P(CD_3)_3$ occurs at a rate which is comparable to the rate of reductive elimination of the metallacycle hydride unit. Thus, dissociation of PMe_3 from $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ to give the 16-electron intermediate $[W(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$ cannot be significantly faster than that for reductive elimination.

(21) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219.

(22) This argument requires that protonation at the metal center would allow the two W–H ligands in the intermediate to exchange positions. If protonation occurred at a selective site at the metal, and this was followed by selective transfer to carbon, then the observed result would be indistinguishable from direct attack at the W–C bond.

Scheme IV. Reactions of (a) Four-Membered and (b) Five-Membered Oxametallacycles with H_2

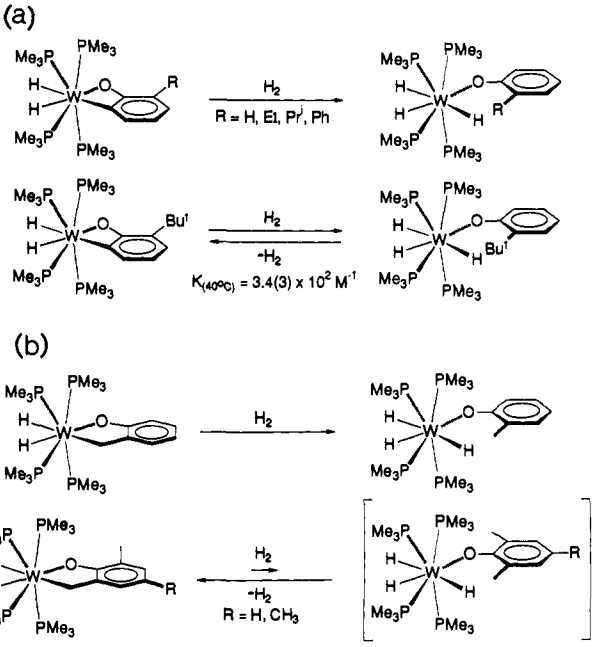


Table III. Equilibrium and Rate Constants for Hydrogenation of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Bu^t)$ to $W(PMe_3)_4H_3(OC_6H_4Bu^t)$ [$K = k_f/k_r$]

T/°C	K/M^{-1}	k_f/M^{-1} s^{-1}	k_r/s^{-1}
40	3.4 (3) × 10^2	0.13 (1)	3.9 (4) × 10^{-4}
60	1.2 (1) × 10^2	0.28 (3)	2.3 (2) × 10^{-3}
80	5.6 (6) × 10^1	0.44 (4)	7.9 (8) × 10^{-3}
100	1.7 (2) × 10^1		

step is reversible on the time scale of the reactions between $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and phenols. Evidence for the reversibility of the C–H bond activation step would be provided by trapping the 16-electron intermediate $[W(PMe_3)_4H(OC_6H_3R)]$ obtained by reductive elimination of the oxametallacycle–hydride unit. In this regard, we have investigated the reactivity of the oxametallacycles toward hydrogen, with the aim of trapping the 16-electron intermediate by oxidative addition (eq 6). We have

$$W(PMe_3)_4H_2(OAr) \rightleftharpoons [W(PMe_3)_4H(OArH)] \xrightarrow{H_2} [W(PMe_3)_4H_3(OArH)] \quad (6)$$

observed that both the 4- and the 5-membered oxametallacycles react rapidly with H_2 at room temperature to give the aryloxy–trihydride derivatives, as summarized in Scheme IV.[23] However, the equilibrium between the aryloxy–trihydride and the oxametallacycle is *extremely sensitive* to the presence of substituents on the aryl ring.

As illustrated in Scheme IVa, the formation of the aryloxy–trihydride complexes $W(PMe_3)_4H_3(OC_6H_4R)$ [R = H, Me, Et, Pr^i, Ph] proceeds to completion, whereas the *tert*-butyl derivative $W(PMe_3)_4H_3(OC_6H_4Bu^t)$ is only obtained as an equilibrium mixture with the oxametallacycle in the presence of 1 atm of H_2. Measurement of the equilibrium constant as a function of temperature (Table III) allows $\Delta H° = -11.2$ (7) kcal mol^{-1} and $\Delta S° = -24$ (2) eu for the hydrogenation reaction to be determined.[8] Furthermore, measurement of the rate of approach to equilibrium (Table III) allows determination of the activation parameters for the hydrogenation. At 40 °C these values are $\Delta G^{\ddagger}_f = 19.6$ (1) kcal mol^{-1}, $\Delta G^{\ddagger}_r = 23.2$ (1) kcal mol^{-1}, and $\Delta G° = -3.6$ (1) kcal mol^{-1}. Although the reaction is proposed to occur via the 16-electron intermediate $[W(PMe_3)_4H(OC_6H_4Bu^t)]$, our present data do not distinguish between (i) a preequilibrium with $[W(PMe_3)_4H(OC_6H_4Bu^t)]$, followed by rate-determining oxidative addition of H_2, or (ii) rate-determining formation of $[W(PMe_3)_4H(OC_6H_4Bu^t)]$, followed by rapid oxidative addition of H_2.

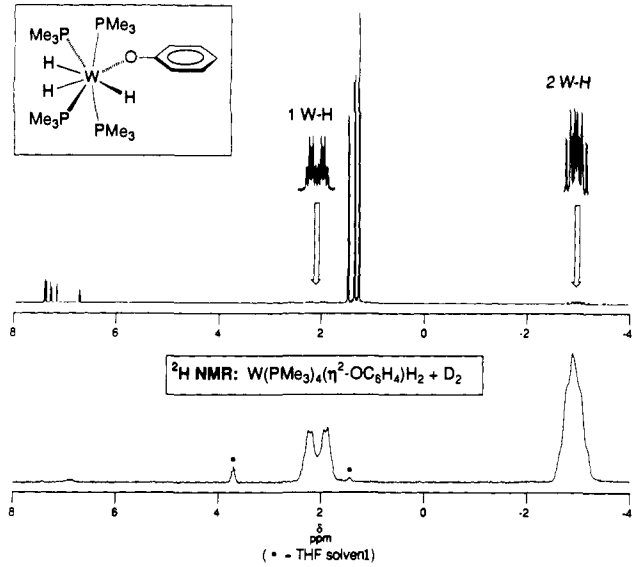
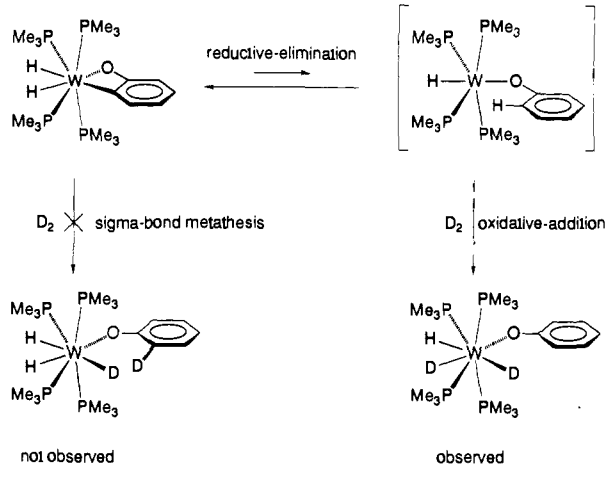


Figure 8. Upper trace: ^{1}H NMR spectrum of $W(PMe_3)_4H_3(OC_6H_5)$ in C_6D_6. Lower trace: ^{2}H NMR spectrum for the reaction of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ with D_2 (in THF).

