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Investigations Directed at Catalytic Carbon−Carbon and Carbon−Oxygen Bond Formation via C−H Bond Activation

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A potential catalytic cycle for the formation of new C−C and C−O linkages from hydrocarbon feedstocks and readily available olefin and ketone substrates mediated by Cp′M(NO)(L) (M = Mo, W; Cp′ = Cp*, Cp; L = Lewis base) fragments has been investigated. The cycle is based on three steps: (1) oxidative addition of the hydrocarbon substrate to the metal center, (2) subsequent hydrometalation of the olefin or the ketone, and (3) final reductive elimination of the coupled product. Of the various Cp′M(NO)(L) groups examined, the Cp*W(NO)(PPh_3) fragment has been found to be the best candidate for mediating these catalytic steps since it is not prone to form unreactive Cp*W(NO)$(PPh_3)_2$ as are some of the other fragments that readily decompose to 18*e* Cp′M(NO)L_2 complexes. Hence, Cp*W(NO)(PPh_3) has been utilized to determine if the oxidative addition and hydrometalation steps can occur sequentially under one-pot experimental conditions. However, olefins are too π-acidic and readily form stable 18*e* Cp*W(NO)(PPh_3)(η^2-olefin) adducts, which prevent oxidative addition of the hydrocarbon substrate to the tungsten center. Similarly, benzophenone, Ph_2CO, and diisopropyl ketone, $^iPr_2CO$, also form 1:1 η^2-C=O adducts with the π-basic tungsten center in the 16*e* fragment. Nevertheless, oxidative addition and hydrometalation do occur sequentially to form the desired aryl alkoxide complex, Cp*W(NO)(OCH^iPr_2)(Ph), in addition to the Cp*W(NO)(η^2-OC^iPr_2)(PPh_3) adduct, when benzene and diisopropyl ketone are employed as the two substrates. The solid-state molecular structures of *cis*-Cp*W(NO)[η^2-(CH_2-NMe)P$(NMe_2)_2$](H), Cp*W(NO)(OCH^iPr_2)(Ph), and Cp*W(NO)(η^2-OC^iPr_2)(PPh_3) have been established by single-crystal X-ray crystallographic analyses.

Introduction

A principal goal of C−H activation chemistry is the efficient catalytic functionalization of commodity hydrocarbon feedstocks to compounds of practical and commercial relevance. However, the cleavage of strong carbon−hydrogen bonds such as those that exist in methane (105 kcal/mol) and benzene (110 kcal/mol) is not a trivial matter. Furthermore, most desirable transformations such as the dehydrogenation and carbonylation of alkanes are often thermodynamically unfavorable at room temperature.[1] Industrial reactions of hydrocarbon feedstocks thus rely on either demanding reaction conditions or the presence of reactive species to effect the desired chemistry. Consequently, the development of catalytic systems that effect selective transformations of hydrocarbons under mild conditions remains a priority to which considerable effort continues to be devoted.[2]

One of our recent contributions to this area of chemistry involves the intermolecular activation of hydrocarbon C−H bonds initiated by the tungsten hydrocarbyl hydrido complexes Cp*W(NO)(R)(H)(PMe_3) (R = alkyl, aryl).[3a] In our view the single C−H activation processes described in that report constitute the requisite first steps in the development of these organometallic nitrosyl complexes as catalysts for the selective functionalization of hydrocarbons. In particular, this chemistry suggests to us that specific members of the general family of complexes, Cp′M(NO)(R)(H)(L) (M = Mo, W; Cp′ = Cp, Cp*; R = alkyl, aryl; L = Lewis base), may well be capable of functioning as homogeneous catalysts for organic coupling reactions of the type depicted in Scheme 1. We have previously demonstrated the three individual steps shown, namely, (1) C−H bond activation by oxidative addition of R′−H to M,[3] (2) insertion of C=Y (in which Y may be more electronegative than C) into the M−H linkage,[4] and (3) reductive elimination of R′−Y−C−H for particular complexes.[5] The challenge remains to discover complexes that effect all three steps, preferably in a sequential manner.

In this report we present the results of our initial investigations of the viability of the catalytic cycle presented in Scheme 1. Specifically, we first describe which Cp′M(NO)(R)(H)(L) complex has been found to be best suited for effecting the indicated transformations. We then employ this optimum nitrosyl complex to ascertain the conditions necessary for effecting step 1 (oxidative addition) and step 2 (hydrometalation) of the

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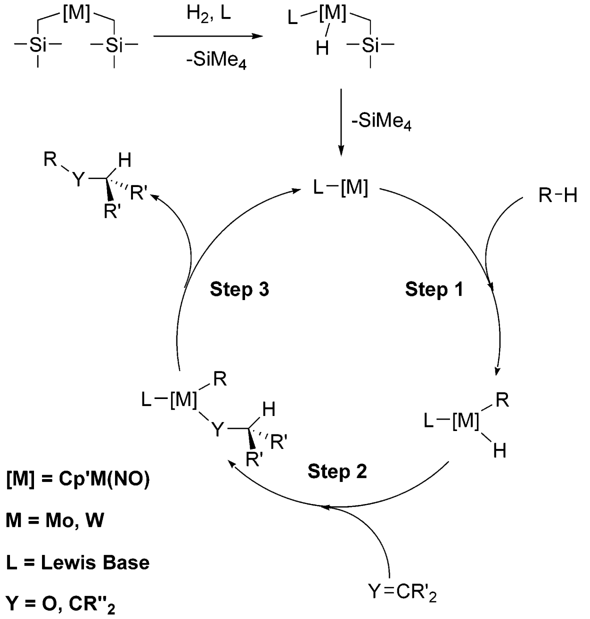
Scheme 1



catalytic cycle in a sequential and effective manner. To put these studies in their proper context, we should note at this point that other examples of carbon−carbon[6] and carbon−oxygen[7] bond-forming reactions via C−H bond activation have been reported previously.

Results and Discussion

C−H Bond-Activating Abilities of Various Cp′M(NO)-(PMe_3) Fragments. As noted above, we have previously shown that Cp*W(NO)(PMe_3)(CH_2SiMe_3)(H) activates a C−H bond of benzene under ambient conditions and cleanly forms Cp*W-(NO)(PMe_3)(Ph)(H).[3] Therefore, as the first step during these investigations, we set out to synthesize other Cp′M(NO)(PMe_3)-(R)(H) complexes in order to assess the relative abilities of the different Cp′M(NO)(PMe_3) fragments (Cp′ = Cp, Cp*; M = Mo, W) to effect step 1 in the catalytic cycle shown in Scheme 1. As illustrated at the top of Scheme 1, the customary method for synthesizing these hydrido alkyl complexes involves treatment of the appropriate Cp′M(NO)R_2 precursors with dihydrogen in the presence of the Lewis base.

Consistent with our previous findings, exposure of CpMo-(NO)$(CH_2SiMe_3)_2$ to H_2 in the presence of excess PMe_3 does indeed produce the desired hydrido alkyl complex, CpMo(NO)-(PMe_3)(CH_2SiMe_3)(H), as indicated by ^1H NMR spectroscopy. However, this compound is not isolable since it quickly eliminates Me_4Si and is coordinated by a second equivalent of PMe_3 to produce unreactive CpMo(NO)$(PMe_3)_2$.[8] In contrast, hydrogenation of the less Lewis acidic Cp*Mo(NO)$(CH_2SiMe_3)_2$ in the presence of excess PMe_3 affords Cp*Mo(NO)(PMe_3)(CH_2-$SiMe_3$)(H) as a yellow, crystalline solid. Although Cp*Mo(NO)-(PMe_3)(CH_2SiMe_3)(H) does eliminate Me_4Si in benzene at room temperature, it does not activate benzene. The only detectable molybdenum-containing species in the final solution is the bis-(phosphine) complex, Cp*Mo(NO)$(PMe_3)_2$, as shown by NMR spectroscopy. It thus appears that neither the CpMo(NO)(PMe_3) or the Cp*Mo(NO)(PMe_3) fragment is capable of acting as the desired mediating species since their greater Lewis acidity favors the eventual formation of stable bis(phosphine) complexes over C−H bond activation. In a similar manner, previous work in these laboratories has established that thermolysis of CpW(NO)-($PMePh_2$)(CH_2SiMe_3)(H) in C_6H_6 results only in the formation of low yields of CpW(NO)$(PMePh_2)_2$.[3b] Taken together, these experimental observations indicated to us that we should focus our subsequent efforts exclusively on fragments containing the Cp*W(NO) entity.

