C−O Bond Homolysis in a Tungsten Alkoxide: The Mechanism of Alcohol Deoxygenation by $WCl_2(PMe_3)_4$ and $WH_2Cl_2(PMe_3)_4$

Thomas J. Crevier[1] and James M. Mayer*

Contribution from the Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

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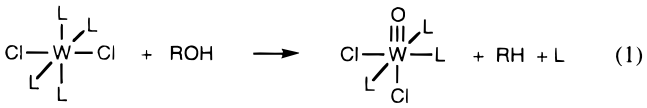
Abstract: Reactions of alcohols with $WCl_2(PMe_3)_4$ (**1**) or $WH_2Cl_2(PMe_3)_4$ (**2**) yield $W(O)Cl_2(PMe_3)_3$ (**3**), PMe_3, and hydrocarbons. Cyclopropanemethanol is deoxygenated to give 1-butene and a trace of *trans*-2-butene as the organic products; benzyl alcohol yields toluene and bibenzyl. These products indicate the intermediacy of organic radicals. Benzyl radicals in the reaction of **1** with $PhCH_2OH$ can be trapped by added **2** or by 9,10-dihydroanthracene (DHA), leading to increased yields of toluene vs bibenzyl. With $WD_2Cl_2(PMe_3)_4$ (**2**-d_2) or DHA-d_{12}, $PhCH_2D$ is formed. The reaction of methanol with **1** proceeds similarly in the presence of DHA, forming **3** and methane. Kinetic studies on the reaction of **1** with benzyl alcohol indicate that the reaction proceeds via alkoxide intermediates. A mechanism involving homolysis of the C−O bond in an alkoxide intermediate is suggested by these results. The thermodynamics of this unusual transformation are discussed.

Introduction

The activation of C−O bonds by transition metal complexes has received increasing attention in recent years due to the importance of such steps in catalytic and stoichiometric transformations.[2] Cleavage of C−O bonds is important in the conversion of alkoxide precursors to metal oxide ceramics.[3] Additionally, C−O bond cleavage reactions may provide insight into the reverse reaction, C−O bond formation, which is of importance in hydrocarbon oxidation. The tungsten complexes WCl_2L_4 (L = PMe_3 (**1**), $PMePh_2$ (**4**)) activate C−O bonds in a wide variety of organic substrates, including ketones, epoxides, isocyanates, sulfoxides, CO_2, and alcohols.[4] WCl_2L_4 complexes are unusual in their ability to deoxygenate non-allylic alcohols (eq 1), as first reported by Wilkinson[5] and subsequently explored in our labs.[4,6,7]



(1)

The deoxygenation of alcohols is a more complicated process than the oxygen atom transfer pathway often utilized by **1** and related reductants.[4b,8,9] The mechanistic data reported here indicate that reaction 1 occurs via a tungsten alkoxide intermediate which eliminates an alkyl radical to form a tungsten−oxo species. This conclusion is opposite to that in our preliminary report,[6] in which we overlooked the evidence for radical intermediates. The C−O bond homolysis is surprising given the stability of most metal alkoxide complexes[10] and the strength of this bond in alcohols, 81 kcal/mol in benzyl alcohol and 94 kcal/mol in methanol.[11] To our knowledge, there are only two other well-characterized examples of C−O bond homolysis in alkoxide complexes: thermolysis of homoleptic titanium(IV) alkoxides at 550−700 °C gives titanium oxides by a number of pathways including homolysis[3a] and a molybdenum/titanium μ-nitrido *tert*-butoxide has recently been reported to lose ^{t}Bu$^\bullet$ under mild conditions.[12] Homolytic cleavage of C−O bonds is a likely mechanism in other systems, such as in the titanium-mediated reductive coupling of alcohols to hydrocarbons which proceeds through L_nTi−OR intermediates.[13] The microscopic reverse, trapping of an alkyl or aryl radical by a metal−oxo complex to form an alkoxide, is a common mechanism of C−O bond formation. For instance, permanganate traps alkyl radicals at near the diffusion limit,[14] and the cytochrome P-450 rebound mechanism is a closely related process.[15] The ability of the tungsten alkoxide to homolyze its

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(7) For L = $PMePh_2$, the bisalkoxide complex, $W(OR)_2Cl_2(PMePh_2)_2$, is also formed.

(8) $W_2(OCH_2{}^tBu)_6(py)_2$ deoxygenates alcohols by a nonradical process: Yang, Y.; Chisholm, M. H. *Polyhedron* **1992**, *11*, 2813−2815.

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(11) Bond strengths calculated from gas phase heats of formation, for instance $D(PhCH_2{-}OH) = -\Delta H_f^\circ(PhCH_2OH) + \Delta H_f^\circ(PhCH_2^\bullet) + \Delta H_f^\circ(OH^\bullet)$. Data from: (a) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744−65 and references therein. (b) *Thermodynamic Tables: Hydrocarbons* and *Thermodynamic Tables: Non-Hydrocarbons*; Thermodynamic Research Center, Texas A&M University, College Station, Texas. (c) Bordwell, F. G.; Liu, W.-Z. *J. Am. Chem. Soc.* **1996**, *118*, 10819−10823.

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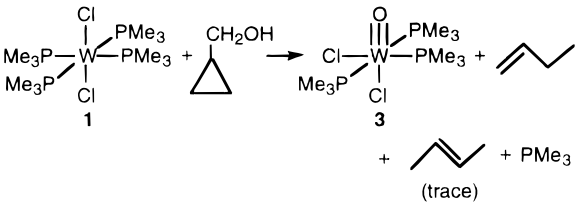
C−O bond can be understood through a thermodynamic analysis of the homolysis step, on the basis of bond strengths in the reactants and products.

Results

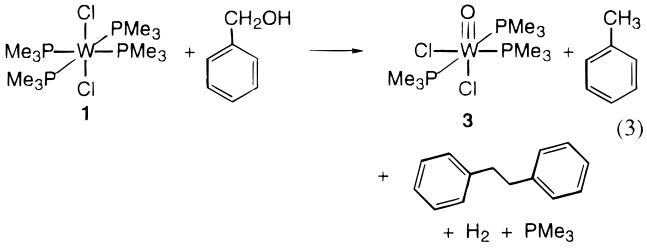
Reaction of $WCl_2(PMe_3)_4$ (1) with Alcohols. $WCl_2(PMe_3)_4$ reacts with 2 equiv of cyclopropanemethanol in benzene at 80 °C over 20 h to give a mixture of $W(O)Cl_2(PMe_3)_3$ (**3**), PMe_3, 1-butene, and a trace amount of *trans*-2-butene (eq 2). The



(2)

butenes were identified by GC and ^{1}H NMR and compared with authentic samples. No methyl cyclopropane was detectable by these techniques. A small amount of $WH_2Cl_2(PMe_3)_4$ (**2**)[16] is formed but it is consumed by the end of the reaction.