The equilibrium constants for hydrogenation of the 5-membered oxametallacycles are even more sensitive to substitution effects than those observed for the 4-membered oxametallacycles. Thus, although the aryloxy–trihydride complex $[W(PMe_3)_4H_3\{OC_6H_4Me\}]$ is rapidly obtained from the reaction of $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_4(CH_2)\}$ with H_2 within minutes at room temperature, the corresponding derivatives $[W(PMe_3)_4H_3\{OC_6H_3Me_2\}]$ and $[W(PMe_3)_4H_3\{OC_6H_2Me_3\}]$, with methyl groups in *both* ortho positions of the phenyl ring, *cannot* even be spectroscopically observed as products of the corresponding reactions of the 5-membered oxametallacycles with H_2 after 2 days at 110 °C. Evidence that this observation is a thermodynamic consequence, and not a kinetic effect, has been provided by a combination of ^{1}H and ^{2}H NMR spectroscopies. Thus, examination of the ^{2}H NMR spectrum of the complexes $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_3Me(CH_2)\}$ and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$ in the presence of D_2 demonstrates that rapid deuterium incorporation is observed into not only the tungsten–hydride site, but also the W–CH_2 and *o*-methyl groups. Similarly, examination by ^{1}H NMR spectroscopy reveals a decrease in intensity of the appropriate resonances. Incorporation of deuterium into both the W–CH_2 and *o*-methyl group strongly implicates the presence of the aryloxy–trihydride intermediates $[W(PMe_3)_4H_3\{OC_6H_3Me_2\}]$ and $[W(PMe_3)_4H_3\{OC_6H_2Me_3\}]$. Thus, the aryloxy species are indeed kinetically accessible but are thermodynamically unstable with respect to elimination of dihydrogen and formation of the 5-membered oxametallacycles. In this regard, it is striking to observe such a dramatic reversal of thermodynamics by incorporation of a single methyl group into an ortho position. Although we are currently not in a position to address completely this issue, it is likely that the origin of this effect is due to increased steric interactions between the more highly substituted aryloxy ligand (i.e., with two ortho substituents) and the PMe_3 ligands.[24] The formation of a 5-membered oxa-

(23) The phenoxy complex $W(PMe_3)_4H_3(OC_6H_5)$ has been synthesized previously by a different procedure.[23a] However, the reported NMR data do not correspond with our data, shown in Figure 8. In particular, the original report does not describe *two* very distinct hydride environments for the complex. We have also characterized $W(PMe_3)_4H_3(OC_6H_5)$ *crystallographically*,[23b] and although our crystal was not isomorphous with that previously reported,[23a] essential structural details of the molecules are identical. (a) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204–1211. (b) Orthorhombic, *Pcmn*, $a = 10.717$ (3) Å, $b = 13.868$ (4) Å, $c = 17.855$ (5) Å, $V = 2652$ (1) Å^3, $Z = 4$.

Scheme V. Proposed Mechanism for the Reaction of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ with H_2



metallacycle may be expected to relieve such interactions.

The formation of the aryloxy–trihydride derivatives $W(PMe_3)_4H_3(OC_6H_4R)$ supports the proposal that reductive elimination of the oxametallacycle–hydride unit is facile, giving the 16-electron intermediate $[W(PMe_3)_4H(OC_6H_3R)]$ which may be trapped by H_2. However, an alternative mechanism involving direct attack of H_2 at the W–C bond, in a σ-bond metathesis fashion, cannot be neglected. In order to distinguish between these mechanistic possibilities, we have examined the reactions between the oxametallacycles and D_2. The ^2H NMR spectrum of the reaction between $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ and D_2 (Figure 8) demonstrates that deuterium is located specifically on the tungsten center, with no incorporation into the phenoxy ligand. Such an observation strongly supports a mechanism that only involves oxidative addition of H_2 to the 16-electron intermediate $[W(PMe_3)_4H(OC_6H_5)]$, as illustrated in Scheme V. Similar results are obtained for the reactions of the 4-membered oxametallacycles $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3R)$ (R = Et, Pr^i), with deuterium incorporation specifically at the tungsten center. However, the reactions of the 4-membered oxametallacycles $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3R)$ (R = Bu^t, Ph) with D_2 *do not* give specifically products in which the deuterium is located only on the tungsten center but also give significant amounts of the isotopomer in which deuterium is incorporated into the ortho position of the aryl group, as determined by both ^1H and ^2H NMR spectroscopies. Furthermore, the reaction of the 5-membered oxametallacycle $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_4(CH_2)\}$ with D_2 *does not* give specifically $W(PMe_3)_4HD_2(OC_6H_4CH_3)$, in which the deuterium is located only on the tungsten center, but also gives a significant quantity of the isotopomer $W(PMe_3)_4H_2D(OC_6H_4CH_2D)$, in which deuterium is located in the methyl group of the aryloxy ligand. Two possible pathways for incorporation of deuterium into the aryl groups of these complexes involve (i) initial rapid exchange of the W–H ligands of the oxametallacycles with D_2 prior to the reductive-elimination step and (ii) direct σ-bond metathesis with the W–C bond of the oxametallacycle. At present our data cannot distinguish between these two possibilities. However, for the purposes of our argument, it is only important that our data demonstrate that the reductive-elimination process is one of the mechanisms that operate for all the compounds.

The above study of the reactions of the 4- and 5-membered oxametallacycles with D_2 clearly demonstrates that reductive elimination of the metallacycle–hydride unit is kinetically accessible at room temperature. However, we have not yet addressed the issue of whether C–H bond activation at a different site in the aryloxy ligand of the 16-electron intermediate $[W(PMe_3)_4H(OC_6H_4R)]$ may take place. Evidence for these processes may be obtained by examining isotopic exchange between the aryloxy–trihydride complexes $W(PMe_3)_4H_3(OC_6H_4R)$ and D_2, using a combination of ^1H and ^2H NMR spectroscopies. As illustrated in Scheme VI, the observation of deuterium incorporation into the various ligand groups may be indicative of C–H bond activation of those groups by the 16-electron intermediate $[W(PMe_3)_4H(OC_6H_4R)]$, obtained by reductive elimination of H_2. In all cases, rapid exchange (ca. 30 min at room temperature) of deuterium into the W–H sites is observed, presumably via a reductive-elimination/oxidative-addition sequence and not σ-bond metathesis, since H_2 (and not HD) is observed to be eliminated initially. For the complex $W(PMe_3)_4H_3(OC_6H_4Me)$, exchange of deuterium into the ortho position was observed after a period of 1 day at room temperature. Significantly, this exchange process was *not* accompanied by any observable exchange of deuterium into the methyl substituent, which requires heating at 55 °C for 1 day to result in observable incorporation. Statistical exchange into the *o*-H, methyl, and W–H sites is observed after 3 days at 55 °C. Furthermore, no exchange is observed into the PMe_3 groups. Thus, the observation of faster exchange into the ortho positions, rather than the methyl group, demonstrates that C–H bond activation of the sp^2 o-C–H bond in the 16-electron intermediate $[W(PMe_3)_4H(OC_6H_4Me)]$ is kinetically favored over that for the sp^3 C–H bond of the methyl group. Since the observed product of the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with 2-methylphenol is indeed the 5-membered oxametallacycle $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_4(CH_2)\}$, these results suggest that although the formation of the 4-membered derivative $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Me)$ is kinetically favored, the formation of the 5-membered oxametallacycle $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_4(CH_2)\}$ is thermodynamically favored. These results are illustrated in the qualitative energy profile shown in Figure 9. We have also used a similar approach to gain information concerning the formation of the 4-membered oxametallacycles derived from the other 2-alkylphenols. Thus, a combination of ^1H and ^2H NMR spectroscopies

