1,2-Bis(dimethylphosphino)ethanehydridomesitylidynetungsten(IV). Hydride Activation via the Trans Influence

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The synthesis of the tungsten carbyne hydride complex *trans*-W(CMes)(dmpe)$_2$H, **7**, which is obtained from the borohydride complex *trans*-W(CMes)(η^1-BH$_4$)(dmpe)$_2$, **6**, (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) is reported. **6** is readily prepared from *trans*-W(CMes)(dmpe)$_2$Cl, **5**, which is prepared from [W(CO)$_5$C(O)Mes][N(CH$_3$)$_4$] via the isolable intermediates *trans*-W(CMes)(CO)$_2$(Py)$_2$Cl, **2**, and *trans*-W(CMes)(CO)[P(OMe)$_3$]$_3$Cl, **3**. **7** was spectroscopically fully characterized, and reactivity studies have revealed its potential in hydrogen transfer reactions. The results of studies into the reactivity of the W−H bond toward small unsaturated molecules, such as propionaldehyde, benzaldehyde, acetone, acetophenone, and benzophenone, to give the corresponding alkoxides *trans*-W(CMes)(dmpe)$_2$(OCHR′R″) (R′ = H, R″ = Pr **9**, R′ = H, R″ = Ph **10**, R′ = R″ = Me **11**, R′ = Me, R″ = Ph **12**, R′ = R″ = Ph **13**) are presented. Facile insertion of the C=O moiety into the W−H bond was also observed with CO$_2$ to yield the formato-O-complex *trans*-W(CMes)(dmpe)$_2$(OCHO), **8**. Reaction of **7** with pyridine-2-carbaldehyde yields the insertion product *trans*-W(CMes)(η^1-methoxypyridine)(dmpe)$_2$, **14**, but only at temperatures below 0 °C. **14** decomposes within minutes at room temperature. Treating **7** with 4-hydroxybenzaldehyde affords *trans*-W(CMes)(η^1-4-formylphenoxy)(dmpe)$_2$, **15**, via a simple acid−base reaction with concomitant evolution of H$_2$.

Introduction

The M−H bond plays an important role in organometallic chemistry and in particular in homogeneous catalysis, where metal hydrides undergo insertion or hydride transfer reactions with a wide variety of unsaturated compounds and thus are involved in many crucial reductive transformations of organic molecules. However, the M−H bond in many cases appears to be quite strong and reluctant to undergo the aforementioned types of reaction. Therefore, it would be of great general interest to elucidate how ancillary ligands are able to influence the M−H bond and subsequently activate it.

In 1973, E. O. Fischer and co-workers[1] reported the first mononuclear carbyne complex. Such complexes contain one of the strongest metal−ligand π-interactions in the form of formal M≡C triple bond. Since then, numerous carbyne complexes have been prepared, and their importance is now well appreciated in organometallic chemistry.[2,3]

Transition metal complexes containing both a hydride and a carbyne ligand are expected to display unusual properties. In recent years, our group has studied the chemistry of activated transition metal hydrides. Systematic investigations have been carried out into how ancillary ligands might activate the M−H bond. It has been shown that the nitrosyl ligand plays a significant role in the electronic activation of a hydride ligand,[4] especially those disposed *trans* to NO. The carbyne ligand CR (R = alkyl, aryl) is regarded as a three-electron donor, and in this sense, it is comparable to the linear nitrosyl ligand. Of special interest, as with the nitrosyl ligand, is that the carbyne ligand is also known to exert a strong *trans* influence[5] on the hydride and, concomitant with that, significant polarization of the *trans*-carbyne disposed W−H bond. The carbyne moiety is also similar to the NO group in that it is a good π-acceptor. It is therefore of interest to compare the reactivity pattern of *trans*-W(CR)L$_4$H with the related NO-substituted species *trans*-W(NO)L$_4$H (L = phosphorus donor).

Our CR residue of choice is the sterically demanding mesityl carbyne ligand, for which, in our case, the nondesirable nucleophilic attack at the carbyne carbon has been estimated to be less feasible.[6] Furthermore, electronically an aryl group acts as a π-donor,[3] which lowers the electrophilicity of the carbyne moiety.

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It has been shown that tungsten carbyne hydrides of the type *trans*-W(CMes)$(CO)_nHL_{4-n}$ (L = phosphorus donor) are thermally unstable, probably as a result of hydride migration and carbene formation.[9] Therefore, to increase the stability of the complexes,[1] the replacement of carbonyl ligands by additional phosphorus donors was sought. Stronger σ-donating phosphines such as the bidentate dmpe (1,2-bis(dimethylphosphino)ethane) were expected to stabilize our hydride complexes. However, overall we envisaged that there might be a weakening of the M−H bond, which might exhibit enhanced reactivity with potential for insertion reactions.[6,7]

Results and Discussion

1. Synthesis of *trans*-W(CMes)(dmpe)$_2$Cl (5). The synthetic procedures described in this work are largely based on chemistry previously outlined by E. O. Fischer and his group,[8] with some modifications used by Mayr, based on the abstraction of oxide from suitable metal carbonyl acylates.[10]

The only previously reported *trans*-carbyne hydride complex with H^{t-CR} is the *trans*-W$(CCMe_3)$(dmpe)$_2$H species,[7] which was obtained from the reaction of W(dmpe)$(CH_2CMe_3)(CHCMe_3)(CCMe_3)$ with dmpe at 120 °C for 15 h. However, the preparation of this compound, as described in the literature, is not suitable as a general procedure.

We have previously reported the preparation of the *trans*-W(CMes)$(CO)[P(OMe)_3]_3Cl$ (**3**) complex via a direct reaction of *trans*-W(CMes)$(CO)_2(py)_2Cl$ (**2**) with a 10-fold excess of neat $P(OMe)_3$ in THF at 67 °C for 16 h.[9] The synthesis of complex **2** was achieved following the literature procedure[9] (Scheme 1).