Screening of Different Lewis Bases for the Cp*W(NO) Fragment. Since Cp*W(NO)(PMe_3)(CH_2SiMe_3)(H) slowly undergoes the undesirable transformation to Cp*W(NO)$(PMe_3)_2$ during the activation of benzene,[3] we next attempted to find a Lewis base (L) for which the formation of such Cp*W(NO)-$(L)_2$ complexes is disfavored. After screening numerous potential bases including phosphine oxides, phosphine sulfides, and coordinating solvents such as pyridine, it became apparent to us that only bases that coordinate through a phosphorus atom are capable of stabilizing the 16-electron Cp*W(NO)(CH_2-$SiMe_3$)(H) entity. We therefore hypothesized that the best way to stop the formation of the undesirable Cp*W(NO)$(L)_2$ complexes would be to utilize bulkier phosphines.

Hydrogenolysis of Cp*W(NO)$(CH_2SiMe_3)_2$ in the presence of excess PEt_3 in benzene-d_6 reveals an interesting series of transformations that appear to be quantitative when monitored by NMR spectroscopy (Scheme 2). As expected, the hydrido alkyl complex Cp*W(NO)(PEt_3)(CH_2SiMe_3)(H) is formed initially as evidenced by the growth of resonances attributable to Me_4Si and the tungsten hydride in the ^1H NMR spectrum and a singlet resonance in the ^{31}P NMR spectrum attributable to the PEt_3 ligand bound to the tungsten center. Cp*W(NO)-(PEt_3)(CH_2SiMe_3)(H) is, however, thermally unstable at room temperature and subsequently eliminates a second equivalent of Me_4Si. In contrast to the related molybdenum system described in the preceding section, it then preferentially activates a benzene molecule rather than associating with a second PEt_3 and converts to Cp*W(NO)(PEt_3)(C_6D_5)(D) as evidenced by the elimination of a second equivalent of Me_4Si and the appearance of a 1:1:1 triplet in the ^{31}P NMR spectrum. Unfortunately, C_6D_6 is then eliminated, and a second PEt_3 molecule coordinates to the tungsten center to produce orange Cp*W(NO)$(PEt_3)_2$, which does not react further.

When the larger P^iPr_3 is used as the Lewis base, only an intractable mixture of products is obtained upon hydrogenolysis of Cp*W(NO)$(CH_2SiMe_3)_2$. Interestingly, the strong σ-donor $P(NMe_2)_3$ does coordinate to the tungsten center, but Me_4Si is again eliminated, and in this case the cyclometalated product, *cis*-Cp*W(NO)[η^2-(CH_2NMe)P$(NMe_2)_2$](H), is obtained as the only isolable organometallic complex (Scheme 2). Since the steric demands and the σ-donating ability of P^iPr_3 and $P(NMe_2)_3$ are fairly similar, a possible explanation for this difference in reactivity could be that the C−H bond of the NMe_2 group is easier to activate than that of the isopropyl group. Unfortunately, thermolysis of *cis*-Cp*W(NO)[η^2-(CH_2NMe)P$(NMe_2)_2$](H) in benzene-d_6 does not lead to activation of the C−D bonds of the solvent but rather to isomerization of the reactant to its trans isomer. This latter transformation resembles the similar interconversion of the cis and trans isomers of Cp*W(NO)(CH_2-$SiMe_3$)(H)(PMe_3) that we have recently documented.[3a]

Both *cis*- and *trans*-Cp*W(NO)[η^2-(CH_2NMe)P$(NMe_2)_2$](H) have been fully characterized by conventional spectroscopic methods, and the solid-state molecular structure of the cis isomer has been established by a single-crystal X-ray crystallographic

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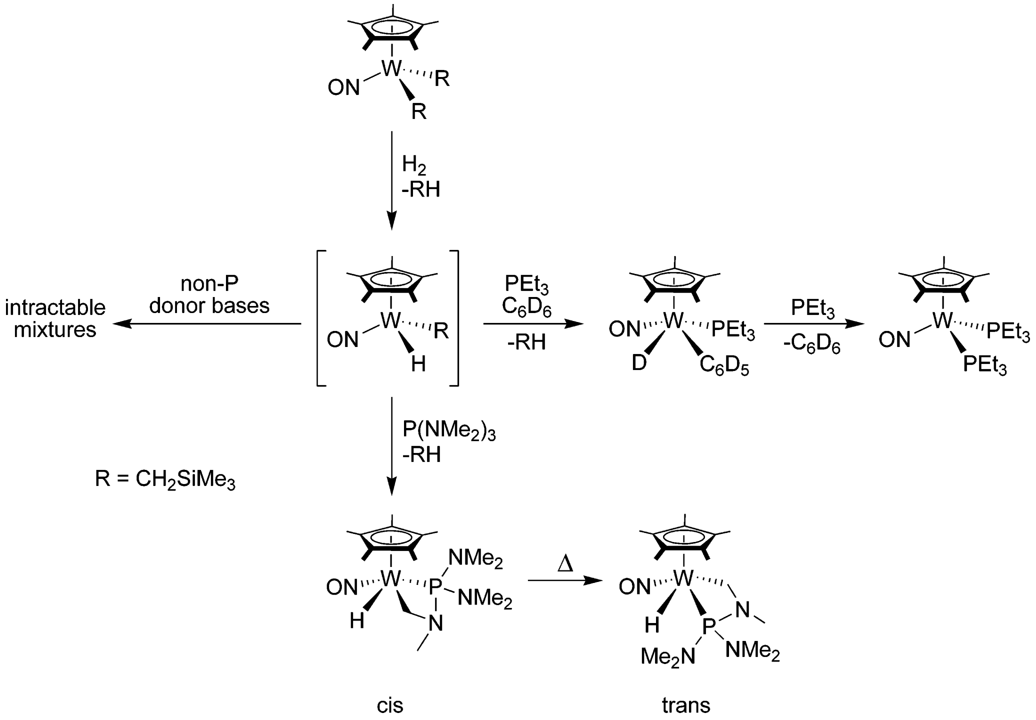
Scheme 2



analysis (Figure 1). As expected,[3a] the signal due to the hydrido ligand in the trans isomer exhibits the larger $^2J_{HP}$ coupling constant in the ^1H NMR spectrum of the complex in C_6D_6, thereby permitting a differentiation of the two isomers. During the X-ray diffraction study, the hydride ligand in the cis isomer [H(01) in Figure 1] was located in a difference Fourier map. Its isotropic thermal parameter was subsequently kept fixed while its coordinates were refined, thereby affording a final W(1)−H(01) separation of 1.57 Å. This distance is comparable to other W−H bond lengths determined by X-ray diffraction.[9]

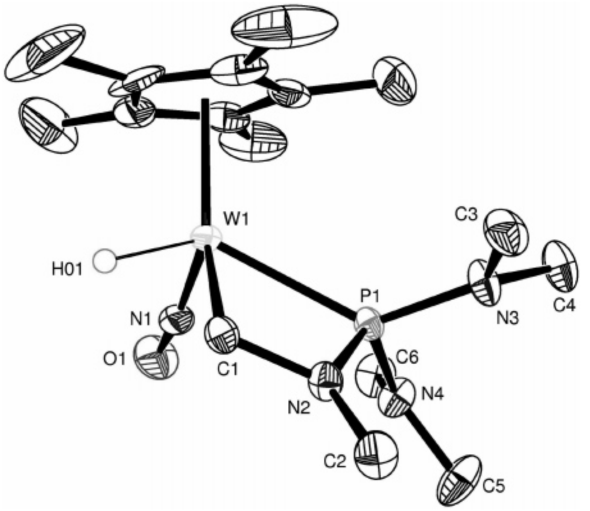


Figure 1. Solid-state molecular structure of *cis*-Cp*W(NO)[η^2-(CH_2NMe)P(NMe_2)$_2$](H) with 50% probability thermal ellipsoids. The hydride atom has been modeled on the basis of residual electron density. Selected interatomic distances (Å) and angles (deg): W(1)−P(1) = 2.5087(11), W(1)−C(1) = 2.242(4), N(2)−C(1) = 1.452(5), P(1)−N(2) = 1.626(4), P(1)−N(3) = 1.680(3), P(1)−N(4) = 1.644(4), W(1)−N(1) = 1.766(4), N(1)−O(1) = 1.210(5), P(1)−W(1)−C(1) = 61.58(11), P(1)−N(2)−C(1) = 104.9(3), W(1)−P(1)−N(2) = 88.73(13), N(2)−C(1)−W(1) = 104.4(3), W(1)−N(1)−O(1) = 168.3(4).