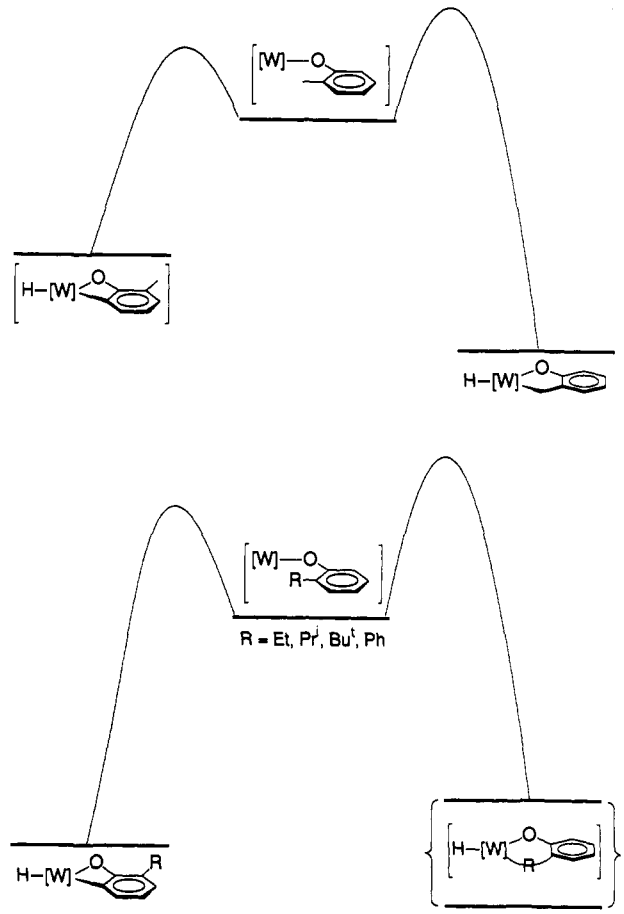
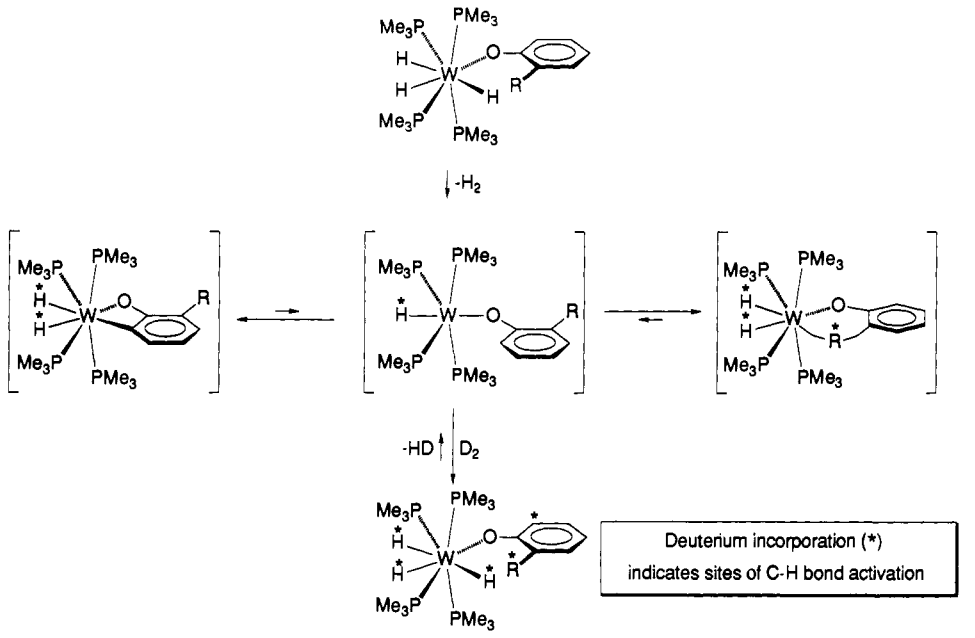


Figure 9. Qualitative energy surfaces for competitive C–H bond activation within $[W(PMe_3)_4H(OC_6H_4R)]$ ($[W] = W(PMe_3)_4H$).

(24) In support of this statement we note that, of the 4-membered oxametallacycles, it is only the bulky *tert*-butyl-substituted derivative which is not completely hydrogenated and gives an equilibrium mixture with the aryloxy–trihydride.

Scheme VI. Probing sites of C-H Activation in [$W(PMe_3)_4H(OC_6H_4R)$] by Observing Deuterium Incorporation



demonstrates that, whereas H/D exchange is observed (after 1 day at room temperature) into the ortho positions of $W(PMe_3)_4H_3(OC_6H_4Et)$, H/D exchange is *not* observed into any position of the ethyl group after 3 days at 55 °C. These results demonstrate that, as for the intermediate $[W(PMe_3)_4H(OC_6H_4Me)]$, sp^2 *o*-C–H bond activation in $[W(PMe_3)_4H(OC_6H_4Et)]$ is kinetically favored over that for the sp^3 C–H bond of the ethyl group. However, since no H/D exchange was observed into the ethyl group, we are presently not in a position to comment upon the relative thermodynamics of this situation, in which the 4-membered oxametallacycle may or may not be the thermodynamic product. A partial energy profile is also illustrated in Figure 9.

In summary, the above results suggest that, for the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with 2-alkylphenols, not only are the 4-membered oxametallacycles the kinetic products, but only for the 2-methylphenol derivative is the 5-membered oxametallacycle also kinetically accessible. From this study we can also conclude that the 5-membered oxametallacycle derived from 2-methylphenol is the thermodynamic product, but we cannot address this issue for the other derivatives for which 5- or 6-membered oxametallacycles cannot be kinetically accessed. Thus, it is most likely that the formation of 4-membered vs 5- or 6-membered oxametallacycles in this system represents a kinetic preference. It is worthwhile to contrast the propensity for the formation of 4-membered metallacycles in this system, with the marked tendency of *o*-alkyl groups in other systems to undergo facile metalation resulting in the formation of 5- or 6-membered oxametallacycles.[18,19] Although a detailed comparison with other systems is not possible, we note that a contributing factor may be a consequence of the 18-electron configuration of the tungsten centers in these oxametallacycles. The 6-membered oxametallacycle complexes that are derived from aryloxy ligands typically possess electron-deficient metal centers. Structural studies on these oxametallacycles demonstrate that formation of the 6-membered ring allows larger M–O–C bond angles, thus enabling favorable lone pair donation from oxygen to the electron-deficient metal center.[18] However, for the 18-electron complexes described here, lone pair donation would not be expected to contribute significantly to oxametallacycle stability, and thus the preference for 6-membered ring formation would be lessened, both in the ground and transition states.