Under forcing conditions, it was possible to obtain the tetrakis(trimethyl phosphite) carbyne complex **4** by subsequent transformation of complex **3** in excess, neat $P(OMe)_3$ at 120 °C, which gave **4** in good yield. Although it was not possible to obtain a satisfactory elemental analysis for **4**, the isolated material was sufficiently pure to be used in further reactions.

The trimethyl phosphite-substituted complexes **3** and **4** readily undergo substitution of their phosphite ligands. Reaction of **3** or **4** with 1,2-bis(dimethylphosphino)-ethane in xylene at 140 °C for 4 days gave the complex *trans*-W(CMes)(dmpe)$_2$Cl (**5**) in yields of 85 and 82%, respectively, as orange crystals after recrystallization from dichloromethane/pentane.

During the formation of **5**, it was possible, by ^{31}P NMR spectroscopy, to detect two intermediate products, **3a** and **4a** (Scheme 1).[9] **3a** displays three signals at δ 175.0 ppm (dd, $^1J_{PW}$ = 460 Hz, $P(OMe)_3$), δ 16.1 ppm (d, $^1J_{PW}$ = 247 Hz, P(trans $P(OMe)_3$), and δ 12.9 ppm (dd, $^1J_{PW}$ = 203 Hz, P(trans CO)). **4a** shows four signals at δ 20.5 ppm (dd, $^1J_{PW}$ = 257 Hz, P_1), δ 7.2 ppm (m, $^1J_{PW}$ = 196 Hz, P_2), δ −9.5 ppm (m, $^1J_{PW}$ = 240 Hz, P_3), and δ −48.2 ppm (d, P_4).

The structure and composition of compound **5** has been established by IR spectroscopy with the metal−carbon triple bond stretching mode $\nu_{(W\equiv C)}$ at 928 cm^{-1} in THF solution, by NMR spectroscopy, mass spectrometry, and elemental microanalysis. The mass spectrum shows the correct isotope pattern for the *trans*-W(CMes)-(dmpe)$_2Cl^+$ ion. No higher mass peaks were found. The ^{31}P NMR spectrum in toluene-d_8 displays a singlet at 23.1 ppm, which corresponds to the four equivalent phosphorus atoms. This signal shows tungsten satellites with a value for $^1J_{PW}$ of 282 Hz, in agreement with those previously reported.[29] The ^1H and ^{13}C NMR spectra in toluene-d_8 of **5** are also consistent with this formulation.

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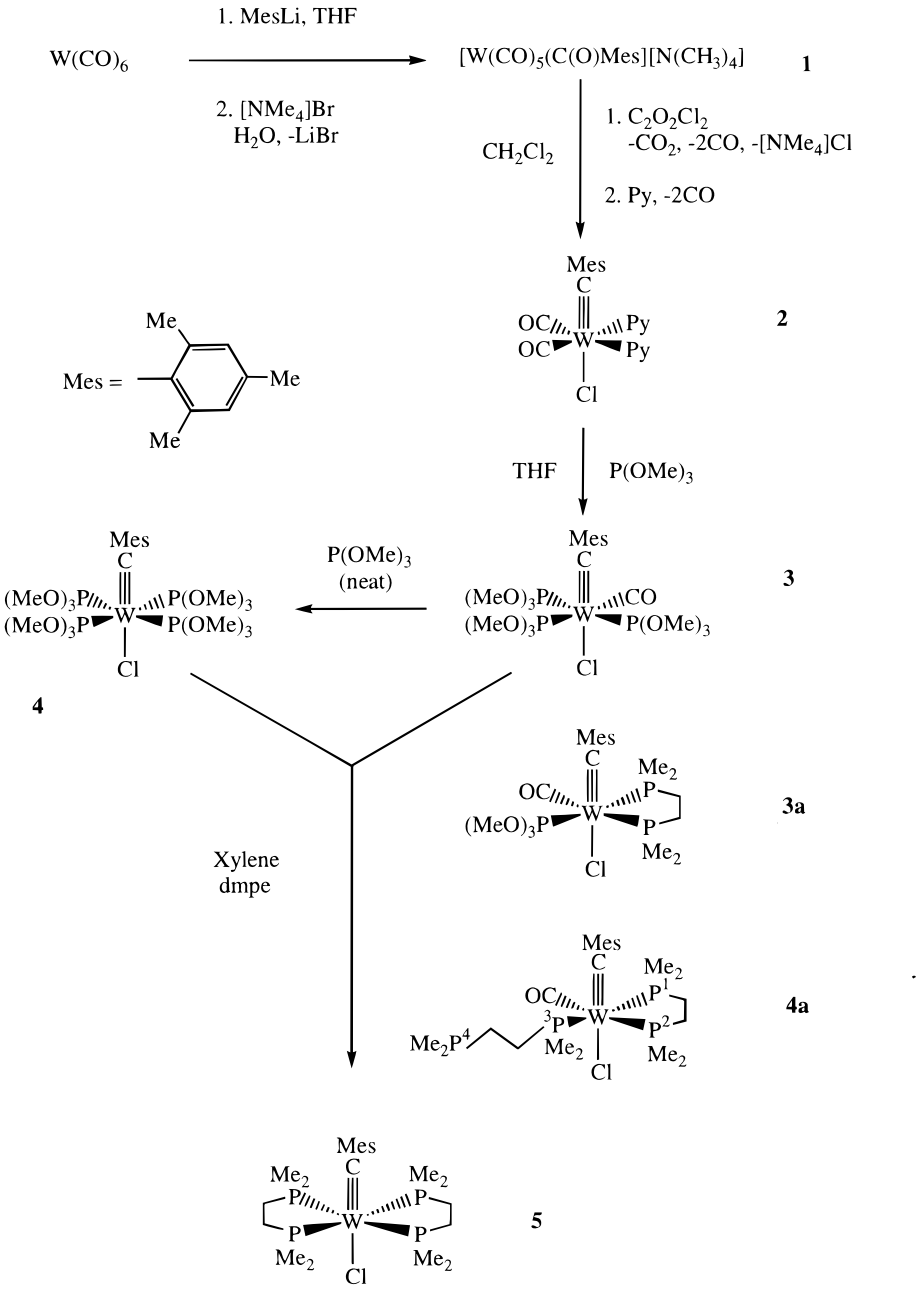
Scheme 1



The ^{1}H NMR spectrum shows four broad signals at 1.55, 1.47, 1.43, and 1.18 ppm corresponding to the two dmpe ligands. The signal for the mesitylidyne α-carbon is found at 260.4 ppm with $^2J_{CP} = 10$ Hz. This low-field chemical shift is typical for metal carbyne complexes.