Thus, *cis*-Cp*W(NO)[η^2-(CH_2NMe)P(NMe_2)$_2$](H) exhibits a four-legged piano-stool molecular structure with intramolecular metrical parameters reflective of it being an 18*e* species. The coordination geometry of the η^2-(CH_2NMe)P(NMe_2)$_2$ group resembles that found in other complexes having P(NMe_2)$_3$ ligands.[10]

When PPh_3 is employed as the Lewis base for the Cp*W(NO) fragment, the situation improves markedly. We have previously shown that the ortho-metalated phenyl ring and hydride of *cis*-Cp*W(NO)[η^2-(C_6H_4)PPh_2](H) (a complex similar to *cis*-Cp*W(NO)[η^2-(CH_2NMe)P(NMe_2)$_2$](H) discussed in the preceding paragraphs) are capable of effecting intramolecular reductive elimination to provide the requisite Cp*W(NO)(PPh_3). The 16*e* Cp*W(NO)(PPh_3) fragment has an open coordination site at the metal center and is a strong π-donor that readily coordinates a variety of π-acids in an η^2-fashion.[11] We have also found that gentle thermolysis of *cis*-Cp*W(NO)[η^2-(C_6H_4)-PPh_2](H) in benzene affords the hydrido phenyl complex Cp*W(NO)(PPh_3)(Ph)(H), presumably via C−H oxidative addition of benzene to the Cp*W(NO)(PPh_3) fragment.[12] Most importantly, Cp*W(NO)(PPh_3)$_2$ is not readily formed as a byproduct during this latter transformation even when harsher conditions are employed. Since the Cp*W(NO)(PPh_3) fragment appears to best fit our desired criteria for a potential catalyst for Scheme 1, the precursor *cis*-Cp*W(NO)[η^2-(C_6H_4)PPh_2](H) complex was used in all our subsequent studies.

Reactions of *cis*-Cp*W(NO)[η^2-(C_6H_4)PPh_2](H) with Benzene and Olefins. In order to test the ability of *cis*-Cp*W(NO)-

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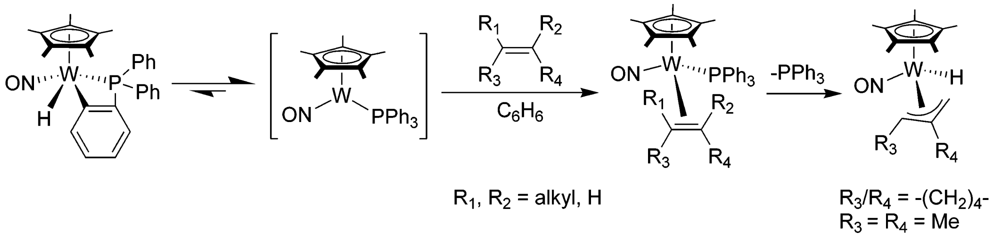
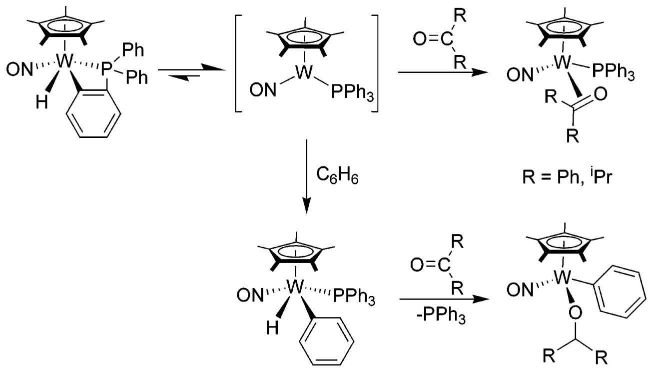
Scheme 3



Scheme 4



[η^2-(C_6H_4)PPh_2](H) to activate benzene and then hydrometalate olefins, benzene solutions of *cis*-Cp*W(NO)[η^2-(C_6H_4)PPh_2](H) and various olefins have been heated and monitored by ^{1}H and ^{31}P NMR spectroscopies. The reactions are clean since monitoring by ^{31}P{^{1}H} NMR spectroscopy reveals the growth of only single resonances in the region 34 to 36 ppm diagnostic of olefin complexes. In the case of less sterically demanding olefins such as cyclohexene and *cis*/*trans*-2-butene, thermally stable Cp*W(NO)(η^2-olefin)(PPh_3) complexes are formed in high yield and may be isolated (Scheme 3). However, in no case is there any evidence for either activation of the benzene or hydrometalation of the olefin. More sterically demanding olefins such as 2-methyl-2-butene or 1-methylcyclohexene form similar Cp*W(NO)(η^2-olefin)(PPh_3) complexes initially. However, further thermolysis of these compounds in C_6D_6 results in the growth of resonances in the ^{1}H NMR spectra attributable to the formation of stable allyl hydride complexes and free PPh_3 (Scheme 3). Thus, the η^2-1-methylcyclohexene complex converts to the allyl hydride complex Cp*W(NO)(η^3-C_7H_{11})(H), which we have previously described.[13] Again, there is no evidence for either activation of the benzene or hydrometalation of the olefin.

Reactions of *cis*-Cp*W(NO)[η^2-(C_6H_4)PPh_2](H) with Benzene and Carbonyl-Containing Molecules. Reactions similar to those described in the preceding section were next performed with ketones to see if these substrates would allow the activation of benzene and then be subsequently hydrometalated by the resulting hydrido aryl complex. To discourage dihapto coordination of the ketones to the tungsten center in the Cp*W(NO)(PPh_3) fragment (as occurs with the olefinic substrates), sterically encumbered ketones were utilized.

The sequential conversions were first attempted by heating a C_6D_6 solution of *cis*-Cp*W(NO)[η^2-(C_6H_4)PPh_2](H) and excess diisopropyl ketone. This operation results in the formation of a final wine red solution whose spectroscopic analysis indicates the presence of two organometallic complexes and some free PPh_3. Attempts to separate the two organometallic products either by chromatography or by fractional crystallization have not yet been successful. Nevertheless, the spectroscopic evidence suggests that they are the desired phenyl alkoxide complex Cp*W(NO)(OCH^{i}Pr$_2$)(Ph) and the η^2-adduct Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh_3) (Scheme 4). In order to confirm this inference, both complexes have been independently synthesized and fully characterized.

In order to synthesize Cp*W(NO)(OCH^{i}Pr$_2$)(Ph), the activation of benzene and the hydrometalation of diisopropyl ketone have been effected successfully in a stepwise manner. Thus, *cis*-Cp*W(NO)[η^2-(C_6H_4)PPh_2](H) can be first converted to Cp*W(NO)(PPh_3)(Ph)(H) by gentle thermolysis in benzene.[12] Following isolation by crystallization, this precursor complex is then allowed to react in neat diisopropyl ketone overnight at 50 °C to obtain a wine red solution. ^{1}H NMR spectroscopic analysis reveals the major organometallic product to be Cp*W(NO)(OCH^{i}Pr$_2$)(Ph) as evidenced by the appearance of a triplet at 4.52 ppm attributable to OC*H*^{i}Pr$_2$. Correlation spectroscopy shows this signal to be associated with a new resonance at 102 ppm in the HMQC spectrum and with the methine protons of the isopropyl groups in the ^{1}H−^{1}H COSY spectrum. All attempts to prepare analytically pure Cp*W(NO)(OCH^{i}Pr$_2$)(Ph) on a preparative scale have been problematic, as this species is not amenable to chromatography and it is extremely soluble in organic solvents. Fortunately, on one occasion we were able to grow single crystals of the complex from pentane. An X-ray crystallographic analysis of these crystals has established the solid-state molecular structure of the complex to be that shown in Figure 2. The metrical parameters of this structure resemble those previously reported for similar alkoxide complexes.[14]

Likewise, the η^2-ketone-containing product, Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh_3), can be prepared by thermolysis of *cis*-Cp*W(NO)[η^2-(C_6H_4)PPh_2](H) at 50 °C overnight in neat diisopropyl ketone. The complex is isolable as a yellow crystalline solid, and it has been fully characterized by conventional methods including single-crystal X-ray crystallography. (The crystal was a three-component twin with a disordered THF molecule in the unit cell. Despite these difficulties, the structure was refined to a final *R* value of 3.4%.) The solid-state molecular structure of the compound (Figure 3) shows the side-on-bound nature of the ketone ligand in which the carbonyl carbon is now approximately sp^3-hybridized and the carbon−oxygen bond is lengthened, thereby attesting to the strong π-donor nature of the tungsten center.