Conclusion

In summary, the homoleptic tungsten complex $W(PMe_3)_6$ may be readily obtained by the reduction of WCl_6 with Na(K) alloy in PMe_3 solvent. Dissociation of PMe_3 from $W(PMe_3)_6$ is facile and results in the formation of the metalated complex $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, with which it is in equilibrium. These electron-rich tungsten complexes react rapidly with phenols to form 4- and 5-membered oxametallacycle complexes, in contrast to the more commonly observed 6-membered derivatives that are obtained for electron-deficient metal complexes. Mechanistic studies suggest that the formation of the oxametallacycles in the reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with phenols does not proceed via oxidative addition of the O–H group at the tungsten center, but rather by direct reaction at the W–C bond of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$. In all cases the the 4-membered oxametallacycles formed have been identified as the kinetic products of the reaction, and for the complex derived from 2-methylphenol, the 5-membered oxametallacycle was also identified as the thermodynamic product.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques.[25] Solvents were purified and degassed by standard procedures. ^1H, ^{13}C, and ^{31}P NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers. *J* values are given in hertz. ^{31}P NMR spectra are referenced relative to 85% H_3PO_4. IR spectra were recorded as Nujol mulls or KBr pellets on a Perkin-Elmer 1420 spectrophotometer and the data are reported in cm^{-1}. Elemental analyses were measured using a Perkin-Elmer 2400 CHN elemental analyzer. $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ was prepared as reported previously.[3] Complete NMR spectroscopic data for all new complexes are given in the supplementary material, and only partial data are presented after the synthesis of each compound.

Synthesis of $W(PMe_3)_6$. PMe_3 (30 mL) was condensed onto Na(K) alloy (1:3 w/w, 5 g) at −78 °C in a glass ampule, equipped with a large bore Teflon valve and a *glass*-covered stir bar.[26] The ampule was maintained at −78 °C, and WCl_6 (5 g) was added to the ampule via a Tygon tube under an argon atmosphere. The ampule was evacuated at −78 °C and then allowed to warm to room temperature. The mixture was stirred at room temperature for 10 days, after which the PMe_3 was removed in vacuo and the product was extracted into pentane (6 × 300 mL) at room temperature (ca. 30 min/extraction). After each extraction the filtrate was immediately concentrated, without warming. The extracts were combined and further concentrated to ca. 30 mL to give $W(PMe_3)_6$ as a yellow microcrystalline solid (4.3 g, 53%) that was isolated pure by filtration, free from $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$. The filtrate consisted of a mixture of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and W-

(25) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. *ACS Symp. Ser.* **1987**, *357*, 6–23. (b) Burger, B. J.; Bercaw, J. E. *ACS Symp. Ser.* **1987**, *357*, 79–97.

(26) Teflon-covered stir bars may react violently with Na(K) alloy, so glass-covered stir bars are strongly recommended.

$(PMe_3)_6$. Note that in order to isolate $W(PMe_3)_6$ in preference to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, it is critical to extract the product as quickly as possible. We observe that an extraction cycle (including filtration) of 30 min gives good yields of $W(PMe_3)_6$, whereas extraction overnight gives $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$. CAUTION: **Mixtures of metal halides, alkali-metal reducing agents, and PMe_3 have been reported to explode violently.**[27] However, we have never observed such an incident following the above procedure exactly. Single crystals of $W(PMe_3)_6$ for the X-ray diffraction study were obtained by slow formation from a concentrated solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ in PMe_3 at room temperature (vide infra). Anal. Calcd for $C_{18}H_{54}P_6W$: C, 33.8; H, 8.5. Found: C, 33.8; H, 9.3. ^1H NMR: δ 1.49 [54 H, s, 6 $P(CH_3)_3$]. $^{31}P\{^1H\}$ NMR: δ −41.5 [s, J_{P-W} = 294, 6 $P(CH_3)_3$]. IR: 926 (ν_{P-C}).

Kinetics and Thermodynamics of the Conversion of $W(PMe_3)_6$ to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$. The quantitative conversion of $W(PMe_3)_6$ to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, accompanied by elimination of PMe_3, was confirmed by comparison of the ^1H and ^{31}P NMR data with those of a sample of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ prepared by the literature method.[3,4] Rate constants for the conversion of $W(PMe_3)_6$ to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ were obtained by monitoring the decrease in intensity of the ^1H NMR resonance of $W(PMe_3)_6$ in C_6D_6 solutions (typically 5–10 mM). Samples were maintained in a thermostat with temperatures constant to within ±1 °C. After measured time intervals, the samples were removed from the thermostat, cooled immediately in an ice bath, and monitored by ^1H NMR spectroscopy. Good first-order plots were obtained for the reactions without additional PMe_3, indicating only slight inhibition. Under these conditions, the rate-determining step is specifically dissociation of PMe_3 from $W(PMe_3)_6$. $\Delta G^\ddagger$ was calculated from the Eyring equation $\Delta G^\ddagger = RT \ln (\kappa k_B T/kh)$, assuming a transmission coefficient (κ) of 1. A plot of $\ln (k/T)$ vs $1/T$ yielded the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the dissociation of PMe_3. The kinetics of the conversion of $W(PMe_3)_6$ to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ was also measured in the presence of excess PMe_3 using the method of initial rates.

Equilibrium constants (K) were determined at several temperatures (see Table I) in the presence of variable amounts of added PMe_3. Equilibrium temperatures were constant to within ±1 °C. $\Delta G°$ for the dissociation was calculated from the equilibrium constant using the expression $\Delta G° = -RT \ln K$, and a plot of $\ln K$ vs $1/T$ yielded $\Delta H°$ and $\Delta S°$.

Synthesis of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$. (a) A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.62 g, 1.10 mmol) in pentane (40 mL) was treated with a solution of C_6H_5OH (0.10 g, 1.06 mmol) in pentane (40 mL). The mixture was filtered after stirring for 15 min at room temperature, and the filtrate was concentrated to ca. 15 mL and placed at −78 °C, giving yellow crystals of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$, which were isolated by filtration and dried in vacuo (0.39 g, 63%). Anal. Calcd for $C_{18}H_{42}OP_4W$: C, 37.1; H, 7.3. Found: C, 37.2; H, 7.1. ^1H NMR: δ 1.21 [18 H, vt, J_{H-P} = 3.3, 2 $P(CH_3)_3$], 1.34 [9 H, d, J_{H-P} = 7.1, 1 $P(CH_3)_3$], 1.42 [9 H, d, J_{H-P} = 7.9, 1 $P(CH_3)_3$], −3.42 [2 H, ddt, $J_{H-P}(d)$ = 35, $J_{H-P}(d)$ = 55, $J_{H-P}(t)$ = 39, 2 W*H*]. $^{31}P\{^1H\}$ NMR: δ −24.0 [t, J_{P-P} = 13, J_{P-W} = 201, 2 $P(CH_3)_3$], −16.6 [m, 2 $P(CH_3)_3$]. IR: 1858 (ν_{W-H}).

(b) A solution of $W(PMe_3)_6$ (10 mg, 0.016 mmol) in C_6D_6 (ca. 0.7 mL) was treated with C_6H_5OH. $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ was observed to be formed by ^1H NMR spectroscopy after ca. 8 h at room temperature.