The bromide analogue of **5** was also isolated from a Schrock carbyne complex, via a reductive procedure.[10] As before, the anionic acyl complex **1** was allowed to react at low temperature with oxalyl bromide, BrC(O)-COBr, to give the unstable intermediate *trans*-halotetracarbonylcarbyne complex, which then reacts with bromine in the presence of a 10-fold excess of dimethoxyethane (DME) to afford the trihalometalalkylidyne complex [W(CMes)Br$_3$(dme)] (**5a**) as a brown, crystalline material. ^{1}H and ^{13}C NMR spectra suggest that **5a** is octahedral with three bromide ligands *cis* to the mesitylidyne ligand. The ^{13}C NMR spectrum displays a resonance at δ 324.1 ppm for the mesitylidyne α-carbon. **5a**, a Schrock type carbyne tungsten (VI) complex, then undergoes a two-electron reduction by zinc in the presence of dmpe in acetonitrile to give complex **5b** with a yield of approximately 36% (Scheme 2).

We have thus shown that both Fischer and Schrock

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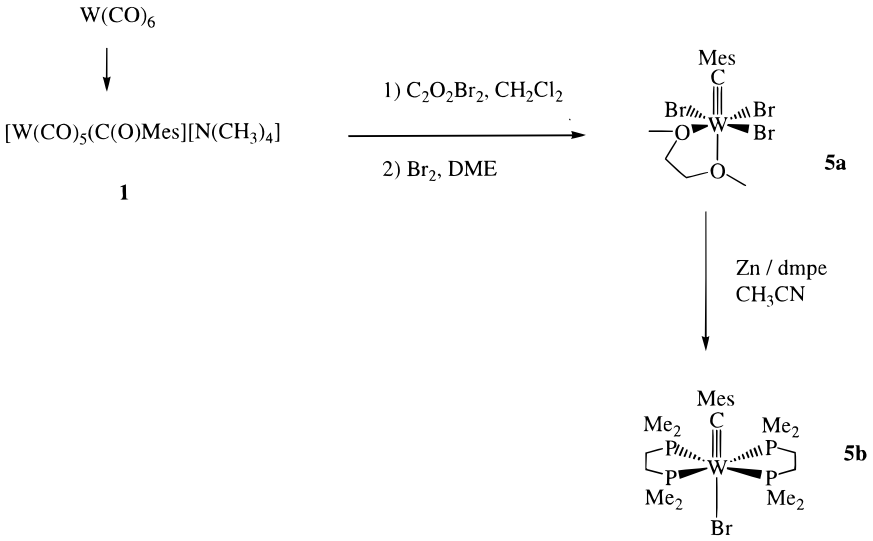
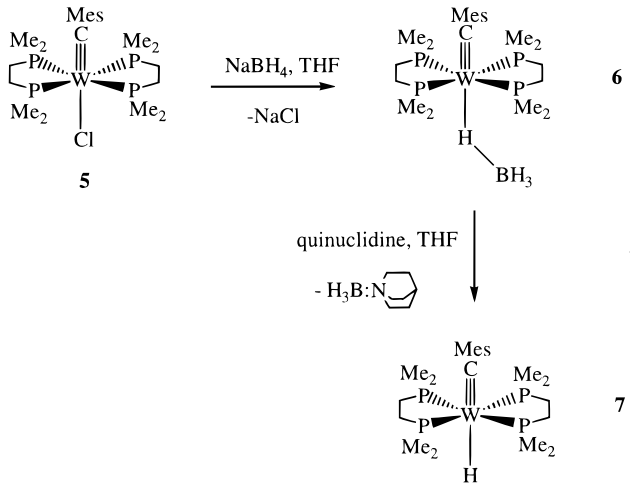
Scheme 2



Scheme 3



type carbyne complexes are accessible from the same starting material.

2. Synthesis of *trans*-W(CMes)(dmpe)$_2$H (7). Considering the preparation of carbyne hydride complexes, we first isolated the respective borohydride compounds, since their existence and potential use as synthetic intermediates were inferred from the earlier carbyne hydride and the supposedly analogous nitrosyl hydride chemistry.[12]

Compound **5** could not directly be transformed into **7** by stoichiometric reaction with $LiBH_4$ or $NaBH_4$ in diethyl ether at room temperature or in THF at 50 °C. However, in the latter case reaction of **5** with an excess of the potential hydride anion donor $NaBH_4$ at 50 °C in THF for 12 h gave the borohydride complex *trans*-W(CMes)(η^1-BH_4)(dmpe)$_2$, **6**. Further reaction of **6** with quinuclidine (3 equiv) in THF at 45 °C for 6 h then gave the desired tungsten hydride **7** in good yield (Scheme 3).

Compound **6** was obtained as brown microcrystals after recrystallization from diethyl ether at −30 °C in a yield of over 90%. The ^{1}H NMR spectrum of **6** shows a broad doublet at δ −2.30 ppm with a characteristic ^{11}B coupling ($^1J_{HB}$ = 80 Hz), which was assigned to the protons of the BH_4 group. ^{1}H NMR spectroscopy was carried out between −80 and 80 °C, but any fluxionality in the BH_4 moiety was not resolved. The ^{31}P NMR spectrum displays a singlet at 22.4 ppm for the four equivalent phosphorus nuclei.[9] The signal for the mesitylidyne α-carbon is found at δ 266.5 ppm with $^2J_{CP}$ = 9 Hz. It was not possible to analyze the ^{183}W nucleus of **6** by indirect NMR spectroscopy, as the W−*H*−B proton relaxes too fast, even at low temperature.