Benzene solutions of **1** react with excess benzyl alcohol at 80 °C over 40 h to give **3**, toluene, bibenzyl, PMe_3, and dihydrogen (eq 3). Again **2** is produced and consumed by the end of the reaction. The reaction is quite clean, with >97%

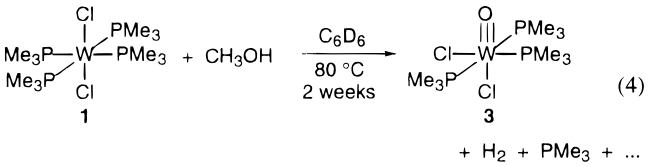


(3)

mass balance observed when the reaction is carried out in a sealed NMR tube and referenced to Me_4Si. The final molar ratio of toluene to bibenzyl is 0.8:1 when a 2.0×10^{-2} M solution of **1** is reacted with 6 equiv of $PhCH_2OH$. The addition of 20 equiv of PMe_3 stops reaction 3, with no appreciable change observed by NMR after 1 week at 80 °C. When $PhCH_2OD$ is the substrate, the reaction is slower. Both $PhCH_2D$ and $PhCH_3$ are produced, in a roughly 3:1 ratio (^{1}H NMR) which remains roughly constant throughout the reaction. No deuterium incorporation into the bibenzyl is observed by ^{2}H NMR. $WD_2Cl_2(PMe_3)_4$ (**2**-d_2) is observed as an intermediate, while $WH_2Cl_2(PMe_3)_4$ and $WHDCl_2(PMe_3)_4$ are not detected by ^{1}H{^{31}P} NMR at any point during the reaction. Thus, the hydride ligands in **2** derive from the hydroxyl proton of the benzyl alcohol.

The formation of both $PhCH_2D$ and $PhCH_3$ from $PhCH_2OD$ indicates that the hydroxyl is not the sole source of the hydrogen added to the benzyl group. Reaction of $WCl_2[P(CD_3)_3]_4$ (**1**-d_{36}) with $PhCH_2OD$ gives $PhCH_2D$ and $PhCH_3$ in the same ratio as observed from protio-**1** plus $PhCH_2OD$, indicating that the phosphine ligands are not involved. When a mixture of **1** and **2**-d_2 is reacted with $PhCH_2OH$, $PhCH_2D$ is the major initial product; protiotoluene and bibenzyl are produced as the reaction proceeds. Thus, the $PhCH_2D$ can come from the hydride ligands in **2**.

$WCl_2(PMe_3)_4$ reacts with several equivalents of methanol in benzene solution over a period of 2 weeks at 80 °C to produce $W(O)Cl_2(PMe_3)_3$ and H_2, as identified by ^{1}H NMR (eq 4).



(4)

Significant amounts of **2** are produced during the reaction and are only slowly consumed. Also seen as the reaction progresses is a small amount of $W_2(\mu\text{-O})(\mu\text{-Cl})(PMe_3)_5Cl_3$, known to form slowly under these conditions from **1** and **3**.[17] This reaction is not very clean, as several small, unidentified peaks appear in the ^{1}H NMR over the course of the reaction. However, there is no evidence under these conditions for the methoxide intermediate reported by Wilkinson.[5] Following the reaction of excess CD_3OD with **1** by ^{2}H NMR shows only the disappearance of the starting material; there is no observable product containing the methyl group.

The methyl product is seen as methane when the reaction of $WCl_2(PMe_3)_4$ and 7 equiv of methanol is run in the presence of 10 equiv of 9,10-dihydroanthracene (DHA). The reaction also produces $W(O)Cl_2(PMe_3)_3$, PMe_3, and H_2, just as in the absence of DHA. The methane was identified by comparison of its ^{1}H NMR with that of an authentic sample and by gas phase IR analysis. Methane (0.2 equiv) is observed in solution by NMR but this is a minimum yield as some is present in the gas phase. No reaction is observed between DHA and **1** or **2** over days at 80 °C in benzene solution in the absence of alcohol. These data are consistent with DHA acting as a trap for methyl radicals.[18]

The addition of 6 equiv of DHA to the reaction of **1** plus 7 equiv of benzyl alcohol (benzene, 80 °C, 2 days) produces predominantly toluene with only a trace of bibenzyl, in addition to **3** and PMe_3. This contrasts with the 0.8:1 ratio observed in the absence of DHA. Increasing the amount of DHA from 6 to 10 equiv results in no bibenzyl being observed by ^{1}H NMR. A similar reaction in the presence of 10 equiv of perdeutero-9,10-dihydroanthracene (DHA-d_{12}) produces **3**, PMe_3, trace bibenzyl, and both $PhCH_3$ and $PhCH_2D$ (∼1:2 by ^{1}H NMR). These data again suggest that DHA is a radical trap, in this case for benzyl radicals. Complex **2** is not observed in reactions containing DHA (^{1}H NMR), and surprisingly, no anthracene is visible by ^{1}H NMR or by GC. When $PhCH_2OD$ is used, deuterium incorporation into the 9,10 positions of DHA is seen by ^{2}H NMR.

The kinetics of the reaction of **1** with benzyl alcohol at 70.0 °C in sealed NMR tubes were monitored by ^{1}H NMR using Me_4Si as an internal standard. The ^{1}H NMR spectrum of paramagnetic **1** is a broad singlet, the chemical shift of which is quite temperature dependent. To obtain base line resolution from the Ph*CH*$_2$OH resonance (δ 4.25 in C_6D_6), we acquired spectra at 55 °C, when the peak due to **1** is shifted to 3.3 ppm (from δ 4.1 at ambient temperatures). As noted above, this reaction is inhibited by added PMe_3 which is a product of the reaction. To achieve pseudo-first-order conditions of phosphine initially and yet still have the reaction proceed at a reasonable rate, we added roughly 1 equiv of PMe_3. Plots of ln[**1**] vs time were reasonably linear for approximately half of a half-life, after

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(18) We have not found a rate constant for $CH_3^\bullet$ + DHA, but DHA should react faster than Ph_3CH (which has a weaker C−H bond). The rate constant for $CH_3^\bullet$ + Ph_3CH can be estimated as 10^4 M^{-1} s^{-1} based on data in: (a) Asmus, K.-D.; Bonifačić, M. Carbon-Centered Radicals II. In *Radical Reaction Rates in Liquids*; Landolt-Börnstein New Series; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13. b.

which point the plots became concave upward (as expected from the buildup of PMe_3). Pseudo-first-order rate constants, k_{obsd}, were obtained from the slopes of the first-order plots over the first half of a half-life. At the same PMe_3 concentration, k_{obsd} is independent of the initial tungsten concentration (for $[\mathbf{1}]_i$ = 17.7 and 35.4 mM, $k_{obsd} = 1.5(\pm0.2) \times 10^{-5}$ and $1.2(\pm0.2) \times 10^{-5}$ s^{-1} at 70.0 °C) and is directly related to the benzyl alcohol concentration (for $[PhCH_2OH] = 0.62$ and 1.24 M, $k_{obsd} = 1.5 \times 10^{-5}$ and 2.7×10^{-5} s^{-1}). These data and the inhibition by phosphine are consistent with the rate law of eq 5. The reaction of $PhCH_2OD$ under the same conditions shows an isotope effect $k_{ROH}/k_{ROD} = 3.3 \pm 0.5$.