Synthesis of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Et)$. A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.51 g, 0.90 mmol) in pentane (50 mL) was treated with 2-EtC_6H_4OH (98 μL, 0.83 mmol). The mixture was filtered after stirring for 30 min at room temperature, and the filtrate was concentrated to ca. 10 mL and placed at −78 °C giving yellow crystals of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Et)$, which were isolated by filtration and dried in vacuo (0.42 g, 83%). Anal. Calcd for $C_{20}H_{46}OP_4W$: C, 39.4; H, 7.6. Found: C, 39.4; H, 7.5. ^1H NMR: δ 1.19 [18 H, vt, J_{H-P} = 3.3, 2 $P(CH_3)_3$], 1.35 [9 H, d, J_{H-P} = 7.1, 1 $P(CH_3)_3$], 1.43 [9 H, d, J_{H-P} = 8.0, 1 $P(CH_3)_3$], −3.41 [2 H, ddt, $J_{H-P}(d)$ = 35, $J_{H-P}(d)$ = 55, $J_{H-P}(t)$ = 39, 2 W*H*]. $^{31}P\{^1H\}$ NMR: δ −24.0 [t, J_{P-P} = 14, J_{P-W} = 202, 2 $P(CH_3)_3$], −17.0 [m, 2 $P(CH_3)_3$]. IR: 1851 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Pr^i)$. A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.64 g, 1.13 mmol) in pentane (50 mL) was treated with 2-$Pr^iC_6H_4OH$ (152 μL, 1.13 mmol). The mixture was filtered after stirring for 10 min, and the filtrate was concentrated to ca. 10 mL and placed at −78 °C, giving yellow crystals of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Pr^i)$, which were isolated by filtration and dried in vacuo (0.58 g, 82%). Anal. Calcd for $C_{21}H_{48}OP_4W$: C, 40.4; H, 7.8. Found: C, 40,7; H, 7.4. ^1H NMR: δ 1.19 [18 H, vt, J_{H-P} = 3.3, 2 $P(CH_3)_3$], 1.35 [9 H, d, J_{H-P} = 6.8, 1 $P(CH_3)_3$], 1.43 [9 H, d, J_{H-P} = 7.6, 1 $P(CH_3)_3$], −3.42 [2 H, ddt, $J_{H-P}(d)$ = 35, $J_{H-P}(d)$ = 54, $J_{H-P}(t)$ = 39, 2 W*H*]. $^{31}P\{^1H\}$ NMR: δ −24.0 [s, J_{P-W} = 203, 2 $P(CH_3)_3$], −16.9 [m, 2 $P(CH_3)_3$]. IR: 1855 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Bu^t)$. A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.64 g, 1.13 mmol) in pentane (50 mL) was treated with 2-$Bu^tC_6H_4OH$ (174 μL, 1.13 mmol). The mixture was filtered after stirring for 10 min at room temperature, and the filtrate was concentrated to ca. 10 mL and placed at −78 °C, giving yellow crystals of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Bu^t)$, which were isolated by filtration and dried in vacuo (0.32 g, 44%). Anal. Calcd for $C_{22}H_{50}OP_4W$: C, 41.4; H, 7.9. Found: C, 41.3; H, 7.6. ^1H NMR: δ 1.21 [18 H, vt, J_{H-P} = 3.3, 2 $P(CH_3)_3$], 1.34 [9 H, d, J_{H-P} = 6.5, 1 $P(CH_3)_3$], 1.43 [9 H, d, J_{H-P} = 7.3, 1 $P(CH_3)_3$], −3.53 [2 H, m, 2 W*H*]. $^{31}P\{^1H\}$ NMR: δ −24.5 [s, J_{P-W} = 202, 2 $P(CH_3)_3$], −16.6 [s, J_{P-W} = 162, 2 $P(CH_3)_3$]. IR: 1838, 1870 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Ph)$. A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.71 g, 1.26 mmol) in pentane (40 mL) was treated with a solution of 2-PhC_6H_4OH (0.21 g, 1.23 mmol) in pentane (40 mL). The mixture was filtered after stirring for 15 min at room temperature, and the filtrate was concentrated to ca. 15 mL and placed at −78 °C, giving orange crystals of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Ph)$, which were isolated by filtration and dried in vacuo (0.66 g, 81%). Anal. Calcd for $C_{24}H_{46}OP_4W$: C, 43.8; H, 7.0. Found: C, 43.9; H, 6.9. ^1H NMR: δ 1.14 [18 H, vt, J_{H-P} = 3.3, 2 $P(CH_3)_3$], 1.34 [9 H, d, J_{H-P} = 7.0, 1 $P(CH_3)_3$], 1.40 [9 H, d, J_{H-P} = 7.6, 1 $P(CH_3)_3$], −3.37 [2 H, ddt, $J_{H-P}(d)$ = 35, $J_{H-P}(d)$ = 55, $J_{H-P}(t)$ = 39, 2 W*H*]. $^{31}P\{^1H\}$ NMR: δ −24.2 [t, J_{P-P} = 12, J_{P-W} = 201, 2 $P(CH_3)_3$], −16.7 [m, 2 $P(CH_3)_3$]. IR: 1835, 1872 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_4(CH_2)\}$. A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.26 g, 0.46 mmol) in pentane (20 mL) was treated with a solution of 2-MeC_6H_4OH (0.05 