We assume that the tetrahydroborate anion adopts a monodentate coordination mode, as it has already been observed in our group by a single-crystal X-ray diffraction study on a similar compound, *trans*-W(NO)(dmpe)$_2$(η^1-BH_4).[14] In the solution IR spectrum of **6** (THF), four different bands were observed at 927 (m) $\nu_{(W\equiv C)}$, 2352 (s) $\nu_{(B-Ht)}$, 2035 (s) $\nu_{(B-Hb)}$, and 1740 (m br) $\nu_{(W-Hb)}$. Compound **6** gave a satisfactory elemental analysis and the expected mass spectrum. Overall, the structural features of the η^1-BH_4 complex remain a rarity among the versatile bonding modes found for BH_4 units.[15]

Treatment of **6** with 3 equiv of the cyclic amine quinuclidine in THF at 45 °C for 6 h gave the hydride **7**. A strong Lewis base is required to abstract the borane, and for this, quinuclidine seems to be an ideal choice, since it does not compete with the phosphorus donors for coordination to the metal center, but rather selectively scavenges the BH_3.

An alternative, albeit more expensive, method could also be employed, using 15 equiv of PMe_3 instead of quinuclidine, in THF for 3 days, at room temperature. In both cases, thermally stable **7** was isolated in good yield, 98 and 96% respectively, after recrystallization from CH_2Cl_2/pentane. The ^{1}H NMR spectrum in toluene-d_8 at room temperature displays among other characteristic resonances that of the hydride ligand, which appears as a 1:4:6:4:1 quintet at δ −6.58 ppm ($^2J_{HP}$ = 32 Hz), which has ^{183}W satellite peaks ($^1J_{HW}$ = 32 Hz) and is quite high field for a tungsten hydride complex. In fact, this hydride resonance is approaching the values observed for hydrogen atoms bridging two tungsten atoms.[4] The ^{31}P NMR spectrum displays a singlet at about δ 25 ppm with tungsten satellites, and the ^{13}C NMR spectrum shows a charateristic low-field resonance for the carbyne carbon at δ 260.4 ppm (quintet, $^2J_{CP}$ = 10 Hz). We have also carried out some solid-state

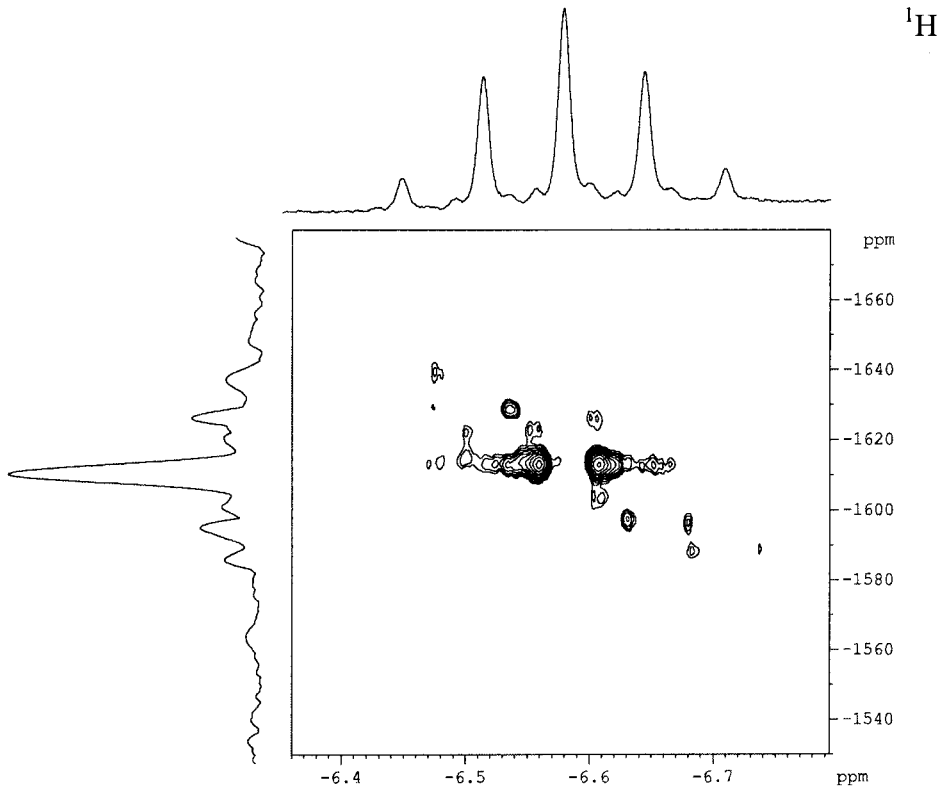


Figure 1. (^{1}H, ^{183}W)-HMQC spectrum shown in its magnitude representation (toluene-d_8, 298 K).

NMR measurements on **7**. Various spinning rates between 2.0 and 13.5 kHz were used in order to distinguish between isotropic shifts and rotational sidebands. As expected from the solid-state structure (vide infra), the spectrum obtained was quite similar to that of ^{1}H NMR liquid spectrum, apart from rotational sidebands. Since the ^{183}W nucleus is relatively abundant (14% natural abundance), (^{1}H, ^{183}W)-HMQC correlations have been used to characterize the ^{183}W chemical shift at δ −1612 ppm (pseudo-quintet, $^1J_{WP} = 281$ Hz). It was also possible to see the coupling with the hydride hydrogen (Figure 1).