An analysis of the NMR spectra of the one-pot reaction mixture confirms that the two organometallic species formed in the in situ reaction (Scheme 4) are indeed the same as the products of the independent syntheses described above. It also reveals that the major product is Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh_3) and that the minor product is Cp*W(NO)(OCH^{i}Pr$_2$)(Ph). The products are formed in a ratio of approximately 1.7:1 depending on the concentration of the ketone and the reaction conditions

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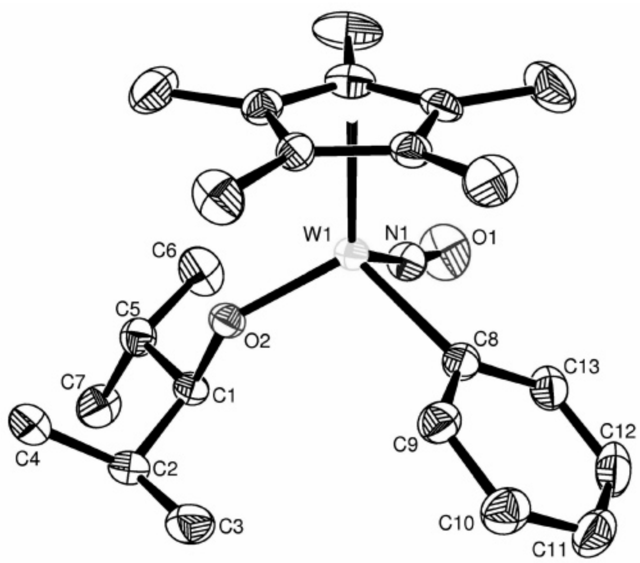

Figure 2. Solid-state molecular structure of Cp*W(NO)(OCH-^{i}Pr$_2$)(Ph) with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−O(2) = 1.899(2), O(2)−C(1) = 1.433(4), W(1)−C(8) = 2.142(3), W(1)−N(1) = 1.759(3), N(1)−O(1) = 1.227(3), W(1)−O(2)−C(1) = 135.7(2), O(2)−C(1)−C(2) = 106.4(3), O(2)−C(1)−C(5) = 111.0(3), C(2)−C(1)−C(5) = 114.8(3), W(1)−N(1)−O(1) = 170.2(3).

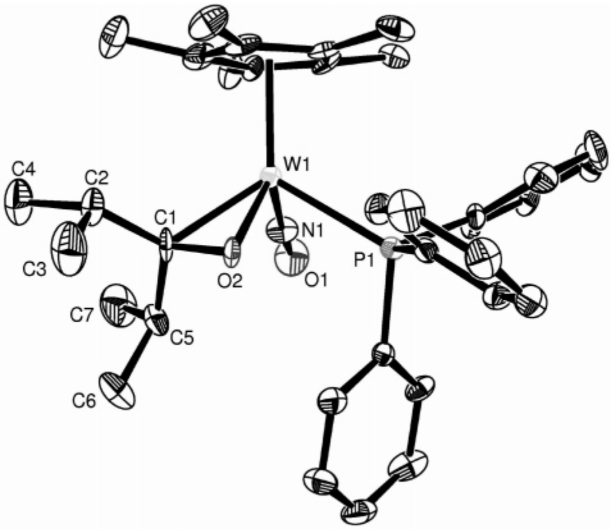

Figure 3. Solid-state molecular structure of Cp*W(NO)(η^2-OC-^{i}Pr$_2$)(PPh$_3$) with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): W(1)−O(2) = 2.043(4), W(1)−C(1) = 2.211(6), O(2)−C(1) = 1.388(7), W(1)−P(1) = 2.4863(16), W(1)−N(1) = 1.774(5), N(1)−O(1) = 1.222(6), O(2)−C(1)−C(2) = 110.7(5), O(2)−C(1)−C(5) = 110.9(5), C(2)−C(1)−C(5) = 120.5(6), W(1)−N(1)−O(1) = 173.6(5).

employed. In other words, the strong π-basicity of the Cp*W(NO)(PPh$_3$) fragment leads preferentially to irreversible formation of the Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh$_3$) adduct rather than C−H activation of benzene. Initial screening suggests that benzophenone behaves similarly toward Cp*W(NO)(PPh$_3$).

Previous investigations in these laboratories have demonstrated that the rate of formation of η^2-ester adducts by the Cp*W(NO)(PPh$_3$) fragment is markedly slower than the formation of η^2-ketone adducts.[11] Hence, we next investigated bulky esters as possible substrates for steps 1 and 2 in the catalytic cycle. Unfortunately, thermolyses of *cis*-Cp*W(NO)[η^2-(C$_6$H$_4$)-PPh$_2$](H) in mixtures of benzene and various esters (ethyl acetate, methyl isobutyrate, etc.) all afforded intractable mixtures of products, as did thermolysis of Cp*W(NO)(PPh$_3$)(η^2-EtC(O)OMe) itself. In no case was there any evidence for hydrometalation of the ester by Cp*W(NO)(PPh$_3$)(Ph)(H).

Epilogue

Our initial investigations into the viability of the catalytic cycle presented in Scheme 1 have provided some useful insights. Of the potential Cp′M(NO)(L) fragments studied, only Cp*W(NO)(L) systems are capable of effecting the necessary C−H activation required in step 1. Furthermore, the Lewis base (L) must be a phosphine, and of these, the sterically encumbered triphenylphosphine best fits the requisite criteria since the Cp*W(NO)(PPh$_3$) fragment does not readily convert to the unreactive bis(phosphine) complex, Cp*W(NO)(PPh$_3$)$_2$. However, the Cp*W(NO)(PPh$_3$) fragment is a strong π-base that is incapable of sequentially activating benzene and hydrometalating olefins since it instead forms stable olefin adducts of the type Cp*W(NO)(PPh$_3$)(η^2-olefin). Similar reactivity occurs with ketones, which also form adducts via dihapto coordination of their C=O linkages to the tungsten center. Nevertheless, some sequential benzene activation followed by hydrometalation of ketone does occur in the one-pot reaction involving C$_6$H$_6$ and ^{i}Pr$_2$CO as evidenced by the formation of Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh$_3$) and Cp*W(NO)(OCH^{i}Pr$_2$)(Ph) in a ratio of approximately 1.7:1. These observations thus illustrate a frequently encountered feature of such systems, namely, that the electronic properties of the fragment that facilitate C−H activation via oxidative addition to the metal center also impart Lewis-basic characteristics to that center. Consequently, with such metal-containing fragments capable of reacting with a variety of organic substrates in different ways, the C−H activation step must be the kinetically preferred one in order to utilize this methodology productively for the formation of new C−C and C−O bonds.[15]

Experimental Section

General Methods. All reactions and subsequent manipulations involving organometallic reagents were performed under rigorously anaerobic and anhydrous conditions either at a vacuum-nitrogen dual manifold or in an inert-atmosphere glovebox. The gloveboxes used were Innovative Technologies LabMaster 100 and MS-130 BG dual-station models equipped with freezers maintained at −30 °C. General procedures routinely employed in these laboratories have been described in detail elsewhere.[3a,16] Thermolysis reactions were performed in thick-walled glass pressure vessels equipped with Kontes greaseless stopcocks, and NMR spectroscopic analyses were conducted on samples in J. Young NMR tubes. All glassware and metal utensils were dried in an oven at 250 °C for a minimum of 24 h prior to use.

All solvents were dried and distilled prior to use or were vacuum transferred directly from the appropriate drying agent. Hydrocarbons, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl. Deuterated benzene was purchased from Cambridge Isotope Laboratories and was also distilled from sodium benzophenone ketyl. Trimethylphosphine (Aldrich) was dried and stored over sodium. Celite and neutral alumina I (60−325 mesh) were oven-dried for a minimum of 48 h and cooled under vacuum

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(15) For a very recent example illustrating this feature, see: Foley, N. A.; Lail, M.; Lee, J. P.; Gunnoe, T. B.; Cundari, T. R.; Petersen, J. L. *J. Am. Chem. Soc.* **2007**, *129*, 6765.