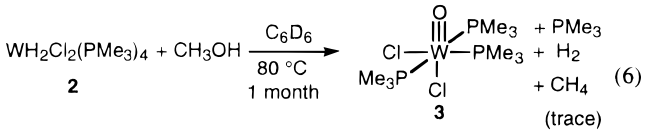
$$\frac{d[WCl_2(PMe_3)_4]}{dt} = -k_1 \frac{[WCl_2(PMe_3)_4][PhCH_2OH]}{[PMe_3]} \qquad (5)$$

Reaction of $WH_2Cl_2(PMe_3)_4$ (2) with Alcohols. A benzene solution of **2** and benzyl alcohol converts over 60 h at 80 °C to $W(O)Cl_2(PMe_3)_3$ (**3**), PMe_3, toluene, bibenzyl, and H_2—similar to the reaction of **1** except slower. In the initial stages, toluene is the sole product, but toward the end of the reaction both toluene and bibenzyl are being formed. The final ratio of toluene to bibenzyl is 1:1 when a 1.8×10^{-2} M solution of $WH_2Cl_2(PMe_3)_4$ is reacted with 6 equiv of $PhCH_2OH$. The addition of 20 equiv of PMe_3 to the reaction results in only minor quantities of the products being observable after 1 week of heating at 80 °C. Running the reaction under 0.60 atm of H_2 has no observable effect on the rate of the reaction. Qualitatively, the reaction proceeds faster at higher initial alcohol concentrations.

Reaction of **2** with $PhCH_2OD$ gives both $PhCH_3$ and $PhCH_2D$. Early in the reaction, the toluene produced is primarily protio, with toluene-d_1 becoming a more significant product as the reaction nears completion. $^1H\{^{31}P\}$ NMR shows the formation of $WHDCl_2(PMe_3)_4$ (**2**-d_2) as the reaction proceeds. Species **2**-d_1 exhibits an intrinsic upfield isotopic shift of 42 ppb in the hydride resonance vs **2**, higher than the 20 ppb shift reported for $WH_2Cl_2(PMe_2Ph)_4$.[19] No deuterium incorporation into the bibenzyl is observed.

The reaction of $WD_2Cl_2(PMe_3)_4$ (**2**-d_2) with $PhCH_2OH$ behaves identically to the reaction of protio-**2** with benzyl alcohol, except that both $PhCH_3$ and $PhCH_2D$ are produced. The final molar ratio of toluene to bibenzyl is 1.2:1 when a 3.0×10^{-2} M solution of $WD_2Cl_2(PMe_3)_4$ is reacted with 6 equiv of $PhCH_2OH$ at 80 °C. The toluene produced early in the reaction is primarily $PhCH_2D$, with protiotoluene becoming a more significant product toward the end of the reaction. Deuterium incorporation into the OH group of the benzyl alcohol is seen over the course of the reaction by ^2H NMR, indicating exchange of hydride and hydroxide protons.

The reaction of cyclopropanemethanol with **2** is very similar to its reaction with **1**, forming 1-butene and a trace amount of *trans*-2-butene as the only observed organic products. The reaction with **2** is slower, taking 2 days at 80 °C for completion vs 20 h for **1**. H_2 is also observed as a product of the reaction. The reaction of **2** with methanol in benzene solution is again about a factor of 2 slower than that of **1**, requiring 3−4 weeks of heating at 80 °C to go to completion (eq 6). In addition to **3**, PMe_3, and H_2, a small amount of methane is observed by ^1H NMR. *p*-Cresol reacts with **2** over a period of weeks at 80 °C to give a bis-*p*-cresolate complex and H_2 (eq 7). Again, reaction with **2** gives the same product as found for **1**,[20] though slower.



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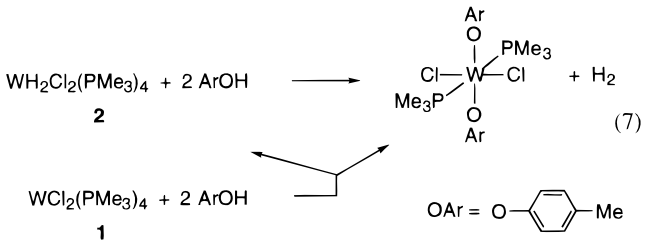
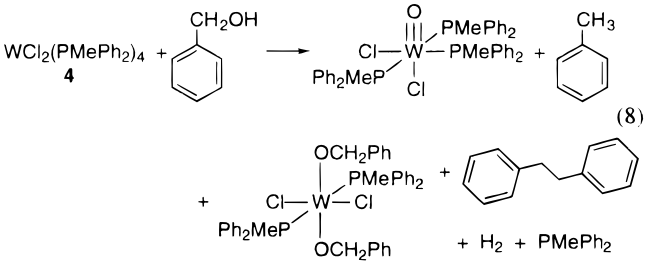


(7)

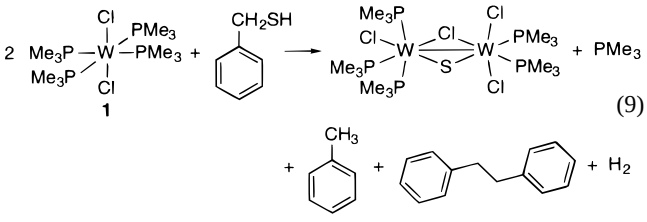
Reactions of $WCl_2(PMePh_2)_4$ (4) with Alcohols. As previously reported,[6] reactions of **4** with alcohols ROH give a mixture of RH + $W(O)Cl_2(PMePh_2)_3$ and H_2 + bis-alkoxides $W(OR)_2Cl_2(PMePh_2)_2$. More careful examination of the reaction with benzyl alcohol at room temperature for 15 h reveals bibenzyl in addition to the above products (eq 8). No dihydride products



(8)

are observed; $WH_2Cl_2(PMePh_2)_4$ is not known and does not appear to be a stable compound.[21] When the reaction is run in the presence of 10 equiv of DHA, toluene is the only detectable organic product.