We were able to estimate the degree of ionic bond character (*i*) in the covalent M−H bond. This was done using deuterium NMR spectroscopy, by determining the DQCC of ^{2}H measuring the T_{1min} relaxation time values in toluene-d_8 solution at different temperatures.[16] A value of $i = 85.0\%$ was obtained. A detailed theoretical analysis of this phenomenon will be presented elsewhere.[33] The deuteride analogue of **7** was prepared by using $NaBD_4$ instead of $NaBH_4$ in the last two steps of the synthesis to afford the complexes **6a** and **7a**. As previously noted by Schrock for *trans*-W(CCMe$_3$)-(dmpe)$_2$H, a W−H or W−D stretching mode in the IR spectrum is not observed, although many different solvents have been tried in the search for them.[7b,20] The W−H vibration seems to be of very low IR intensity, which is quite frequently the case in transition metal hydride chemistry.[13,17] A solid-state Raman spectrum of **7** displays the W−H vibration at 1600 cm^{-1}. The position of this band at very low vibrational energies allows us to suggest that the W−H bond of **7** seems to be relatively weak. The W≡C vibration was found at about 920 cm^{-1}, which is consistent with those reported by Hopkins and co-workers.[18]

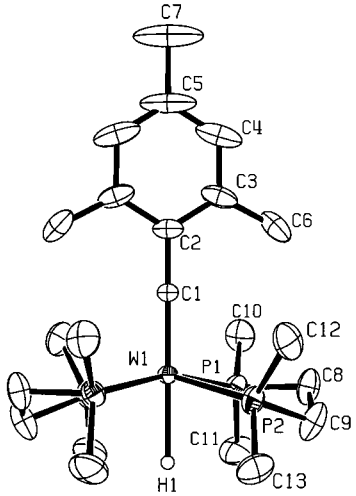


Figure 2. X-ray structure of complex **7** (ORTEP representation). The hydrogen atoms, except H1, have been omitted for clarity. Labeling of symmetry-related atoms *i* for C3, C4, C6, P1, P2, and C8−C13 is not shown (sym. op. $i = 1-x, y, 1.5-z$).

The structure of this *trans*-mesitylidyne hydride

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) in *trans*-W(CMes)(dmpe)$_2$H[a]

selected bond distances (Å)	selected angles (deg)
W(1)−C(1) 1.863(6)	W(1)−C(1)−C(2) 180.0
W(1)−H(1) 2.0088	H(1)−W(1)−C(1) 180.0
C(1)−C(2) 1.448(9)	P(1)−W(1)−P(2) 81.07(5)
W(1)−P(1) 2.4281(14)	P(1)−W(1)−P(2i) 81.07(5)
W(1)−P(2) 2.4208(15)	P(1)−W(1)−H(1) 81.64(3)
W(1)−P(1i) 2.4281(14)	P(1i)−W(1)−H(1) 81.64(3)
W(1)−P(2i) 2.4208(15)	P(2)−W(1)−H(1) 77.39(4)
	P(2i)−W(1)−H(1) 77.39(4)
	P(1i)−W(1)−P(1) 163.28(7)
	C(1)−W(1)−P(2) 102.61(4)
	C(1)−W(1)−P(1) 98.36(3)
	P(1)−W(1)−P(2i) 95.26(5)

[a] See Figure 2 for atom designations. Symmetry operator for *i* = 1−*x*, *y*, 1.5−*z*.

complex **7** was finally unequivocally established by a single-crystal X-ray diffraction study (Figure 2). Suitable crystals were obtained by slow cooling of a saturated CH_2Cl_2/pentane solution to −30 °C. Selected bond distances (Å) and bond angles (deg) are listed in Table 1.

7 adopts a pseudooctahedral geometry with the two dmpe ligands in equatorial positions and the hydride and carbyne ligands axial and *trans* to each other. This type of structure has previously been observed for similar M(CR)L$_4$X complexes (M= Cr, Mo, W; L = phosphorus donor).[6] This X-ray structure indicates a W−H bond of about 2 Å; this distance has to be taken with caution, but it is significantly longer than expected on the basis of previous X-ray crystallographic studies (around 1.8 Å).[21] However, this could be due to a strong *trans*-influence of the carbyne ligand. The strong σ-donor dmpe ligands may also contribute to this elongation and as a result increase the "hydridic" character of H; that is, greater separation of charge across M−H bond (less covalent, more ionic) occurs. The tungsten carbon triple bond distance is about 1.86 Å, which is unremarkable and similar to those calculated[22] or observed in the literature.[5b,6,23]

The dmpe ligands do not lie exactly in the equatorial plane but are bent away from the carbyne unit, presumably due to unfavorable steric interactions between the mesityl *ortho*-methyl groups and the methyl groups attached to phosphorus.

3. Reactivity Patterns of *trans*-W(CMes)(dmpe)$_2$H (7). Compound **7** was expected to undergo facile intermolecular hydride transfer reactions, i.e., insertions with a wide variety of unsaturated compounds such as CO_2, aldehydes, ketones, and metal carbonyls, to afford principally compounds with W−O bonds. Aldehydes and ketones have only rarely been demonstrated to insert into transition metal hydrogen bonds,[24] with ketones being particularly reluctant to undergo such transformations. These types of insertions, however, have been invoked as key steps in catalytic reduction with transition metal compounds.[25] Insertion of CO_2 into a metal hydride bond is a reaction of growing interest,[19] since it is assumed to be the initial step in the hydrogenation of CO_2.[26] **7** reacts readily with 1 bar of CO_2 in THF to give the η^1-formate species **8**. The reaction was complete after a few minutes at −25 °C. This complex was isolated in 85% yield as analytically pure orange crystals after recrystallization from diethyl ether (Scheme 4).

The ^{1}H NMR spectrum of **8** displays a singlet at δ 8.25 ppm, which is assigned to the formate proton, and the ^{13}C NMR spectrum shows a singlet resonance at δ 165.9 ppm, attributed to the formate carbon. On heating a solution of **8** to +50 °C, no signal was observed corresponding to an η^2-CO_2 insertion product. The THF solution IR spectrum of **8** exhibits two bands at 1621 and 1337 cm^{-1} for the formate ligand, in accordance with other reported η^1-formate complexes in the literature.[30f,g] **8** has been further characterized by elemental analyses and mass spectrometry. Formate, like most carboxylate ligands, tends to be a bis(chelate) or bridging ligand, and relatively few η^1-formate complexes have been characterized to date.[30] Here we present the structure of **8**, which has been studied by single-crystal X-ray diffraction (Figure 3). Suitable crystals were obtained by slow cooling of a saturated diethyl ether solution to −30 °C. Selected bond distances (Å) and bond angles (deg) are listed in Table 2.