(16) Legzdins, P.; Rettig, S. J.; Ross, K. J.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1995**, *14*, 5579.

prior to use. $Cp^*W(NO)(CH_2SiMe_3)_2$[17] and *cis*-$Cp^*W(NO)[\eta^2-(C_6H_4)PPh_2](H)$[11] were prepared according to literature procedures. Benzophenone, Ph_2CO (Fisher), and triphenylphosphine, PPh_3 (99%, Aldrich), were recrystallized from saturated diethyl ether solutions and dried under vacuum. Diisopropyl ketone, $^{i}Pr_2CO$ (98% Aldrich), was first stirred over Drierite for 3 days and then stirred with anhydrous alumina overnight. It was then distilled, and the distillate was finally passed through a column of alumina. Acetone was distilled from Drierite into a vessel containing 4 Å molecular sieves. All other reagents were purchased from commercial suppliers and were used as received.

All IR samples were prepared as Nujol mulls sandwiched between NaCl plates, and their spectra were recorded on a Thermo Nicolet model 4700 FT-IR spectrometer. NMR spectra were recorded at room temperature, unless otherwise noted, on Bruker AV300 or AV400 spectrometers. ^1H and ^{13}C chemical shifts are specified in ppm relative to the residual proton or natural-abundance carbon signal(s) of the solvents employed; coupling constants are reported in Hz. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Correlation and assignment of ^1H and ^{13}C NMR resonances were aided by 2D COSY, HMQC, HMBC, and 1D NOE experiments when necessary. No-D NMR spectra were locked by using an external sample of an equivalent volume of deuterated solvent. Low-resolution mass spectra (EI, 70 eV) were recorded by Mr. M. Lapawa of the UBC mass spectrometry facility using a Kratos MS-50 spectrometer. Elemental analyses were performed by Mr. M. Lakha of the UBC microanalytical facility. Melting points were determined using a Gallenkamp melting-point apparatus.

Monitoring of the Reaction of $CpMo(NO)(CH_2SiMe_3)_2$ with PMe_3 and Dihydrogen in C_6D_6. A C_6D_6 solution of $CpMo(NO)(CH_2SiMe_3)_2$ (20 mg, 0.05 mmol) in a J. Young NMR tube was frozen in liquid nitrogen, and an excess of PMe_3 (5−10 equiv) was added by vacuum transfer. The NMR tube was pressurized with dihydrogen (1 atm), sealed, and allowed to warm to room temperature, whereupon the purple solution quickly became yellow. Analysis of the yellow solution by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy revealed only the presence of $CpMo(NO)(PMe_3)_2$.[8]

Synthesis of $Cp^*Mo(NO)(CH_2SiMe_3)(PMe_3)(H)$. Into a thick-walled glass bomb were added $Cp^*Mo(NO)(CH_2SiMe_3)_2$ (0.50 g, 1.14 mmol) and hexanes (50 mL). This solution was frozen in liquid nitrogen on a Schlenk line, and an excess of PMe_3 (1 mL, 9.7 mmol) was added by vacuum transfer. The vacuum was replaced by dihydrogen (1 atm), and the mixture was allowed to warm to room temperature and was stirred for approximately 5 h, whereupon the deep purple solution became brown. Removal of the volatile components under reduced pressure afforded a brown solid, which was recrystallized from pentane at −30 °C to obtain yellow crystals of $Cp^*Mo(NO)(CH_2SiMe_3)(PMe_3)(H)$ (0.36 g, 73%).

Anal. Calcd for $C_{17}H_{36}NOPSiMo$: C, 47.99; H, 8.53; N, 3.29. Found: C, 48.33; H, 8.68; N, 3.69. IR (Nujol): $\nu_{NO} = 1569$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 1.73 (s, 15H, C_5Me_5), 1.01 (d, 9H, PMe_3), 0.49 (s, 9H, CH_2SiMe_3), −0.7 (m, 2H, CH_2SiMe_3), −2.2 (br dt, $^2J_{HP} = 104$ Hz, $^3J_{HH} = 6$ Hz, 1H, W*H*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 107.1 (C_5Me_5), 19.7 (PMe_3), 11.7 (CH_2SiMe_3), 4.7 (C_5Me_5), −0.3 (CH_2SiMe_3). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6): δ 2.9 (PMe_3).

Monitoring the Conversion of $Cp^*Mo(NO)(CH_2SiMe_3)(PMe_3)(H)$ to $Cp^*Mo(NO)(PMe_3)_2$. $Cp^*Mo(NO)(CH_2SiMe_3)(PMe_3)(H)$ (47 mg, 0.1 mmol) was dissolved in benzene-d_6, and the resulting solution was sealed in an NMR tube and allowed to react for 24 h under ambient temperature. The resulting brown solution was then chromatographed on alumina (0.5 × 5 cm), from which an orange band was eluted with Et_2O. The solvent was removed in vacuo to obtain $Cp^*Mo(NO)(PMe_3)_2$ as an orange powder (11 mg, 66%), which was identified by comparison of its spectroscopic properties listed below with those exhibited by the known $Cp^*W(NO)(PMe_3)_2$.[3a]

IR (Nujol): $\nu_{NO} = 1561$ cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 1.87 (s, 15H, C_5Me_5), 1.20 (d, $^2J_{HP} = 7$ Hz, 18H, PMe_3). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 101.2 (C_5Me_5), 23.0 (d, $^1J_{CP} = 10$ Hz, PMe_3), 12.3 (C_5Me_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 17.4 (PMe_3).

Monitoring of the Reaction of $Cp^*W(NO)(CH_2SiMe_3)_2$ with PEt_3 and Dihydrogen in C_6D_6. A C_6D_6 solution of $Cp^*W(NO)(CH_2SiMe_3)_2$ (20 mg, 0.04 mmol) in a J. Young NMR tube was frozen in liquid nitrogen, and an excess of PEt_3 (5−10 equiv) was added by vacuum transfer. The NMR tube was pressurized with dihydrogen (1 atm), sealed, and left to stand at room temperature. The deep purple solution slowly became yellow-orange, and the progress of the transformations described in the text was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies.

$Cp^*W(NO)(CH_2SiMe_3)(PEt_3)(H)$: ^1H NMR (300 MHz, C_6D_6): δ 1.80 (s, 15H, C_5Me_5), 1.61 (m, 6H, $P(CH_2CH_3)_3$), 0.78 (m, 9H, $P(CH_2CH_3)_3$), 0.46 (s, 9H, CH_2SiMe_3), −0.5 (m, 2H, CH_2SiMe_3), −1.0 (m, 1H, W-*H*). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6): δ 7.3 (satellites $^1J_{PW} = 192$ Hz, PEt_3).

$Cp^*W(NO)(C_6D_5)(PEt_3)(D)$: ^1H NMR (300 MHz, C_6D_6): δ 1.68 (s, 15H, C_5Me_5), 1.51 (m, 6H, $P(CH_2CH_3)_3$), 0.84 (m, 9H, $P(CH_2CH_3)_3$. $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6): δ 31.9 (t, $^2J_{PD} = 14$ Hz, satellites $^1J_{PW} = 212$ Hz, PEt_3).

$Cp^*W(NO)(PEt_3)_2$: ^1H NMR (300 MHz, C_6D_6): δ 1.92 (s, 15H, C_5Me_5), 1.85 (m, 6H, $P(CH_2CH_3)_3$), 1.54 (m, 6H, $P(CH_2CH_3)_3$), 0.98 (m, 18H, $P(CH_2CH_3)_3$). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6): δ 12.7 (satellites $^1J_{PW} = 453$ Hz, PEt_3).

Synthesis of *cis*-$Cp^*W(NO)[\eta^2-(CH_2NMe)P(NMe_2)_2](H)$. In a glovebox, a thick-walled glass bomb was charged with $Cp^*W(NO)(CH_2SiMe_3)_2$ (0.50 g, 0.96 mmol), hexanes (50 mL), and $P(NMe_2)_3$ (0.156 g, 1 equiv). The resulting solution was frozen in liquid nitrogen on a Schlenk line, the vessel was evacuated, and dihydrogen (1 atm) was added. The mixture was then allowed to warm to room temperature and was stirred under a dihydrogen atmosphere for 24 h. During this time the solution became brown, and a yellow powder precipitated. This powder was collected by filtration, washed with pentane (ca. 50 mL), and recrystallized from Et_2O at −30 °C to obtain yellow crystals of *cis*-$Cp^*W(NO)[\eta^2-(CH_2NMe)P(NMe_2)_2](H)$ (0.32 g, 65%).