Reactions with Thiols. Benzene solutions of **1** react with excess benzyl thiol in 3 h at 80 °C to form $W_2(\mu\text{-}S)(\mu\text{-}Cl)(PMe_3)_5Cl_3$, PMe_3, toluene, bibenzyl, and H_2 (eq 9). The



(9)

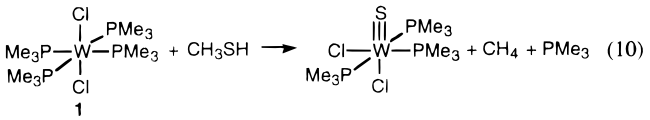
tungsten μ-sulfido dimer has been previously reported as the product of conproportionation of **1** and $W(S)Cl_2(PMe_3)_3$.[17] This reaction is not as clean as the reactions with alcohols, as yields of dimer are 80−90% and many small peaks are observed in the ^1H NMR. In the presence of 10 equiv of DHA, toluene is the only identifiable organic product and $W_2(\mu\text{-}S)(\mu\text{-}Cl)(PMe_3)_5Cl_3$ is still the observed tungsten product. Excess methane thiol reacts with **1** in C_6D_6 over 5 h at 80 °C to form $W(S)Cl_2(PMe_3)_3$, methane, and PMe_3 (eq 10). The methane is clearly observed

(19) Rothfuss, H.; Huffman, J.; Caulton, K. *Inorg. Chem.* **1994**, *33*, 2946−2953.

(20) Atagi, L. M.; Mayer, J. M. *Angew. Chem., Int. Ed. Eng.* **1993**, *32*, 439−441.

(21) $WH_2Cl_2(PMe_3)_4$ (**2**) and $WH_2Cl_2(PMePh_2)_4$ are formed by H_2 oxidative addition,[16,19] but **4** + H_2 does not give $WH_2Cl_2(PMePh_2)_4$.

in the ^{1}H NMR, and added DHA does not have a sizable effect on the methane yield.



(10)

Discussion

Formation of an Alkoxide Intermediate. The rate of deoxygenation of benzyl alcohol by $WCl_2(PMe_3)_4$ (**1**) is first order in both **1** and alcohol and inhibited by added PMe_3 (eq 5). This implies pre-equilibrium loss of a phosphine ligand, as is typical of the reactions of WX_2P_4 compounds.[4,22] The k_{OH}/k_{OD} isotope effect of 3.3 shows that $PhCH_2O-H$ bond cleavage occurs in the rate-limiting step. Pre-equilibrium oxidative addition of the O−H bond is calculated to have an isotope effect of only 2.4, on the basis of stretching frequencies $\nu_{OH} = 3600$ cm^{-1} and $\nu_{WH} = 2000$ cm^{-1}. These data indicate a pathway of oxidative addition of the O−H bond to an unsaturated tungsten species (eq 11). The O−H oxidative addition to tungsten(II) also occurs in the formation of $WH_3(OR)(PMe_3)_4$ from $WH_2(PMe_3)_5$ and MeOH or $PhCH_2OH$[23,24] and likely occurs in the reaction of **1** with phenols to form $W(OAr)_2Cl_2(PMe_3)_2$ and H_2.[20]

$$WCl_2(PMe_3)_4 \rightleftarrows PMe_3 + [WCl_2(PMe_3)_3] \xrightarrow{ROH} [W(OR)HCl_2(PMe_3)_3] \longrightarrow \quad (11)$$

$WH_2Cl_2(PMe_3)_4$ (**2**) is observed to grow in and then be consumed in all of the reactions of **1** with alcohols. It is likely formed by ligand redistribution reactions of intermediate tungsten hydride complexes. It is also likely that **2** forms by the known addition of H_2 to **1**,[16] as H_2 is an observed product. Oxidative addition of H_2 to the iodide derivative $WI_2(PMe_3)_4$ has been shown to occur by initial phosphine loss analogous to eq 11.[22]

Complex **2** also deoxygenates benzyl alcohol, as shown by independent reactions. These do not proceed by initial formation of **1**, since **2** is thermally stable to reductive elimination of H_2.[16] In addition, pre-equilibrium loss of H_2 is ruled out by the lack of inhibition of alcohol deoxygenation by 0.6 atm of H_2. These data and the inhibition by added PMe_3 indicate that **2** reacts by pre-equilibrium loss of phosphine followed by reaction with $PhCH_2OH$, presumably to form a nine-coordinate, 18-electron tungsten(VI) alkoxy−hydride species, $WH_3Cl_2(OR)(PMe_3)_3$ (eq 12). The $PhCH_2OH$ oxidative addition appears to be reversible

$$WH_2Cl_2(PMe_3)_4 \rightleftarrows PMe_3 + [WH_2Cl_2(PMe_3)_3] \xrightleftharpoons{ROH} [W(OR)H_3Cl_2(PMe_3)_3] \rightarrow H_2 + [W(OR)HCl_2(PMe_3)_3] \longrightarrow \quad (12)$$

as H/D exchange is observed by ^{1}H and ^{2}H NMR in reactions of $WD_2Cl_2(PMe_3)_4 + PhCH_2OH$ and $WH_2Cl_2(PMe_3)_4 + PhCH_2OD$. A similar mechanism of reversible phosphine loss and dihydrogen oxidative addition has been proposed by Caulton and co-workers to explain isotopic exchange between D_2 and the closely related $WH_2Cl_2(PMe_2Ph)_4$.[19] Nine-coordinate hydride complexes of the form $WH_6(PR_3)_3$ are known[25] but the chloride derivatives are unstable to reductive elimination. Therefore, it is likely that $W(OR)H_3Cl_2(PMe_3)_3$ reductively eliminates H_2 to give the tungsten(IV) complex $W(OR)HCl_2(PMe_3)_3$ (as in eq 11). The pathways for deoxygenation of alcohols by **1** and **2** therefore appear to converge, not by initial conversion of **2** to **1** but by H_2 loss after oxidative addition of ROH (Scheme 1). We cannot, however, rule out that H_2 loss occurs even later in the pathway from **2**, perhaps after C−O cleavage (Scheme 1).