g, 0.46 mmol) in pentane (15 mL). The mixture was filtered after stirring for 15 min at room temperature, and the filtrate was concentrated to ca. 10 mL and placed at −78 °C, giving yellow crystals of $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_4(CH_2)\}$, which were isolated by filtration and dried in vacuo (0.14 g, 50%). Anal. Calcd for $C_{19}H_{44}OP_4W$: C, 38.3; H, 7.4. Found: C, 37.8; H, 7.4. ^1H NMR: δ 1.07 [18 H, vt, J_{H-P} = 3.2, 2 $P(CH_3)_3$], 1.29 [9 H, d, J_{H-P} = 7.5, 1 $P(CH_3)_3$], 1.41 [9 H, d, J_{H-P} = 7.0, 1 $P(CH_3)_3$], −3.41 [2 H, m, 2 W*H*]. $^{31}P\{^1H\}$ NMR: δ −25.5 [t, J_{P-P} = 14, J_{P-W} = 206, 2 $P(CH_3)_3$], −21.8 [dt, $J_{P-P}(d)$ = 44, $J_{P-P}(t)$ = 14, J_{P-W} = 167, 1 $P(CH_3)_3$], −17.3 [dt, $J_{P-P}(d)$ = 44, $J_{P-P}(t)$ = 14, J_{P-W} = 167, 1 $P(CH_3)_3$]. IR: 1850 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_3Me(CH_2)\}$. A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.52 g, 0.92 mmol) in pentane (30 mL) was treated with a solution of 2,6-$Me_2C_6H_3OH$ (0.10 g, 0.82 mmol) in pentane (30 mL). The mixture was filtered after stirring for 1 h at room temperature, and the filtrate was concentrated to ca. 15 mL and placed at −78 °C, giving pale yellow crystals of $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_3Me(CH_2)\}$, which were isolated by filtration and dried in vacuo (0.36 g, 72%). Anal. Calcd for $C_{20}H_{46}OP_4W$: C, 39.4; H, 7.6. Found: C, 39.0; H, 7.4. ^1H NMR: δ 1.06 [18 H, vt, J_{H-P} = 3.1, 2 $P(CH_3)_3$], 1.30 [9 H, d, J_{H-P} = 7.4, 1 $P(CH_3)_3$], 1.45 [9 H, d, J_{H-P} = 7.0, 1 $P(CH_3)_3$], −3.41 [2 H, m, 2 W*H*]. $^{31}P\{^1H\}$ NMR: δ −25.7 [t, J_{P-P} = 15, J_{P-W} = 206, 2 $P(CH_3)_3$], −20.8 [dt, $J_{P-P}(d)$ = 45, $J_{P-P}(t)$ = 15, J_{P-W} = 166, 1 $P(CH_3)_3$], −17.3 [dt, $J_{P-P}(d)$ = 45, $J_{P-P}(t)$ = 15, J_{P-W} = 165, 1 $P(CH_3)_3$]. IR: 1821, 1893 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$. A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (0.50 g, 0.89 mmol) in pentane (30 mL) was treated with a solution of 2,4,6-$Me_3C_6H_2OH$ (0.11 g, 0.81 mmol) in pentane (30 mL). The mixture was filtered after stirring for 1 h at room temperature, and the filtrate was concentrated to ca. 15 mL and placed at −78 °C, giving pale yellow crystals of $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$, which were isolated by filtration and dried in vacuo (0.37 g, 73%). Anal. Calcd for $C_{21}H_{48}OP_4W$: C, 40.4; H, 7.8. Found: C, 40.4; H, 7.6. ^1H NMR: δ 1.07 [18 H, vt, J_{H-P} = 3.2, 2 $P(CH_3)_3$], 1.32 [9 H, d, J_{H-P} = 7.4, 1 $P(CH_3)_3$], 1.44 [9 H, d, J_{H-P} = 6.8, 1 $P(CH_3)_3$], −3.43 [2 H, m, 2 W*H*]. $^{31}P\{^1H\}$ NMR: δ −25.7 [t, J_{P-P} = 15, J_{P-W} = 207, 2 $P(CH_3)_3$], −20.9 [dt, $J_{P-P}(d)$ = 45, $J_{P-P}(t)$ = 15, J_{P-W} = 166, 1 $P(CH_3)_3$], −17.3 [dt, $J_{P-P}(d)$ = 45, $J_{P-P}(t)$ = 15, J_{P-W} = 164, 1 $P(CH_3)_3$]. IR: 1828, 1877 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_3(OC_6H_5)$. A solution of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ (0.31 g, 0.53 mmol) in pentane (50 mL) was stirred under H_2 (ca. 2 atm) in a glass ampule for 15 h at room temperature. The solution was filtered and the solvent removed under reduced pressure, giving $W(PMe_3)_4H_3(OC_6H_5)$ as an off-white solid (0.19 g, 62%). Anal. Calcd for $C_{18}H_{44}OP_4W$: C, 37.0; H, 7.6. Found: C, 37.0; H, 7.4. ^1H NMR: δ 1.27 [18 H, vt, J_{H-P} = 3.2, 2 $P(CH_3)_3$], 1.36 [9 H, d, J_{H-P} = 6.4, 1 $P(CH_3)_3$], 1.48 [9 H, d, J_{H-P} = 8.0, 1 $P(CH_3)_3$], −3.01 [2 H, dddt, $J_{H-H}(d)$ = 6, $J_{H-P}(d)$ = 34, $J_{H-P}(d)$ = 55, $J_{H-P}(t)$ = 38, 2 W*H*], 2.07 [1 H, dtq, $J_{H-P}(d)$ = 92, $J_{H-H}(t)$ = 6, $J_{H-P}(q)$ = 29, 1 W*H*]. $^{31}P\{^1H\}$ NMR: δ −25.0 [dt, $J_{P-P}(d)$ = 50, $J_{P-P}(t)$ = 17, J_{P-W} = 157, 1 $P(CH_3)_3$], −19.9