Anal. Calcd for $C_{16}H_{33}N_4OPW$: C, 37.51; H, 6.49; N, 10.94. Found: C, 37.70; H, 6.49; N, 11.33. IR (Nujol): $\nu_{NO} = 1545$ cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 3.65 (ddd, $^3J_{HP} = 27$ Hz, $^2J_{HH} = 8$ Hz, $^3J_{HH} = 3$ Hz, 1H, $(NMe_2)_2P[N(Me)CH_2]W$), 2.58 (d, $^3J_{HP} = 7$ Hz, 6H, $(NMe_2)_2P[N(Me)CH_2]W$), 2.55 (ddd, $^3J_{HP} = 14$ Hz, $^2J_{HH} = 8$ Hz, $^3J_{HH} = 2$ Hz, 1H, $(NMe_2)_2P[N(Me)CH_2]W$) 2.20 (d, $^3J_{HP} = 7$ Hz, 6H, $(NMe_2)_2P[N(Me)CH_2]W$), 2.30 (br d, overlapping, $^2J_{HP} = 18$ Hz, 1H, W-*H*), 2.27 (d, $^3J_{HP} = 10$ Hz, 3H, $(NMe_2)_2P[N(Me)CH_2]W$), 1.97 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 105.8 (C_5Me_5), 42.6 ($(NMe_2)_2P[N(Me)CH_2]W$), 39.2 ($(NMe_2)_2P[N(Me)CH_2]W$), 38.0 ($(NMe_2)_2P[N(Me)CH_2]W$), 33.7 ($(NMe_2)_2P[N(Me)CH_2]W$), 11.7 (C_5Me_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 68.5 (satellites $^1J_{PW} = 238$ Hz, $(NMe_2)_2P[N(Me)CH_2]W$). MS (EI, probe temperature 120 °C): *m/z* 512 [M^+].

Characterization of *trans*-$Cp^*W(NO)[\eta^2-(CH_2NMe)P(NMe_2)_2](H)$. A C_6D_6 solution of *cis*-$Cp^*W(NO)[\eta^2-(CH_2NMe)P(NMe_2)_2](H)$ (10 mg) was sealed in a J. Young NMR tube and was heated at 80 °C for 48 h, whereupon the pale yellow solution became brown.

^1H NMR (400 MHz, C_6D_6): δ 2.93 (ddd, $^3J_{HP} = 27$ Hz, $^4J_{HH} = 5$ Hz, $^3J_{HH} = 2$ Hz, 2H, $(NMe_2)_2P[N(Me)CH_2]W$), 2.61 (d, $^3J_{HP} = 10$ Hz, 6H, $(NMe_2)_2P[N(Me)CH_2]W$), 2.48 (d, $^3J_{HP} = 9$ Hz, 3H, $(NMe_2)_2P[N(Me)CH_2]W$), 2.27 (d, $^3J_{HP} = 10$ Hz, 6H, $(NMe_2)_2P[N(Me)CH_2]W$), 1.87 (s, 15H, C_5Me_5), 0.91 (br d, $^2J_{PH} = 75$ Hz,

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[17] Veltheer, J. E.; Legzdins, P. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Thieme Verlag: New York, 1997; Vol. 8, pp 79−85.

1H, W-*H*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 105.6 (C_5Me_5), 41.9 ($(NMe_2)_2P[N(Me)CH_2]W$), 38.6 ($(NMe_2)_2P[N(Me)CH_2]W$), 38.1 ($(NMe_2)_2P[N(Me)CH_2]W$), 32.1 ($(NMe_2)_2P[N(Me)CH_2]W$), 11.4 (C_5Me_5) $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 79.8 (satellites $^1J_{PW}$ = 203 Hz, $(NMe_2)_2P[N(Me)CH_2]W$).

Reaction of *cis*-$Cp^*W(NO)[\eta^2\text{-}(C_6H_4)PPh_2](H)$ with Olefins and Benzene as Substrates. These reactions were typically effected in the manner described below.

cis-$Cp^*W(NO)[\eta^2\text{-}(C_6H_4)PPh_2](H)$ (0.25 g, 0.48 mmol) was dissolved in benzene (8 mL), and to this solution was added the olefin (5 to 10 equiv) either by vacuum transfer or by syringe. The mixture was then transferred to a sealable bomb and heated at 45 °C for 24 h. Removal of the volatile components from the final reaction mixtures afforded yellow solids that were either washed with Et_2O or recrystallized from Et_2O to obtain $Cp^*W(NO)(PPh_3)(\eta^2\text{-olefin})$ complexes in good yields.

$Cp^*W(NO)(PPh_3)[\eta^2\text{-}(CH_3)_2CCH(CH_3)]$ (64% yield). Anal. Calcd for $C_{34}H_{43}NOPW$: C, 58.63; H, 6.22; N, 2.01. Found: C, 58.97; H, 6.30; N, 2.06. IR (Nujol): $\nu_{NO} = 1511$ cm^{-1}. ^1H NMR (400 MHz, C_6D_6) major isomer: δ 7.97−7.08 (br m, 15H, PPh_3), 2.22 (d, $^3J_{HH}$ = 6 Hz, 3H, $(CH_3)_2CCH(CH_3)$), 1.58 (s, 3H, $(CH_3)_2CCH(CH_3)$), 1.56 (s, 15H, C_5Me_5), 1.23 (s, 3H, $(CH_3)_2CCH(CH_3)$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) major isomer: PPh_3 carbons not observed, δ 104.9 (C_5Me_5), 48.0 $(CH_3)_2CCH(CH_3)$ 47.2 ($(CH_3)_2CCH(CH_3)$), 34.1 (olefin-CH_3), 27.7 (olefin-CH_3), 20.8 (olefin-CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) major isomer: δ 35.4 (satellites $^1J_{PW}$ = 371 Hz, PPh_3). MS (EI, probe temperature 100 °C): *m/z* 700 [M^+].

$Cp^*W(NO)(PPh_3)[\eta^2\text{-}(1\text{-}Me\text{-}C_6H_9)]$ (71% yield). Anal. Calcd for $C_{36}H_{45}NOPW$: C, 59.84; H, 6.28; N, 1.94. Found: C, 59.81; H, 5.98; N, 2.19. IR (Nujol): $\nu_{NO} = 1519$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.97−7.09 (br m, 15H, PPh_3), 3.05 (m, 2H, cyclohexene-CH_2), 2.45 (m, 2H, cyclohexene-CH_2), 1.79 (m, 2H, cyclohexene-CH_2), 1.67 (s, 3H, $Me\text{-}C_6H_9$), 1.58 (s, 15H, C_5Me_5), 1.44 (m, 2H, cyclohexene-CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): PPh_3 carbons not observed, δ 104.7 (C_5Me_5), 51.6 ($Me\text{-}C_6H_9$), 49.9 (cyclohexene-$CH{=}C(Me)CH_2-$), 37.2 (cyclohexene-CH_2-), 34.5 (cyclohexene-$CH{=}C(Me)CH_2-$), 31.8 (cyclohexene-CH_2-), 24.8 (cyclohexene-CH_2-), 24.2 (cyclohexene-CH_2-), 11.0 (C_5Me_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 35.8 (satellites $^1J_{PW}$ = 375 Hz, PPh_3). MS (EI, probe temperature 150 °C) *m/z* 720 [M^+].