C−O Bond Homolysis and Radical Trapping. The cleavage of C−O bonds in alcohols and alkoxides is unusual because of the strength of these bonds: $D(PhCH_2-OH) = 81$ kcal/mol and $D(CH_3-OH) = 94$ kcal/mol.[11] These values are pertinent because all of the data point toward a homolytic cleavage of the C−O bond (eq 13). C−O bond cleavage likely occurs in an alkoxide complex, from the kinetic evidence above and the thermodynamic arguments below.

$$L_nW-O-R \rightarrow L_nW{\equiv}O + R^{\bullet} \quad (13)$$

Both **1** and **2** react with cyclopropanemethanol to give primarily 1-butene, indicative of an intermediate cyclopropylcarbinyl radical. This ring opens ($k = 6 \times 10^8$ s^{-1} at 75 °C[26]) to the 3-butenyl radical which is then trapped by addition of a hydrogen atom. The products are not consistent with the formation of cyclopropylcarbinyl cation, since no cyclobutane derivatives are seen.[27] The formation of bibenzyl from benzyl alcohol and either **1** or **2** indicates the presence of free benzyl radicals. The effects of added 9,10-dihydroanthracene (DHA) also imply radical intermediates, as DHA readily traps radicals by hydrogen atom transfer.[28] DHA increases toluene yields over bibenzyl and converts methyl radicals to methane. With perdeutero-DHA (DHA-d_{12}), the major products are $PhCH_2D$ and CH_3D. Larger amounts of bibenzyl are observed when the DHA is deuterated, indicating a significant primary kinetic isotope on hydrogen atom transfer from DHA to $PhCH_2^{\bullet}$. The presence of DHA in the reaction does not have a noticeable effect on the overall rate of alcohol deoxygenation, indicating that it becomes involved after the rate-limiting step. In sum, the deoxygenation reaction can generate not only stabilized radicals such as $PhCH_2^{\bullet}$ but also the highly reactive primary radicals $CH_3^{\bullet}$ and c-$C_3H_5CH_2^{\bullet}$.

ROH compounds are deoxygenated to RH even in the absence of DHA, indicating that these reactions contain other radical traps that can reduce $R^{\bullet}$ to RH. Radical trapping is relatively slow in this system, as no methylcyclopropane is formed and the benzyl radical concentration is high enough to observe bibenzyl. The reaction of **1** with $PhCH_2OD$ results in a 3:1 ratio of $PhCH_2D$ to $PhCH_3$, indicating that the major source of the hydrogen atoms is the hydroxyl proton. Since hydroxyl groups do not trap alkyl radicals, this trapping is done by species derived from ROH, apparently tungsten hydride species formed by RO−H oxidative addition (see above). $WH_2Cl_2L_4$ (**2**) is observed during the reaction and clearly functions as a hydrogen atom donor. For instance, at early times the reaction of **2** plus

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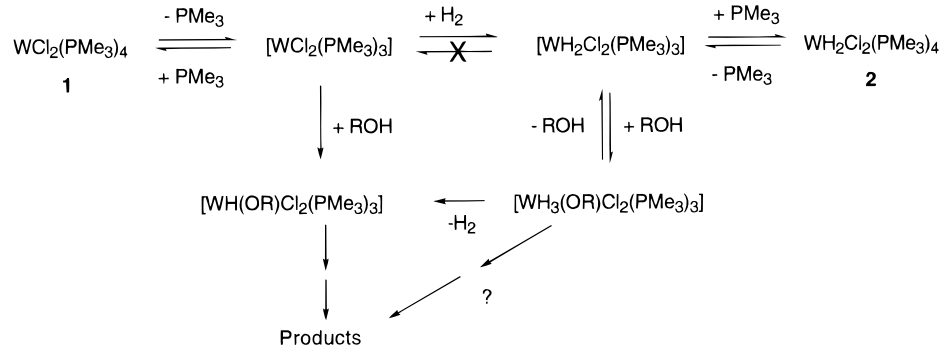
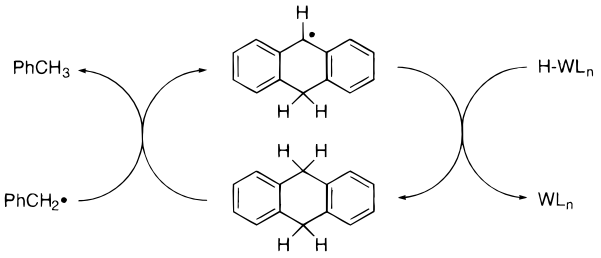
Scheme 1



benzyl alcohol produces toluene with just a trace of bibenzyl but as the reaction proceeds and the concentration of **2** drops, bibenzyl becomes an increasingly significant product. In the reaction of **2**-d_2 with $PhCH_2OH$, the initial product is $PhCH_2D$ but as hydroxyl protons are incorporated into **2** by the reversible addition of the alcohol, $PhCH_3$ is produced in increasing amounts. The ability of **2** to donate a hydrogen atom to an alkyl radical has ample precedent in metal hydride chemistry.[29] In the reaction of **1** with methanol and without DHA, the fate of the methyl fragment is unknown; presumably, the reactive methyl radical shows little selectivity and forms a variety of products.

The formation of $PhCH_3$ as well as $PhCH_2D$ from $PhCH_2OD$ shows that the hydroxyl proton is not the only hydrogen atom source. Too much $PhCH_3$ is formed to be the result of the protic impurity in the $PhCH_2OD$ (<1%), and the $PhCH_2D/PhCH_3$ ratio does not change over the course of the reaction as would be expected for consumption of a small impurity. The reaction of $WCl_2[P(CD_3)_3]_4$ (**1**-d_{36}) with $PhCH_2OD$ gives the same $PhCH_2D/PhCH_3$ ratio as the reaction of protio-**1**, ruling out the PMe_3 ligands as the secondary hydrogen atom donor for benzyl radicals. The source of the hydrogen atoms is likely the methylene protons of the benzyl alcohol, although this has not been demonstrated.[30]

When dihydroanthracene (DHA) is used as the radical trap, no anthracene is produced. Deuterium exchange with the 9,10 positions is however observed in the reaction of **1** + $PhCH_2OD$ + DHA. Reactions that contain DHA also do not show formation of **2**, though **2** is visible in all other reactions of **1** + ROH. In an independent control experiment, no hydrogenation of anthracene by **2** is observed even after reaction for several days at 77 °C. These initially puzzling results indicate that DHA acts as a hydrogen transfer *catalyst*: alkyl radicals are trapped by DHA to give RH and the relatively stable monohydroanthracenyl radical, which is then reduced by trace amounts of **2** or other tungsten hydrides present in the solution (eq 14). The



(14)

monohydroanthracenyl radicals are trapped back to DHA by tungsten hydride species faster than they undergo disproportionation or react with **1** or a second benzyl radical.