The tungsten center adopts a pseudooctahedral geometry, with the carbyne and the η^1-formate ligands *trans* to each other. This X-ray structure indicates a W−O(1) distance of 2.275(10) Å and a W−O(2) distance of about 3.63(1) Å, which is unambiguously nonbonding. These two W−O bond lengths are consistent with most (but not all[30d,e]) of the reported η^1-formate structures, with the conventional bonding description (W−O−CH=O). The other geometric parameters are quite similar to those of compound bis(formate)[Mo(dmpe)$_2$(OCHO)$_2$],[30f] except for the angles P(n)−W−O(1) (n = 1−4), which are about 5° smaller in **8**, probably due to the *trans* sterically large carbyne ligand. The C(1)−W−O(1) angle (175.7(4)°) also deviates from an ideal value.

Aldehydes and ketones have been shown in our laboratory to insert directly into the W−H bond of *trans*,*trans*-W(H)(CO)$_2$(NO)(PMe$_3$)$_2$, *trans*-W(H)(CO)(NO)(PMe$_3$)$_3$, and with their analogous Mo complexes,[13,21,24] apparently without prior coordination of the substrate to the metal, via a mechanism involving direct nucleophilic attack of the hydride ligand at the electrophilic carbon of the aldehyde or ketone. The reactions of **7** demonstrate this conclusively, since it cannot easily be envisaged that **7** provides an open coordination site.

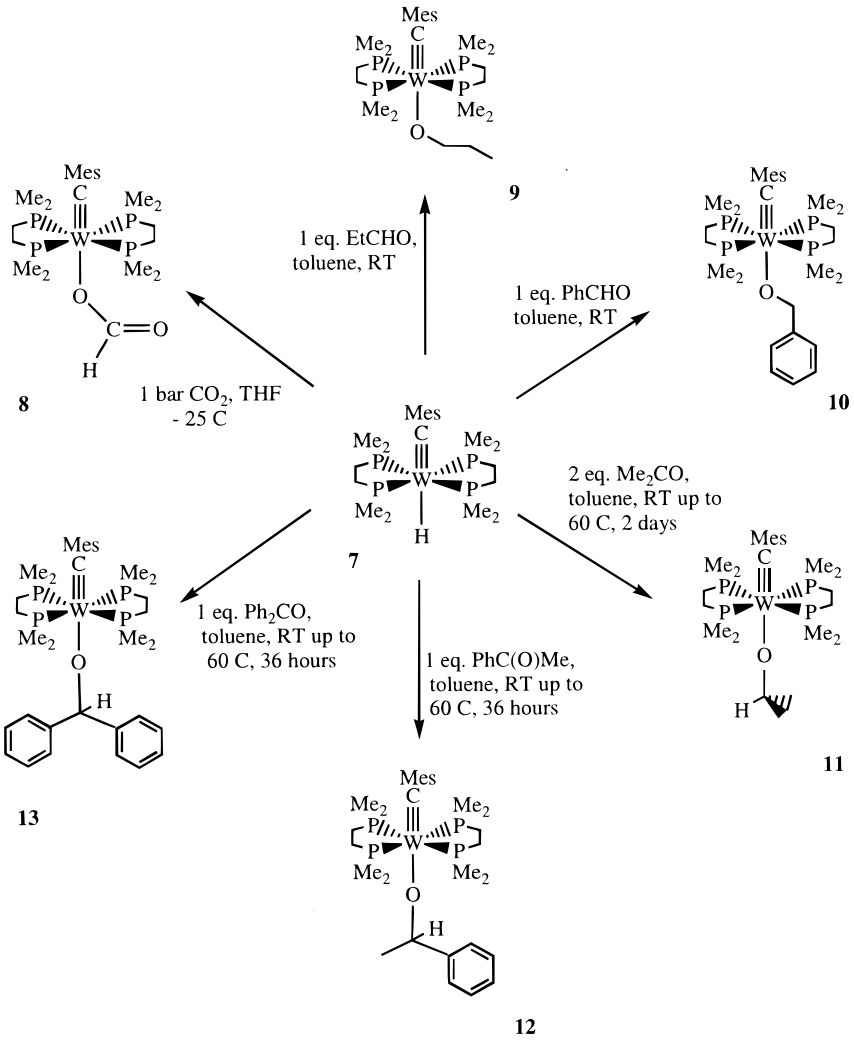
Treatment of **7** with 1 equiv of propionaldehyde or benzaldehyde affords the corresponding alkoxy compounds (Scheme 4).

When the reactions were monitored by ^{1}H NMR spectroscopy in toluene-d_8, a triplet at δ 3.21 ppm ($^3J_{HH}$ = 6.3 Hz) and a singlet at δ 4.23 ppm indicated the formation of the insertion products *trans*-W(CMes)(η^1-OPr)(dmpe)$_2$, **9**, and *trans*-W(CMes)(η^1-OBn)(dmpe)$_2$, **10**, respectively. Compounds **9** and **10** were isolated with yields of 90 and 97%, respectively, after recrystallization from CH_2Cl_2/pentane at −30 °C, and their compositions confirmed by elemental microanalyses.

Reactions of the W−H bond of **7** with ketones were slower. Reduction of these unsaturated compounds were spectroscopically observable by NMR spectroscopy after a few minutes, but the reactions were complete only after 36−48 h, at 60 °C (Scheme 4).