(27) Berry, D. H. *Chem. Eng. News* **1989**, *67* (47), 2.

Table IV. Summary of Crystal and Intensity Collection Data

	$W(PMe_3)_6$	$W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$	$W(PMe_3)_4H_2[\eta^2\text{-}OC_6H_2Me_2(CH_2)]$
formula	$C_{18}H_{54}P_6W$	$C_{18}H_{42}OP_4W$	$C_{21}H_{48}OP_4W$
formula wt	640.3	582.3	624.4
lattice	cubic	monoclinic	monoclinic
cell constants			
a, Å	11.303 (2)	9.713 (2)	9.898 (3)
b, Å		16.008 (5)	28.065 (9)
c, Å		16.283 (2)	10.663 (3)
β, deg		93.51 (1)	104.33 (2)
V, Å^3	1444.1 (6)	2527.1 (9)	2870 (1)
Z	2	4	4
space group	$Im\bar{3}m$ (No. 229)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ(calcd), g cm^{-3}	1.47	1.53	1.45
goodness of fit	1.165	1.055	1.274
R	0.0529	0.0262	0.0455
R_w	0.0645	0.0356	0.0451

[t, J_{P-P} = 17, J_{P-W} = 201, 2 $P(CH_3)_3$], −11.3 [dt, $J_{P-P}(d)$ = 50, $J_{P-P}(t)$ = 17, J_{P-W} = 121, 1 $P(CH_3)_3$]. IR: 1747, 1838 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_3(OC_6H_4Me)$. A solution of $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_4(CH_2)\}$ (0.13 g, 0.22 mmol) in pentane (60 mL) was stirred under H_2 (ca. 2 atm) in a glass ampule for 18 h at room temperature. The solution was filtered and the solvent removed under reduced pressure, giving $W(PMe_3)_4H_3(OC_6H_4Me)$ as an off-white solid (0.11 g, 82%). Anal. Calcd for $C_{19}H_{46}OP_4W$: C, 38.1; H, 7.8. Found: C, 38.0; H, 7.6. ^{1}H NMR: δ 1.25 [18 H, vt, J_{H-P} = 3.0, 2 $P(CH_3)_3$], 1.39 [9 H, d, J_{H-P} = 6.2, 1 $P(CH_3)_3$], 1.49 [9 H, d, J_{H-P} = 7.9, 1 $P(CH_3)_3$], −3.26 [2 H, dddt, $J_{H-H}(d)$ = 6, $J_{H-P}(d)$ = 32, $J_{H-P}(d)$ = 58, $J_{H-P}(t)$ = 38, 2 W*H*], 2.29 [1 H, dtq, $J_{H-P}(d)$ = 97, $J_{H-H}(t)$ = 6, $J_{H-P}(q)$ = 28, 1 W*H*]. $^{31}P\{^1H\}$ NMR: δ −27.9 [dt, $J_{P-P}(d)$ = 55, $J_{P-P}(t)$ = 19, J_{P-W} = 156, 1 $P(CH_3)_3$], −20.2 [t, J_{P-P} = 19, J_{P-W} = 204, 2 $P(CH_3)_3$], −10.1 [dt, $J_{P-P}(d)$ = 55, $J_{P-P}(t)$ = 19, J_{P-W} = 121, 1 $P(CH_3)_3$]. IR: 1769, 1822, 1879 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_3(OC_6H_4Et)$. A solution of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Et)$ (0.17 g, 0.28 mmol) in pentane (50 mL) was stirred under H_2 (ca. 2 atm) in a glass ampule for 18 h at room temperature. The solution was filtered and the solvent removed under reduced pressure, giving $W(PMe_3)_4H_3(OC_6H_4Et)$ as an off-white solid (0.14 g, 82%). Anal. Calcd for $C_{20}H_{48}OP_4W$: C, 39.2; H, 7.9. Found: C, 38.8; H, 7.6. ^{1}H NMR: δ 1.25 [18 H, vt, J_{H-P} = 3.2, 2 $P(CH_3)_3$], 1.40 [9 H, d, J_{H-P} = 6.3, 1 $P(CH_3)_3$], 1.48 [9 H, d, J_{H-P} = 8.0, 1 $P(CH_3)_3$], −3.28 [2 H, dddt, $J_{H-H}(d)$ = 6, $J_{H-P}(d)$ = 34, $J_{H-P}(d)$ = 58, $J_{H-P}(t)$ = 38, 2 W*H*], 2.34 [1 H, dtq, $J_{H-P}(d)$ = 96, $J_{H-H}(t)$ = 6, $J_{H-P}(q)$ = 24, 1 W*H*]. $^{31}P\{^1H\}$ NMR: δ −28.8 [dt, $J_{P-P}(d)$ = 55, $J_{P-P}(t)$ = 19, J_{P-W} = 155, 1 $P(CH_3)_3$], −19.9 [t, J_{P-P} = 19, J_{P-W} = 204, 2 $P(CH_3)_3$], −10.2 [dt, $J_{P-P}(d)$ = 55, $J_{P-P}(t)$ = 19, J_{P-W} = 122, 1 $P(CH_3)_3$]. IR: 1761, 1855 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_3(OC_6H_4Pr^i)$. A solution of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Pr^i)$ (0.49 g, 0.78 mmol) in pentane (50 mL) was stirred under H_2 (ca. 2 atm) in a glass ampule for 18 h at room temperature. The solution was filtered and the solvent removed under reduced pressure, giving $W(PMe_3)_4H_3(OC_6H_4Pr^i)$ as an off-white solid (0.38 g, 78%). Anal. Calcd for $C_{21}H_{50}OP_4W$: C, 40.3; H, 8.1. Found: C, 40.2; H, 7.6. ^{1}H NMR: δ 1.26 [18 H, vt, J_{H-P} = 3.1, 2 $P(CH_3)_3$], 1.40 [9 H, d, J_{H-P} = 6.0, 1 $P(CH_3)_3$], 1.47 [9 H, d, J_{H-P} = 8.0, 1 $P(CH_3)_3$], −3.25 [2 H, dddt, $J_{H-H}(d)$ = 6, $J_{H-P}(d)$ = 33, $J_{H-P}(d)$ = 58, $J_{H-P}(t)$ = 39, 2 W*H*], 2.37 [1 H, dtq, $J_{H-P}(d)$ = 96, $J_{H-H}(t)$ = 6, $J_{H-P}(q)$ = 22, 1 W*H*]. $^{31}P\{^1H\}$ NMR: δ −29.7 [dt, $J_{P-P}(d)$ = 56, $J_{P-P}(t)$ = 19, J_{P-W} = 154, 1 $P(CH_3)_3$], −20.1 [t, J_{P-P} = 19, J_{P-W} = 202, 2 $P(CH_3)_3$], −10.4 [dt, $J_{P-P}(d)$ = 56, $J_{P-P}(t)$ = 19, J_{P-W} = 123, 1 $P(CH_3)_3$]. IR: 1763, 1833, 1890 (ν_{W-H}).

Synthesis of $W(PMe_3)_4H_3(OC_6H_4Ph)$. A solution of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Ph)$ (0.59 g, 0.90 mmol) in pentane (60 mL) was stirred under H_2 (ca. 2 atm) in a glass ampule for 18 h at room temperature. The solution was filtered and the solvent removed under reduced pressure, giving $W(PMe_3)_4H_3(OC_6H_4Ph)$ as a pale orange solid, which was recrystallized from pentane (0.32 g, 54%). Anal. Calcd for $C_{24}H_{48}OP_4W$: C, 43.7; H, 7.3. Found: C, 43.6; H, 7.0. ^{1}H NMR: δ 1.28 [18 H, vt, J_{H-P} = 3.1, 2 $P(CH_3)_3$], 1.00 [9 H, d, J_{H-P} = 6.4, 1 $P(CH_3)_3$], 1.45 [9 H, d, J_{H-P} = 8.0, 1 $P(CH_3)_3$], −3.41 [2 H, dddt, $J_{H-H}(d)$ = 6, $J_{H-P}(d)$ = 33, $J_{H-P}(d)$ = 57, $J_{H-P}(t)$ = 38, 2 W*H*], 2.58 [1 H, dtq, $J_{H-P}(d)$ = 92, $J_{H-H}(t)$ = 6, $J_{H-P}(q)$ = 25, 1 W*H*]. $^{31}P\{^1H\}$ NMR: δ −29.0 [dt, $J_{P-P}(d)$ = 53, $J_{P-P}(t)$ = 19, J_{P-W} = 156, 1 $P(CH_3)_3$], −19.7 [t, J_{P-P} = 19, J_{P-W} = 202, 2 $P(CH_3)_3$], −11.5 [dt, $J_{P-P}(d)$ = 53, $J_{P-P}(t)$ = 19, J_{P-W} = 123, 1 $P(CH_3)_3$]. IR: 1770, 1842, 1887 (ν_{W-H}).

Kinetics and Thermodynamics of the Hydrogenation of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Bu^t)$. In a typical experiment, a solution of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Bu^t)$ (7 mg, 0.011 mmol) in C_6D_6 (0.84 mL) was saturated with H_2 (1 atm at 23 °C). The sample was placed in a constant-temperature oil bath (±1 °C) and removed periodically to monitor (^{1}H NMR) the formation of the equilibrium mixture with the trihydride complex $W(PMe_3)_4H_3(OC_6H_4Bu^t)$. The molar concentration of dihydrogen in solution was estimated by a similar method to that described previously,[21] using a combination of Henry's law with the mole fraction solubilities of H_2 calculated directly or extrapolated from the equation given by Clever.[28] The equilibrium constant K = $[W(PMe_3)_4H_3(OC_6H_4Bu^t)]/[W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_3Bu^t)][H_2]$ (see Table III) was measured over the temperature range temperature 40–100 °C, while the kinetics of the approach to equilibrium (k_f and k_r, where $K = k_f/k_r$) were measured over the temperature range 40–80 °C. Partial ^{1}H NMR for $W(PMe_3)_4H_3(OC_6H_4Bu^t)$: δ 1.29 [18 H, vt, J_{H-P} = 3.1, 2 $P(CH_3)_3$], 1.45 [9 H, d, J_{H-P} = 7.8, 1 $P(CH_3)_3$], 1.47 [9 H, d, J_{H-P} = 6.0, 1 $P(CH_3)_3$], −3.40 [2 H, m, 2 W*H*], 3.00 [1 H, m, 1 W*H*].