The methyldiphenylphosphine complex $WCl_2(PMePh_2)_4$ (**4**) appears to deoxygenate alcohols by a similar mechanism, as bibenzyl is formed from benzyl alcohol. This product was overlooked in our earlier report,[6] leading to the erroneous conclusion that radicals were not involved. This report, which dealt only with $PMePh_2$ compounds, also mentioned the absence of characteristic radical products: no ethane was formed from MeOH, no butane or ethylene was formed from EtOH, and no CH_3D was formed from MeOH in toluene-d_8 solvent. The lack of radical coupling products is understandable because the various radical traps in this system keep the radical concentrations low—and MeOH and EtOH react very slowly with **4**. Little CH_3D is formed because $CH_3^\bullet$ + toluene-d_8 is a slow reaction[31] and proceeds in part by methyl addition rather than by D-atom transfer.[32] The desulfurization of thiols by **1** and **4**[4,6] is also likely to involve alkyl radicals. Thus, benzyl thiol reacts with **1** to give toluene and bibenzyl and added DHA leads to the production of only toluene. Methanethiol is desulfurized to methane by **1**[4] and EtSH plus **4** gives ethane.[6] Presumably the sulfhydryl proton acts as the trap for $Me^\bullet$ and $Et^\bullet$.[33] Homolytic cleavage of C−S bonds has been demonstrated in other systems, such as hydrodesulfurization (HDS) model systems, and there is recent evidence in a catalytic HDS process.[34] Additionally, C−S bonds appear to be cleaved homolytically in some enzymatic reactions.[35]

Our attempts to synthesize isolable alkoxides that would undergo C−O homolysis when thermolyzed are reported elsewhere.[24] $WH_3(OCH_2Ph)(PMe_3)_4$, synthesized by the addition of benzyl alcohol to $WH_2(PMe_3)_5$, does not undergo C−O bond homolysis on heating. Rather, it undergoes C−H bond activation, eventually leading to $WH_2(CO)(PMe_3)_4$ and benzene. Curiously, when thermolysis is conducted in the presence of free benzyl alcohol, the reaction is almost an order of magnitude faster and toluene and bibenzyl are formed in excellent yield. The reason for this change in mechanism to C−O bond homolysis is not understood. Free benzyl alcohol does not seem to be requisite for C−O bond homolysis, as treatment of $WH_3(OCH_2Ph)(PMe_3)_4$ with $CDCl_3$ results in the rapid formation of toluene, bibenzyl, and $W(O)Cl_2(PMe_3)_3$ (**3**). Presumably,

(29) Bullock, R. M. In *Transition Metal Hydrides*; VCH: New York, 1992; pp 263−304.

(30) No benzyl-α-d_1 alcohol was observed by ^{2}D NMR or GC-MS in reactions of $PhCH_2OD$. A reviewer suggested that this might be formed as a minor product from trapping of $Ph\dot{C}HOH$ radicals (although conversion to PhCHO and other products seems equally likely).

(31) The rate constant for $CH_3^\bullet$ abstraction from toluene-h_8 is 10^2-10^3 times smaller than that for abstraction from DHA, and reaction with toluene-d_8 is slower still due to the primary isotope effect.[18a]

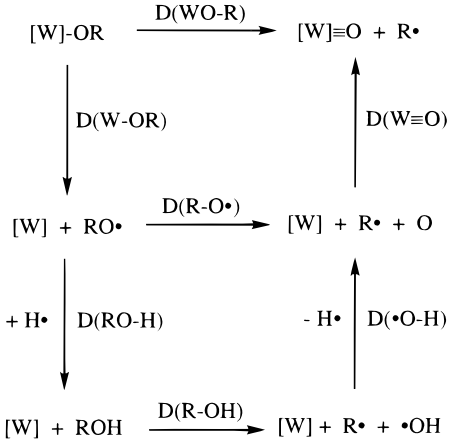
(32) Reference 18a. Leffler, J. E. *An Introduction to Free Radicals*; Wiley: New York, 1993; p 163.

(33) $k(CH_3^\bullet + MeSH \rightarrow CH_4 + MeS^\bullet) = 7 \times 10^7\ M^{-1}\ s^{-1}$ in H_2O at 293 K.[18a]

(34) Dungey, K. E.; Curtis, M. D. *J. Am. Chem. Soc.* **1997**, *119*, 842−843 and references therein.

(35) *The Bioinorganic Chemistry of Nickel*; Lancaster, J. R., Jr., Ed.; VCH: New York, 1988; Chapters 11 and 12.

Scheme 2. Estimation of the L_nWO-R Bond Dissociation Energy



this involves a chlorobenzyloxide complex related to those discussed here (Scheme 1).

Thermodynamics of C−O Bond Homolysis. To our knowledge, the only other well-defined example of alkoxide C−O bond homolysis under mild conditions is the loss of ^{t}Bu• from a molybdenum/titanium complex reported by Cummins *et al.* while this report was in preparation.[12] The key parameter in any homolysis reaction is the strength of the bond being broken, in this case L_nWO-R. This is quite different than the alcohol C−O bond strength, because while C−O cleavage in an alcohol generates a hydroxyl radical, homolysis in an alkoxide compound gives a metal−oxo complex (eq 13 above). To show that this reaction is reasonable, we estimate this bond strength using the thermochemical cycle in Scheme 2. The mechanistic data do not uniquely define which tungsten alkoxide is undergoing homolysis; we assume that homolysis occurs in $W(OR)Cl_2(PMe_3)_3$ in order to use data obtained in other studies. This could be formed from $WH(OR)Cl_2(PMe_3)_3$, generated as in Scheme 1, by hydride redistribution or reductive elimination (see above). Alternatively, the reactive alkoxide could be a hydrido−alkoxide $WH_n(OR)Cl_2(PMe_3)_m$, as long as it has valence electron count of 15 or fewer.

Across the top of Scheme 2 is the W−OR bond dissociation energy, the quantity of interest. Going around the upper cycle counterclockwise involves (i) removing the alkoxide ligand from the metal, (ii) homolyzing the C−O bond, and (iii) reattaching the oxygen to the metal. The values for step ii, $D(R-O^{\bullet})$, are calculated from the lower cycle, given in algebraic form in eq 15. D(R−OH) values are determined from heats of formation

$$D(R-O^{\bullet}) = -D(RO-H) + D(R-OH) + D(^{\bullet}O-H) \quad (15)$$

$$D(WO-R) = D(R-O^{\bullet}) + D(W-OR) - D(W{\equiv}O) = 81 + (90 \pm 10) - (>138)\ \text{kcal/mol} \quad (16)$$

of ROH, R•, and OH•.[11] For R = benzyl, the value for $D(PhCH_2-O^{\bullet})$ is 81 kcal/mol. The upper cycle yields eq 16 for D(W−OR). The tungsten-oxygen triple bond strength has been estimated as at least 138 kcal/mol in $W(O)Cl_2(PMe_3)_3$, on the basis of the ability of **1** to deoxygenate CO_2.[4] The bond strength of the tungsten oxygen single bond is crudely estimated to be 90 ± 10 kcal/mol on the basis of data for $W(OMe)_6$ and a series of homoleptic tantalum alkoxides,[36] although this could vary significantly depending on the exact complex. When these values are used, eq 16 gives an estimate of $<33 \pm 10$ kcal/mol for D(WO−R). This is an exceptionally low bond strength for a C−O bond. This calculation thus provides a rationale for how a C−O bond could cleave under such mild conditions.[37] As suggested elsewhere,[10b] alkoxide ligands should be considered to have activated C−O bonds in systems that make strong metal-oxo bonds.