Treatment of **7** with 1 equiv of acetophenone or benzophenone from room temperature up to 60 °C yielded **12** and **13**, respectively. Compound **12** shows a

Scheme 4



quartet at δ 4.17 ppm for the OC*H*MePh proton ($^3J_{HH}$ = 6 Hz) and a characteristic signal at δ 77.7 ppm in the ^{13}C NMR spectrum which is attributed to the W−O*C*HMePh carbon. **13** displays chemical shifts similar to **12** at δ 5.08 and δ 86.7 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. The compositions of **12** and **13** were further confirmed by elemental microanalyses. Acetone is known to be a more reluctant reagent compared to acetophenone or benzophenone, so a higher stoichiometric ratio (1:2) was used. The phenyl sub-

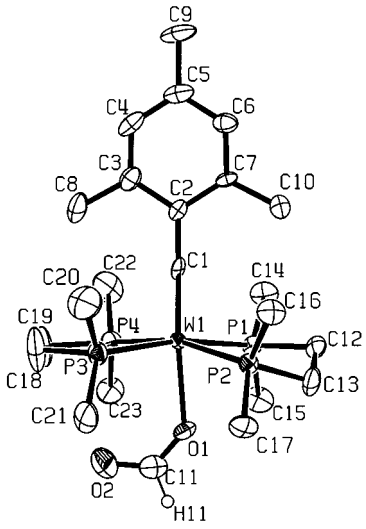


Figure 3. X-ray structure of complex **8** (ORTEP representation). The hydrogen atoms of the mesitylidyne and the dmpe ligands have been omitted for clarity.

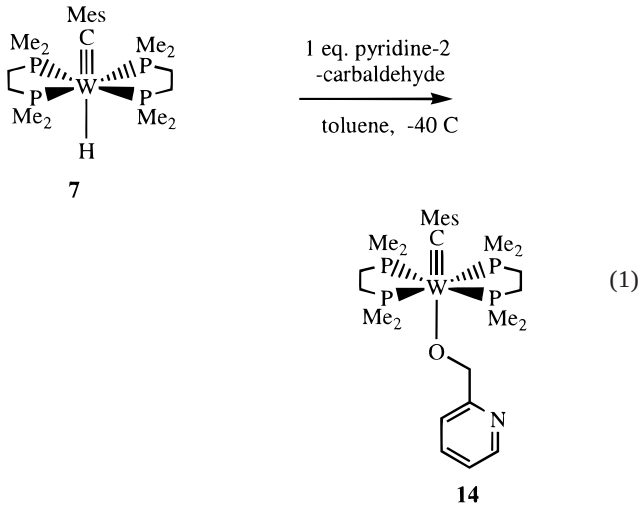
Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) in *trans*-W(CMes)(η^1-OC(O)H)(dmpe)$_2$[a]

selected bond distances (Å)	selected angles (deg)
W(1)−C(1) 1.821(14)	W(1)−C(1)−C(2) 178.6(10)
W(1)−O(1) 2.275(10)	C(1)−W(1)−O(1) 175.7(4)
C(1)−C(2) 1.457(9)	P(1)−W(1)−P(2) 80.87(12)
W(1)−P(1) 2.441(4)	P(3)−W(1)−P(2) 97.51(12)
W(1)−P(2) 2.463(3)	P(4)−W(1)−P(2) 166.24(13)
W(1)−P(3) 2.463(4)	P(4)−W(1)−P(3) 81.51(13)
W(1)−P(4) 2.456(3)	P(1)−W(1)−P(3) 169.97(14)
O(1)−C(11) 1.227(19)	P(1)−W(1)−P(4) 97.69(13)
C(11)−O(2) 1.24(2)	C(1)−W(1)−P(1) 95.7(4)
C(11)−H(11) 0.95	C(1)−W(1)−P(4) 93.9(4)
C(2)−C(3) 1.433(19)	C(1)−W(1)−P(3) 94.3(4)
W(1)−O(2) 3.63(1)	C(1)−W(1)−P(2) 99.8(4)
	O(1)−W(1)−P(1) 80.8(3)
	O(1)−W(1)−P(4) 89.1(3)
	O(1)−W(1)−P(3) 89.2(3)
	O(1)−W(1)−P(2) 77.2(3)
	C(11)−O(1)−W(1) 135.0(11)
	O(1)−C(11)−O(2) 126.7(18)
	O(1)−C(11)−H(11) 116.7
	O(2)−C(11)−H(11) 116.7

[a] See Figure 3 for atom designations.

stituent apparently facilitates these reactions via enhanced electrophilicity of the $C_{carbonyl}$ atom. This was confirmed qualitatively by the apparently longer reaction time with acetone. Hence, **7** with 2 equiv of acetone at 60 °C gave compound **11** in almost spectroscopically quantitative yield after 2 days. At room temperature, however, even after stirring 10 days and with the addition of up to 5 equiv of acetone, the spectroscopic yield of compound **11** was only about 60%. The structure of **11** was assigned on the basis of NMR spectroscopy and its composition confirmed by mass spectrometry. The ^{1}H NMR spectrum of **11** shows a septet at δ 3.56 ppm for the OC*H*Me$_2$ proton and a signal at δ 78.7 ppm in ^{13}C NMR spectrum, which is attributed to the W−O*C*HMe$_2$ carbon.

All the alkoxy compounds produced were found to be relatively stable and could be stored at low temperature (−30 °C) for several months or at room temperature for a few days before decomposing. We have also studied the reactivity of **7** toward modified aldehydes, i.e., aldehydes that contain an additional functional group. Reaction of **7** with 1 equiv of pyridine-2-carbaldehyde (eq 1) leads to the corresponding alkoxy compound **14**.

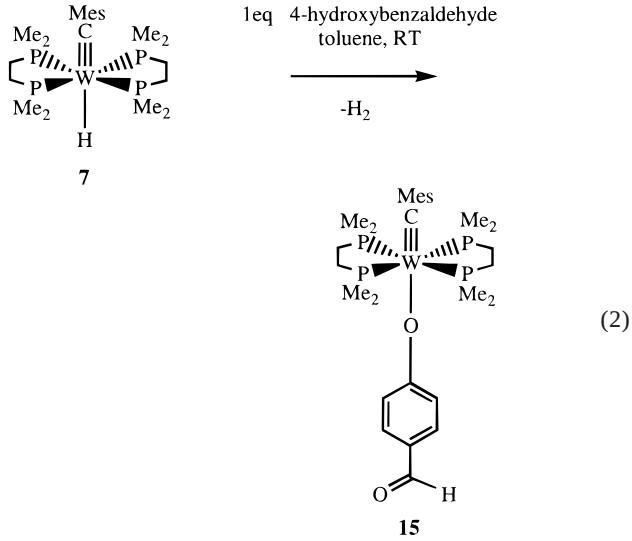


7 **14** (1)

2D NMR experiments such as long-range coupling {^{1}H, ^{13}C} (LR-CH), HSQC {^{1}H, ^{13}C}, and NOESY {^{1}H, ^{1}H} were performed at 500 MHz (at −40 °C to confirm a W−O bond rather than a W−N bond as already seen in our group).[24b] However, attemps to isolate **14** were unsuccessful due to its rapid decomposition at room temperature.