Table V. Selected Bond Lengths (Å) for $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$

W–P(1)	2.422 (2)	W–P(2)	2.467 (2)
W–P(3)	2.491 (2)	W–P(4)	2.491 (2)
W–O	2.177 (5)	W–C(2)	2.213 (7)
O–C(1)	1.349 (9)	C(1)–C(2)	1.397 (10)
C(1)–C(6)	1.405 (11)	C(2)–C(3)	1.388 (12)
C(3)–C(4)	1.407 (13)	C(4)–C(5)	1.390 (14)
C(5)–C(6)	1.373 (12)		

Table VI. Selected Bond Angles (deg) for $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$

P(1)–W–P(2)	132.0 (1)	P(1)–W–P(3)	97.1 (1)
P(2)–W–P(3)	92.5 (1)	P(1)–W–P(4)	96.9 (1)
P(2)–W–P(4)	91.1 (1)	P(3)–W–P(4)	157.6 (1)
P(1)–W–O	146.0 (1)	P(2)–W–O	82.0 (1)
P(3)–W–O	79.6 (1)	P(4)–W–O	79.0 (1)
P(1)–W–C(2)	83.2 (2)	P(2)–W–C(2)	144.8 (2)
P(3)–W–C(2)	83.5 (2)	P(4)–W–C(2)	80.8 (2)
O–W–C(2)	62.8 (2)	W–P(1)–C(11)	116.7 (3)
W–O–C(1)	93.6 (4)	O–C(1)–C(6)	124.9 (7)
O–C(1)–C(2)	112.8 (6)	W–C(2)–C(1)	90.7 (5)
C(2)–C(1)–C(6)	122.1 (7)	C(1)–C(2)–C(3)	116.9 (7)
W–C(2)–C(3)	152.2 (6)	C(3)–C(4)–C(5)	119.2 (8)
C(2)–C(3)–C(4)	121.8 (8)	C(1)–C(6)–C(5)	119.2 (8)
C(4)–C(5)–C(6)	120.6 (9)		

X-ray Structure Determination Procedures. Crystal data, data collection, and refinement parameters for $W(PMe_3)_6$, $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$, and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$ are summarized in Table IV. A typical procedure for the structure determination is as follows. A single crystal was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite monochromated Mo Kα X-radiation (λ = 0.71073 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was solved using Patterson and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[29]

(28) $\ln x_g = -5.5284 - 813.90/(T/K)$. Clever, H. L. In *Hydrogen and Deuterium*; Solubility Data Series, Young, C. L., Ed.; Pergamon: Oxford, 1981; p 159, Vol. 5/6.

(29) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.

Table VII. Selected Bond Lengths (Å) for $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$

W-P(1)	2.426 (4)	W-P(2)	2.479 (4)
W-P(3)	2.494 (4)	W-P(4)	2.496 (4)
W-O	2.145 (8)	W-C(7)	2.290 (11)
O-C(1)	1.354 (14)	C(1)-C(2)	1.359 (19)
C(1)-C(6)	1.420 (18)	C(2)-C(3)	1.402 (17)
C(2)-C(7)	1.488 (16)	C(3)-C(4)	1.403 (22)
C(4)-C(5)	1.368 (26)	C(4)-C(8)	1.515 (21)
C(5)-C(6)	1.410 (22)	C(6)-C(9)	1.505 (24)

Table VIII. Selected Bond Angles (deg) for $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$

P(1)-W-P(2)	128.8 (1)	P(1)-W-P(3)	96.4 (1)
P(2)-W-P(3)	92.8 (1)	P(1)-W-P(4)	97.1 (1)
P(2)-W-P(4)	91.7 (1)	P(3)-W-P(4)	158.5 (1)
P(1)-W-O	152.1 (2)	P(2)-W-O	79.1 (2)
P(3)-W-O	79.7 (2)	P(4)-W-O	80.5 (2)
P(1)-W-C(7)	76.7 (3)	P(2)-W-C(7)	154.5 (3)
P(3)-W-C(7)	83.4 (3)	P(4)-W-C(7)	83.5 (3)
O-W-C(7)	75.4 (4)	W-P(1)-C(11)	115.8 (5)
O-C(1)-C(2)	120.4 (10)	W-O-C(1)	117.6 (8)
C(2)-C(1)-C(6)	122.1 (12)	O-C(1)-C(6)	117.5 (12)
C(1)-C(2)-C(7)	116.5 (10)	C(1)-C(2)-C(3)	119.4 (11)
W-C(7)-C(2)	109.7 (8)	C(3)-C(2)-C(7)	124.0 (12)

For $W(PMe_3)_6$, systematic absences were consistent with several space groups, of which the choice $Im\bar{3}m$ was made since (i) this produced the most successful solution and (ii) this is also the space group for the isostructural complexes $Mo(PMe_3)_6$ and $M(Me_2PCH_2CH_2PMe_2)_3$ (M = Cr, Mo, W, V, Nb, Ta).[1a,6] The methyl groups of the PMe_3 ligands are highly disordered as a result of the presence of both the 3-fold symmetry of PMe_3 and the 4-fold crystallographic symmetry. The disorder was modeled, in a similar manner to that reported for $Mo(PMe_3)_6$, by fixing two carbon atoms on two independent mirror planes that pass through P.[1a] For both $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$, systematic absences were consistent with the space group $P2_1/n$. Hydrogen atoms on carbon were included in calculated positions (d_{C-H} = 0.96 Å; $U_{iso}(H) = 1.2U_{iso}(C)$). Selected bond lengths and angles for $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$ are given in Tables V-VIII.

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Supplementary Material Available: Complete table of ^1H, ^{13}C, and ^{31}P NMR spectroscopic data for all new compounds (8 pages). Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and observed and calculated structure factors and ORTEP drawings for $W(PMe_3)_6$, $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$, and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$ are available as supplementary material to the original communications.[2] Ordering information is given on any current masthead page.

A New Approach to the Study of the Oxygenation Reactions of Transition-Metal Complexes. Formation of the μ-Superoxo Cobalt(III) Complexes in the Oxygenation Reactions of Cobalt(II) Amines

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Abstract: In the reactions of molecular oxygen with cobalt(II) amines, formation of μ-superoxo complexes has been identified on photolysis of cobalt(III) amine complexes $[Co(trien)(NO_2)_2]ClO_4$ (**1**) and $[Co(tetraen)(NO_2)](ClO_4)_2$ (**2**) in oxygen-saturated aqueous solution. The kinetics of oxygenation reactions has been followed by flash photolyzing the complexes **1** and **2** in aqueous and nonaqueous solvents and the rate constants for the formation of mononuclear superoxo complex and the μ-superoxo dinuclear complex has been determined at 25 ± 1 °C. Photochemical routes for the preparation of μ-superoxo cobalt(III) complexes are suggested from this study.

Introduction

Activation of molecular oxygen by cobalt(II) amines is a classic reaction[1,2] and the subject has been extensively investigated.[3] Earlier investigations based on stopped flow kinetics have proposed two steps for the formation of the final product μ-peroxo complex. We have discovered that oxygen activation by cobalt(II) amine species photoproduced from the cobalt(III) complexes opens up possibilities to find new species during the course of the reaction and also more defined mechanistic information on the oxygenation reaction. In this paper we report on the oxygenation reactions of cobalt(II) amine systems by investigating the flash photolysis and steady photolysis of oxygenated aqueous solutions of *cis*-$[Co(trien)(NO_2)_2]ClO_4$ (**1**) and $[Co(tetraen)(NO_2)](ClO_4)_2$ (**2**). By this method the reactant is generated in situ and the coordination environment of the labile cobalt(II) amine is better characterized at the time of the reaction. The subsequent reaction with molecular oxygen could be followed on much shorter time scale compared to stopped flow time scale. In addition, cobalt(II) amine is present at much lower concentration compared to dissolved oxygen and hence the possibility of finding new types of reactions involving dioxygen has been explored.

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