The C−O bond homolysis also occurs in the reactions of **1** with methanol and cyclopropanemethanol. For R = methyl, $D(R-O^{\bullet})$ is 90 kcal/mol,[11] so the estimated D(WO−R) is 12 kcal/mol higher than for benzyl alcohol. In reactions of aryl alcohols, the C−O bond is not cleaved, consistent with a calculated D(WO−Ph) on the order of 80 kcal/mol [$D(Ph-O^{\bullet})$ = 125 kcal/mol[11]], more than 40 kcal/mol stronger than WO−CH_2Ph.

The thermodynamic analysis also provides a rationale for the very rapid trapping of alkyl radicals by oxidizing metal−oxo compounds, the reverse of eq 13. Permanganate, dichromate, and CrO_2Cl_2 have all been shown to trap radicals at close to the diffusion limit.[38] In the tungsten case, which is the least favorable situation because the metal−oxo complex is a reducing agent, addition of R• to M═O is significantly downhill. For an oxidizing metal center such as Mn^{VII}, Cr^{VI}, or Fe^{IV}, this reaction should be even more favorable.

Conclusions

$WCl_2(PMe_3)_4$ (**1**) and $WH_2Cl_2(PMe_3)_4$ (**2**) react with alcohols to give $W(O)Cl_2(PMe_3)_3$ (**3**), PMe_3, hydrocarbons, and H_2. A mechanism involving alkyl radicals is indicated by the products, butenes from cyclopropanemethanol and bibenzyl from benzyl alcohol, and by trapping of radicals by 9,10-dihydroanthracene (DHA) and DHA-d_{12}. Methyl radicals are formed from methanol. Kinetic studies suggest that the reactions proceed through intermediate tungsten alkoxide species. The alkyl radicals are formed by homolysis of the C−O bond in an alkoxide complex, with formation of a stable tungsten−oxo compound. A simple thermochemical analysis indicates that the homolysis step is made more facile by the strength of the tungsten−oxo triple bond, especially by the large difference between W−O and W≡O bonds. Deoxygenation of alcohols by $WCl_2(PMePh_2)_4$ (**4**) and desulfurization of thiols by **1** and **4** appear to proceed by similar mechanisms.

Experimental Section

General Considerations. All experiments were performed under a nitrogen atmosphere or *in vacuo* employing high vacuum line and standard glovebox techniques. Solvents were dried according to standard procedures.[39] Gases were used directly from the cylinder without further purification. All other reagents were degassed on the vacuum line, checked for purity by NMR, and, if necessary, dried by standard means. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Anthracene-d_{10} (Cambridge Isotope) was used without further purification. 9,10-Dihydroanthracene (Aldrich) was recrystallized two times from ethanol prior to use. $WCl_2(PMe_3)_4$ (**1**),[40] $WH_2Cl_2(PMe_3)_4$ (**2**),[16] and $WCl_2(PMePh_2)_4$ (**4**)[40] were prepared following published procedures. PMe_3-d_9 was prepared by Keith Hall from

(36) The mean W−O bond dissociation enthalpy for $W(OMe)_6$ is 86 kcal/mol. Bond dissociation enthalpies for homoleptic tantalum alkoxides lie between 86 and 100 kcal/mol. Connor, J. A. *Topics Curr. Chem.* **1977**, *71*, 71−110.

(37) Except in unusual circumstances, $\Delta H^{\ddagger} \geq \Delta H^{\circ}$. Most homolysis reactions have $\Delta H^{\ddagger} \cong \Delta H^{\circ}$ because the reverse reaction (recombination) has at most a small barrier. Barriers for R• + $L_nM{=}O \rightarrow L_nMOR$ are not known but such reactions can be very rapid.[38]

(38) (a) Reference 14. (b) Al-Sheikhly, M.; McLaughlin, W. L. *Radiat. Phys. Chem.* **1991**, *38*, 203−211. (c) Cook, G. K.; Mayer, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 1855−1868.

(39) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd Ed.; Pergamon: New York, 1989.

(40) Atagi, L. M.; Mayer, J. M. *Polyhedron* **1995**, *14*, 113−125 (as adapted from Sharp, P. R. *Organometallics* **1984**, *8*, 1217−1223 and Sharp, P. R.; Bryan, J. C.; Mayer, J. M. *Inorg. Synth.* **1990**, *28*, 326−332).

CD_3I following the published procedure.[41] $PhCH_2OD$ was prepared by exchange of $PhCH_2OH$ (15 mL) with 3 × 35 mL of D_2O and dried *in vacuo*; ^1H NMR of the sample in C_6D_6 showed no residual alcohol protons, consistent with >98% deuterium incorporation.

NMR spectra were acquired using Bruker WM-500, AM-499, AF-300, or AC-200 at ambient temperatures (24 ± 2° C), except where noted. ^1H NMR spectra were referenced relative to TMS or the residual protons in the solvent. $^{31}P\{^1H\}$ NMR spectra were recorded at 202.5 or 81.0 MHz and were referenced to external 85% H_3PO_4. $^1H\{^{31}P\}$ NMR spectra and ^2H spectra were recorded at 500.0 and 30.7 MHz, respectively, and referenced to ^1H or ^2H in the solvent. IR spectra were recorded on a Perkin-Elmer 1604 FTIR. GC analyses were performed on HP 5790 or 5890 instruments equipped with an FID detector. GC-MS were performed on a Kratos EI mass spectrometer equipped with an HP 5890 instrument.

$WCl_2(P(CD_3)_3)_4$ (1-d_{36}). A solution of **1** (10.3 mg, 19 μmol) in 0.5 mL of C_6D_6 was placed in a sealable NMR tube, degassed, and 300 μmol of $P(CD_3)_3$ was vacuum transferred into the tube. This solution was heated at 80 °C for 48 h. The tube was then cooled to 0 °C, and the volatiles were removed by vacuum. The tube was immersed in a 77 K bath, and 0.5 mL of benzene and 0.30 mmol of $P(CD_3)_3$ were vacuum transferred into the tube, and the solution was heated to 80 °C for 2 days. This was repeated three times. The NMR tube was then sealed under vacuum with a torch, and the sample was determined to be >95% deuterated by ^1H NMR.

$WD_2Cl_2(PMe_3)_4$ (2-d_2). Following the procedure for **2**,[16] a thick-walled glass vessel containing 102 mg of **1**, 1 mL of toluene, and 250 Torr of D_2 gas was heated at 80 °C for 22 h with stirring. Pentane (1 mL) was added, causing the formation of a fluffy bright yellow precipitate. After 3 h of cooling to −78 °C, filtration *in vacuo* yielded 44.5 mg of an air-sensitive yellow solid. ^1H NMR: δ 1.38 (quartet caused by overlapping virtual triplets, 36 H, J_{HP} = 4 Hz).