$Cp^*W(NO)(PPh_3)(\eta^2\text{-}MeCHCHMe)$ (62% yield). Anal. Calcd for $C_{33}H_{41}NOPW$: C, 58.07; H, 6.06; N, 2.05. Found: C, 58.39; H, 6.39; N, 2.40. IR (Nujol): $\nu_{NO} = 1513$ cm^{-1}, br. ^1H NMR (300 MHz, C_6D_6) two isomers in a ratio of 1.14:1: δ 7.80−6.95 (br m, 30H, PPh_3), 2.32 (d, 3H, olefin-CH_3), 2.23 (d, 3H, olefin-CH_3), 2.10−1.90 (m, 4H, $MeCHCHMe$), 1.73 (d, 3H, olefin-CH_3), 1.05 (d, 3H, olefin-CH_3), 1.63 (s, 15H, C_5Me_5), 1.49 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) both isomers: some aryl peaks obscured, δ 135.0 (C_{aryl}), 134.5 (C_{aryl}), 133.2 (C_{aryl}), 133.1 (C_{aryl}), 132.3 (C_{aryl}), 130.4 (C_{aryl}), 129.6 (C_{aryl}), 129.3 (C_{aryl}), 129.2 (C_{aryl}), 104.7 (C_5Me_5), 104.3 (C_5Me_5), 46.4 (olefin-CH_3), 39.1 (olefin-CH_3), 25.5 (olefin-CH_3), 19.5 (olefin-CH_3), 44.6 (C_{olefin}), 41.0 (C_{olefin}), 22.5 (C_{olefin}), 18.9 (C_{olefin}), 11.1 (C_5Me_5), 10.5 (C_5Me_5). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6) both isomers: δ 40.2 (satellites $^1J_{PW}$ = 361 Hz, PPh_3), 39.9 (satellites $^1J_{PW}$ = 372 Hz, PPh_3). MS (EI, probe temperature 150 °C): *m/z* 667 [$M^+ - N$].

$Cp^*W(NO)(PPh_3)(\eta^2\text{-}C_6H_{10})$ (58% yield). Anal. Calcd for $C_{35}H_{43}NOPW$: C, 59.33; H, 6.12; N, 1.98. Found: C, 58.60, H, 5.79; N, 2.00. IR (Nujol): $\nu_{NO} = 1510$ cm^{-1}. ^1H NMR (300 MHz. C_6D_6): δ 7.78−7.04 (br m, 15H, PPh_3), 2.91 (m, 1H, olefinic-CH), 2.67 (br m, 2H, cyclohexene-CH_2), 2.19 (m, 1H, olefinic-CH), 1.88−1.30 (m, overlapping, 6H, cyclohexene-CH_2), 1.51 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): some aryl peaks obscured, δ 135.1 (C_{aryl}), 135.0 (C_{aryl}), 130.3 (C_{aryl}), 104.4 (C_5Me_5), 43.9 (C_{olefin}), 43.0 (C_{olefin}), 30.7 (cyclohexene-CH_2), 29.6 (cyclohexene-CH_2), 26.0 (cyclohexene-CH_2), 25.2 (cyclohexene-CH_2), 10.7 (C_5Me_5). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6): δ 39.1 (satellites $^1J_{PW}$ = 375 Hz, PPh_3). MS (EI, probe temperature 100 °C): *m/z* 693 [$M^+ - O$].

Synthesis of $Cp^*W(NO)(Ph)(H)(PPh_3)$. This complex was synthesized by following a slightly modified version of a previously described procedure.[12] $Cp^*W(NO)[\eta^2\text{-}(C_6H_4)PPh_2](H)$ was dissolved in benzene, and the solution was maintained at 50 °C for 24 h. The solvent was removed in vacuo to obtain a brown solid, which was recrystallized from toluene/hexanes at −30 °C to isolate $Cp^*W(NO)(Ph)(H)(PPh_3)$ as a yellow, crystalline material.

IR (Nujol): $\nu_{NO} = 1572$ cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.63−6.90 (br m, 20H, *Ph* and PPh_3), 1.61 (s, 15H C_5Me_5), 1.20 (d, $^2J_{HP}$ = 94 Hz, 1H, W-*H*). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 166.6 (C_{aryl}), 142.8 (C_{aryl}), 137.1 (C_{aryl}), 136.5 (C_{aryl}), 134.3 (C_{aryl}), 134.2 (C_{aryl}), 129.2 (C_{aryl}), 128.3 (C_{aryl}), 123.9 (C_{aryl}), 123.8 (C_{aryl}), 106.9 (C_5Me_5), 10.2 (C_5Me_5). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6): δ 22.8 (satellites $^1J_{PW}$ = 118 Hz, PPh_3).

Synthesis and Spectroscopic Characterization of $Cp^*W(NO)(OCH^iPr_2)(Ph)$. $Cp^*W(NO)(Ph)(H)(PPh_3)$ (12 mg, 0.019 mmol) was dissolved in C_6D_6 (0.75 mL), and OC^iPr_2 (0.02 mL, 10 equiv) was added by syringe. This solution was then sealed in an NMR tube and was heated for 18 h at 50 °C, during which time the color changed from orange to red. The remaining OC^iPr_2 was removed from solution by repeatedly evaporating the volatiles and replacing the lost volume with C_6D_6. NMR spectroscopic analysis showed the products to be predominantly $Cp^*W(NO)(OCH^iPr_2)(Ph)$ (85% spectroscopic yield) and free PPh_3.

IR (Nujol): $\nu_{NO} = 1572$ cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.97−7.04 (m, overlapping signals, 20H, *Ph* and free PPh_3), 4.52 (t, $^3J_{HH}$ = 6 Hz, 1H, OC*H*), 1.80 (m, overlapping, 1H, ($CHMe_2$)), 1.72 (m, overlapping, 1H, ($CHMe_2$)), 1.65 (s, 15H C_5Me_5), 0.98 (d, $^3J_{HH}$ = 7 Hz, 3H, $CHMe_2$), 0.90 (d, $^3J_{HH}$ = 7 Hz, 3H, $CHMe_2$), 0.83 (d, $^3J_{HH}$ = 7 Hz, 3H, $CHMe_2$), 0.70 (d, $^3J_{HH}$ = 7 Hz, 3H, $CHMe_2$). ^{13}C NMR (100 MHz, C_6D_6): δ 134.7 (C_{aryl}), 134.5 (C_{aryl}), 129.2 (C_{aryl}), 129.1 (C_{aryl}), 128.7 (C_{aryl}), 128.5 (C_{aryl}), 128.3 (C_{aryl}), 127.7 (C_{aryl}), 113.5 (C_5Me_5), 102.3 (O*C*H), 32.9 ($CHMe_2$), 32.7 ($CHMe_2$), 21.0 ($CHMe_2$), 20.2 ($CHMe_2$), 18.8 ($CHMe_2$), 17.9 ($CHMe_2$), 10.1 (C_5Me_5). $^{31}P\{^1H\}$NMR (122 MHz, C_6D_6): δ −4.5 (free PPh_3).

Synthesis of $Cp^*W(NO)(\eta^2\text{-}OC^iPr_2)(PPh_3)$. A thick-walled glass bomb equipped with a Kontes stopcock was charged with a stir bar and a solution of *cis*-$Cp^*W(NO)[\eta^2\text{-}(C_6H_4)PPh_2](H)$ (0.400 g, 0.624 mmol) in $^iPr_2CO$ (5 mL). The solution was stirred overnight at 50 °C, after which time the solvent was removed in vacuo to obtain a brown oil. Hexanes were added to the oil to induce the precipitation of $Cp^*W(NO)(\eta^2\text{-}OC^iPr_2)(PPh_3)$ as a tan powder. The powder was isolated by filtration and was washed with hexanes (3 × 10 mL) before being recrystallized from a minimum amount of a 1:1 THF/hexanes solution maintained at −30 °C overnight (1 crop, 0.10 g, 20% yield). Single-crystal X-ray diffraction and elemental analysis of the yellow crystals showed the $Cp^*W(NO)(\eta^2\text{-}OC(CHMe_2)_2)(PPh_3)$ product to be monosolvated with THF.

Anal. Calcd for $C_{35}H_{44}NO_2PW{\cdot}C_4H_8O$: C, 58.72; H, 6.57; N, 1.76. Found: C, 58.37; H, 6.46; N, 1.97. IR (Nujol): $\nu_{NO} = 1552$, 1537 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.84 − 7.06 (m, overlapping 15H, PPh_3), 2.09 (m, 1H, $CHMe_2$), 1.96 (m, 1H, $CHMe_2$), 1.71 (s, 15H, C_5Me_5), 1.48 (d, $^3J_{HH}$ = 7 Hz, 3H, $CHMe_2$), 1.41 (d, $^3J_{HH}$ = 7 Hz, 3H, $CHMe_2$), 1.31 (d, $^3J_{HH}$ = 7 Hz, 3H, $CHMe_2$), 0.95 (d, $^3J_{HH}$ = 7 Hz, 3H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): some aryl peaks obscured, δ 136.0 (br, C_{aryl}), 121.2 (C_{aryl}), 107.8 (C_5Me_5), 88.2 ($OC(CHMe_2)_2$), 44.0 (br, $CHMe_2$), 41.0 ($CHMe_2$), 26.2 (overlapping, ($CHMe_2$), 23.1 ($CHMe_2$), 20.4 ($CHMe_2$), 11.0 (C_5Me_5). $^{31}P\{^1H\}$ NMR (122 MHz, C_6D_6): δ 25.4 (satellites $^1J_{PW}$ = 339 Hz). MS (EI, probe temperature 150 °C): *m/z* 627 [$M^+ - CH(^iPr)_2$]. Mp: 120.9 °C dec.

Reaction of *cis*-$Cp^*W(NO)[\eta^2\text{-}(C_6H_4)PPh_2](H)$ with C_6D_6 and $^iPr_2CO$ as Substrates. A sealable NMR tube was charged with a solution of *cis*-$Cp^*W(NO)[\eta^2\text{-}(C_6H_4)PPh_2](H)$ (35.0 mg, 0.055

Table 1. X-ray Crystallographic Data for *cis*-Cp*W(NO)[η^2-(CH$_2$NMe)P(NMe$_2$)$_2$](H), Cp*W(NO)(OCH^{i}Pr$_2$)(Ph), and Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh$_3$)·THF

	cis-Cp*W(NO)[η^2-(CH$_2$NMe)P(NMe$_2$)$_2$](H)
Crystal Data	
empirical formula	$C_{16}H_{33}N_4OPW$
cryst habit, color	prism, yellow
cryst size (mm)	0.90 × 0.55 × 0.15
cryst syst	monoclinic
space group	$P2_1/c$
volume (Å^3)	1961.1(4)
a (Å)	15.711(2)
b (Å)	7.7716(8)
c (Å)	17.039(2)
α (deg)	90
β (deg)	109.499(6)
γ (deg)	90
Z	4
density(calcd) (Mg/m^3)	1.735
absorp coeff (cm^{-1})	59.81
F_{000}	1016
Data Collection and Refinement	
measd reflns: total	26 735
measd reflns: unique	4580
final *R* indices[a]	R1 = 0.0295, wR2 = 0.0791
goodness-of-fit on F^2 [b]	1.068
largest diff peak and hole (e Å^{-3})	1.079 and −2.373

	Cp*W(NO)(OCH^{i}Pr$_2$)(Ph)	Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh$_3$)·THF
Crystal Data		
empirical formula	$C_{23}H_{35}NO_2W$	$C_{35}H_{44}NO_2PW\cdot C_4H_8O$
cryst habit, color	irregular, red	prism, yellow
cryst size (mm)	0.2 × 0.1 × 0.1	0.30 × 0.15 × 0.09
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
volume (Å^3)	2259.55(9)	1822.5(5)
a (Å)	8.2752(2)	11.323(2)
b (Å)	18.3553(4)	12.829(2)
c (Å)	15.2157(4)	13.410(2)
α (deg)	90	89.345(5)
β (deg)	102.132(1)	76.520(4)
γ (deg)	90	74.479(4)
Z	4	2
density(calcd) (Mg/m^3)	1.591	1.450
absorp coeff (cm^{-1})	51.29	32.49
F_{000}	1080	808
Data Collection and Refinement		
measd reflns: total	35 475	5127
measd reflns: unique	5384	5127
final *R* indices[a]	R1 = 0.0243, wR2 = 0.0474	R1 = 0.0337, wR2 = 0.0863
goodness-of-fit on F^2 [b]	1.097	1.071
largest diff peak and hole (e Å^{-3})	0.781 and −0.797	1.475 and −1.551

[a] R1 on $F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$ ($I_o > 2\sigma(I_o)$); $wR2 = [(\sum(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$ (all data); $w = [\sigma^2 F_o^2]^{-1}$. [b] $\mathrm{GOF} = [\sum(w(|F_o| - |F_c|)^2)/\text{degrees of freedom}]^{1/2}$.

mmol) in C_6D_6 (0.25 mL) and ^{i}Pr$_2$CO (5 equiv). The solution was heated for 18 h at 50 °C, during which time it changed color from yellow to red. Analysis of the final mixture by ^{1}H NMR spectroscopy revealed the presence of two principal organometallic species, namely, Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh$_3$) and Cp*W(NO)(OCD^{i}Pr$_2$)(Ph-d_5) in a ratio of approximately 1.7:1.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.87−6.88 (m, overlapping), 1.71 (s), 1.65 (s), 1.46 (d), 1.40 (d), 1.28 (d), 0.97 (d), 0.88 (d), 0.82 (d), 0.68 (d). ^{31}P{^{1}H} NMR (122 MHz, C_6D_6): δ 25.4, 4.2.

Signals attributable to Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh$_3$) ^{1}H NMR (400 MHz, C_6D_6): δ 1.71 (s, C$_5$*Me*$_5$), 1.46 (d, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 1.40 (d, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 1.28 (d, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 0.97 (d, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$). ^{31}P{^{1}H} NMR (122 MHz, C_6D_6): δ 25.4 (satellites $^1J_{PW}$ = 339 Hz, *P*Ph$_3$).

Signals attributable to Cp*W(NO)(OCD^{i}Pr$_2$)(Ph-d_5) ^{1}H NMR (C_6D_6, 400 MHz): δ 1.65 (s, C$_5$*Me*$_5$), 0.88 (d, $^3J_{HH}$ = 8 Hz, CH*Me*$_2$), 0.82 (d, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$), 0.68 (d, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$).

X-ray Crystallography. Data collection for each compound was carried out at −100 ± 1 °C on either a Rigaku AFC7/ADSC CCD diffractometer or a Bruker X8 APEX diffractometer, using graphite-monochromated Mo Kα radiation.

Data for *cis*-Cp*W(NO)[η^2-(CH$_2$NMe)P(NMe$_2$)$_2$](H) were collected to a maximum 2θ value of 55.6° in 0.5° oscillations. The structure was solved by direct methods[18] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in fixed positions, except the hydride atom (H01), the position of which was modeled based on residual electron density in the appropriate open space. The final cycle of full-matrix least-squares analysis was based on 4580 observed reflections and 222 variable parameters.

Data for Cp*W(NO)(OCH^{i}Pr$_2$)(Ph) were collected to a maximum 2θ value of 56.0° in 0.5° oscillations. The structure was solved by

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[18] SIR97: Altomare, A.; Burla, M. C.; Cammalli, G.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, A. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

direct methods[18] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 5384 observed reflections and 257 variable parameters.

Data for Cp*W(NO)(η^2-OC^{i}Pr$_2$)(PPh$_3$) were collected to a maximum 2θ value of 50.0° in 0.5° oscillations. The structure was solved by direct methods[18] and expanded using Fourier techniques. The crystal was a three-component twin. The unit cell contained a disordered THF solvent molecule, which was modeled in two orientations using isotropic carbon atoms; four of the eight THF hydrogen atoms were modeled. All non-hydrogen atoms in the organometallic complex were refined anisotropically, and all of its hydrogen atoms were included in fixed positions. The final cycle of full-matrix least-squares analysis was based on 5127 observed reflections and 415 variable parameters.

For each structure neutral-atom scattering factors were taken from Cromer and Waber.[19] Anomalous dispersion effects were included in F_{calc};[20] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[21] The values for mass attenuation coefficients are those of Creagh and Hubbell.[22] All calculations were performed using the CrystalClear software package of Rigaku/MSC,[23] or SHELXL-97.[24] X-ray crystallographic data for the structures are presented in Table 1, and full details of all crystallographic analyses are provided in the Supporting Information.

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Supporting Information Available: CIF files providing full details of crystallographic analyses of complexes *cis*-Cp*W(NO)-[η^2-(CH$_2$NMe)P(NMe$_2$)$_2$](H), Cp*W(NO)(OCH^{i}Pr$_2$)(Ph), and Cp*W-(NO)(η^2-OC^{i}Pr$_2$)(PPh$_3$). This material is available free of charge via the Internet at http://pubs.acs.org.

OM700583Q

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(19) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV.

(20) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781−782.

(21) Creagh, D. C.; McAuley, W. J. *International Tables of X-ray Crystallography*; Kluwer Academic Publishers: Boston, 1992; Vol. C.

(22) Creagh, D. C.; Hubbell, J. H. *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Boston, 1992; Vol. C.

(23) *CrystalClear*, Version1.3.5b20; Molecular Structure Corporation, 2002.

(24) Sheldrick, G. M. *SHELXL97*; University of Göttingen: Germany, 1997.