9,10-Dihydroanthracene-d_{12} (DHA-d_{12}) was synthesized from anthracene-d_{10} by modification of a previously reported procedure for protio-DHA.[42] A 100 mL three-necked round bottom flask was charged with 2.505 g (13.3 mmol) of anthracene-d_{10} and 42 mL of ethanol-d_1. The resulting solution was stirred and heated to 50 °C for 5 min, and then small chunks of sodium metal (total of 3.91 g, 170 mmol) were added over a 5 min period against a counterflow of nitrogen. The resulting slurry was allowed to cool to room temperature. D_2O (50 mL) was added to the reaction mixture. After 10 min of stirring, the solution was filtered and the filtrate was washed with 20 mL of D_2O. This process was repeated three times to remove residual anthracene (detected by GC analysis), yielding 2.24 g (11.7 mmol, 87%) of white powder which was >98% 9,10-dihydroanthracene as analyzed by GC. The product was analyzed by GC-MS and determined to be 96 ± 2% deuterated in the 9,10 positions (assuming the other positions remain 99% enriched).

Reactions were typically run in NMR tubes sealed with a torch. A general procedure follows. **Reaction of $WCl_2(PMe_3)_4$ (1) plus Benzyl Alcohol.** A sealable NMR tube attached to a ground glass joint was charged with 8.9 mg of **1** (16 μmol), 10.0 μL of $PhCH_2OH$ (96 μmol), and 0.5 mL of C_6D_6. The tube was attached to a needle valve, placed on the vacuum line, cooled to 77 K, evacuated, and sealed with a torch. The tube was allowed to warm to ambient temperature and then immersed in an 80 °C oil bath for 24 h. The progress of the reaction was monitored by ^1H and ^{31}P NMR. Using 500 MHz ^1H NMR instruments, $PhCH_3$ and $PhCH_2D$ were base line resolved. Reactions with deuterated reagents ($PhCH_2OD$, DHA-d_{12}, etc.) were run in C_6H_6 and observed by ^2H and ^{31}P NMR.

Reaction of 1 with Cyclopropanemethanol. Following the above procedure, 8.8 mg of **1** (16 μmol), 10 μL of *c*-$C_3H_5CH_2OH$ (123 μmol), and 0.5 mL of C_6D_6 were reacted in a sealed NMR tube at 80 °C for 48 h. When the reaction was completed, the tube was opened in the glovebox and emptied into a 10 mL round bottom flask. The volatiles were then vacuum transferred and analyzed by GC.

Reaction of 1 with Benzyl Alcohol and DHA. By the above procedure, 8.8 mg of **1** (16 μmol), 10 μL of $PhCH_2OH$ (96 μmol), 26.1 mg of DHA (145 μmol), and 0.5 mL of C_6D_6 were reacted in a sealed NMR tube for 2 days at 80 °C. Upon completion of the reaction, tube was broken open in the glove box, the contents were transferred to a small round bottom flask, and the volatiles were removed on the vacuum line. The residual solids were dissolved, in the air, in a 5% ethyl acetate/hexane solution and chromatographed on a small silica column, and analysis of the resulting fractions by GC revealed only bibenzyl and DHA. A trace amount of anthracene was also visible in the GC analysis, but the amount was consistent with the residual anthracene seen in analysis of the initial reaction mixture (ca. 0.1% anthracene remains in DHA samples even after multiple recrystallizations).

Reaction of 1 with Methanol and DHA. A 20 mL thick-walled, sealable reaction vessel was charged with 73.3 mg (0.13 mmol) of **1**, 134 mg (0.74 mmol) of DHA, and 1.5 mL of benzene in the drybox. The vessel was degassed on a vacuum line, and ∼1.5 mmol of methanol was vacuum transferred into the vessel. The vessel was sealed and heated to 77 °C for 12 days, which resulted in a darkening of the solution from bright yellow to a brownish/purple. The vessel was hooked to a gas phase infrared cell via a short-path vacuum transfer apparatus. The apparatus and cell were degassed, and the vessel was immersed in 77 K bath and then opened to the cell. An infrared spectrum of the collected gases revealed bands at 3016 and 1305 cm^{-1} with resolved rotational bands, in agreement with the spectrum of methane.[43]

Reaction of $WH_2Cl_2(PMe_3)_4$ (2) with Methanol. A sealable NMR tube was charged with 7.8 mg of **2** (14 μmol) and 0.5 mL of C_6D_6. Methanol (140 μmol) was transferred into the tube by charging an addition bulb of known size with a known pressure of methanol. The tube was degassed and sealed *in vacuo* with a torch. The tube was heated in an 80 °C oil bath for 2 weeks, during which time the solution turned from yellow to brownish/purple. The same procedure was used for the **reaction of 1** (16 μmol) **with CH_3SH** (120 μmol) which turned from yellow to brownish/purple over 3 h at 80 °C. CH_4 was identified in both reactions as a singlet at 0.14 ppm. A similar color change was observed in the **reaction of 1** (7.7 mg, 13 μmol) **with $PhCH_2SH$** (9.0 μL, 76 μmol) over 5 h at 80 °C.

Reaction of $WCl_2(PMePh_2)_4$ (4) with Benzyl Alcohol. A sealed NMR tube containing 8.7 mg of **4** (8 μmol), 8.0 μL of $PhCH_2OH$ (77 μmol), and 0.5 mL of C_6D_6 was monitored by ^1H NMR at ambient temperatures for 24 h, during which time the solution turned from yellow to purple.

Kinetics of the Reaction of 1 with Benzyl Alcohol. In the drybox, a 5.00 mL stock solution of 49.8 mg of **1** (89 μmol) in C_6D_6 was prepared. Aliquots of this solution (0.50 mL) were transferred into four sealable NMR tubes. To the first was added 25 equiv of $PhCH_2OH$ (32.0 μL, 222 μmol); two times as much $PhCH_2OH$ was added to the second tube. The third was charged with 25 equiv of $PhCH_2OD$. To the fourth were added 5.0 mg of **1** (8.9 μmol) and 25 equiv of $PhCH_2OH$. The tubes were each capped with a needle valve. Into each tube was condensed 8.9 μmol of PMe_3 (1 equiv) and 2.0 μmol of Me_4Si using a gas addition bulb of known volume. The tubes were then flame sealed *in vacuo*. The tubes were heated by complete immersion in a regulated temperature bath at 70.0 °C, and the progress of the reaction was monitored by ^1H NMR measured at 55 °C.

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