In some cases, when the carbonyl substrate contains an acidic functionality, **7** reacts via an acid−base reaction rather than by hydride transfer. For example, **7** reacts with 1 equiv of 4-hydroxybenzaldehyde at room temperature in toluene, and no reduced organic products were observed. The hydride complex acts as a base toward the acidic alcoholic hydrogen of the reagent to give **15** (eq 2).

This complex presumably results from protonation of the transition metal complex and subsequent loss of dihydrogen. The evolution of H_2 can also be traced in the ^{1}H NMR spectrum with the H_2 resonance at about δ 4.25 ppm. The formation of this compound thus confirms the substantial hydridic character of the W−H functionality in **7**.



7 **15** (2)

However, in contrast to *trans*-W(CMes)(CO)H-[P(OMe)$_3$]$_3$,[9] *trans*-W(CMes)(dmpe)$_2$H does not react readily with donor molecules such as acetonitrile, trimethylphosphine, and trimethyl phosphite, even in the presence of a large excess of these reagents. Furthermore, reaction of **7** with camphor was not successful either, probably due to steric factors.

The insertion of carbon monoxide into a M−H bond to produce a formyl species has been proposed as a key step in the homogeneous catalytic hydrogenation of CO.[27] However, the direct product of CO insertion into a M−H bond, a metal-bound formyl group, is rarely observed[28] and generally requires either a strongly hydridic hydride or the presence of a Lewis acidic group, presumably due to the high bond energy of CO. The reaction of **7** with an excess of CO (1 bar), in toluene-d_8, from room temperature up to +50 °C was monitored in a sealed NMR tube experiment over a period of several days. However, after a few days, only decomposition was observed, and no metal-containing product could be traced. The main problem seems here to be the low CO solubility in common solvents.

Conclusion

The tungsten carbyne hydride complex **7** has been prepared and its reactivity toward unsaturated organic molecules studied. Support for the enhanced hydricity and weakness of the W−H bond is indeed provided by physical and chemical evidence. We have also synthesized the isoelectronic analogous nitrosyl complex of **7**, and we are currently comparing the physical properties and the reactions based on the *trans*-influence/effect of the linear nitrosyl and the carbyne ligands, which both are three-electron donor ligands.

Experimental Section

All manipulations of air-sensitive compounds were carried out either in a dry glovebox under recirculating nitrogen or under dry nitrogen by conventional Schlenk techniques. Solvents were distilled from appropriate drying agents[32] and freshly distilled under nitrogen prior to use (e.g., diethyl ether, hexane, pentane, benzene, toluene, xylene, 1,2-dimethoxyethane, and THF were purified by reflux over sodium/benzophenone, dichloromethane was refluxed either over calcium

hydride or over P_2O_5, pyridine was dried over KOH pellets). Quinuclidine, benzophenone, acetophenone, 4-hydroxybenzaldehyde, and 2-pyridine carbaldehyde were dried a few hours under high vacuum. The deuterated solvents (C_6D_6, $CDCl_3$, toluene-d_8, and THF-d_8) were also obtained from commercial suppliers and distilled from appropriate drying agents and vacuum transferred for storage in Schlenk flasks fitted with Teflon stopcocks. The ligands dmpe and PMe_3 were synthesized following modified literature procedures,[31] whereas all other reagents were purchased and used without further purification. ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR spectra were run either on a Varian Gemini-300 operating at 300.1, 75.4, 121.5, and 96.2 MHz, respectively, or on a Bruker DRX-500 spectrometer at 500.2, 125.8, 202.5, and 160.5 MHz, respectively. $\delta(^1H)$, $\delta(^{13}C)$, rel. to $SiMe_4$, $\delta(^{31}P)$ rel. to 85% H_3PO_4, $\delta(^{11}B)$ rel. to BF_3/OEt_2, and $\delta(^{183}W)$ rel. to Na_2WO_4. All solid-state NMR measurements have been carried out at room temperature using a small bore probe for 4 mm rotors. The ^{31}P and ^{13}C spectra were obtained under CP-MAS conditions and high-power proton decoupling during acquisition. Various spinning rates between 2.0 and 13.5 kHz were used in order to distinguish between isotropic shifts and rotation sidebands. Mass spectra (EI or FAB) were recorded on a Finnigan MAT-8230 mass spectrometer. IR spectra: Bio-Rad FTS-45 instrument. Raman spectra: Renishaw Labram Raman microscope. Elemental analyses: LECO CHNS-932

Compounds **1**, **2**, **3**, and **4** were prepared following earlier procedures,[9] and the observed spectroscopic data were in accordance with those reported.

Crystallography. Compound **7** crystallized as red plates in the monoclinic space group, *C*2/*c* with unit cell parameters of $a = 12.8920(10)$ Å, $b = 12.5780(9)$ Å, $c = 16.9976(14)$ Å, $\beta = 97.424(9)°$, $V = 2733.2(4)$ Å^3, $Z = 4$, and $R = 0.0463$ for 3377 observed reflections.

Compound **8** crystallizes as red plates in the monoclinic space group $P2_1/c$ with unit cell parameters of $a = 9.1712(7)$ Å, $b = 8.9647(5)$ Å, $c = 33.982(3)$ Å, $\beta = 94.231(10)°$, $V = 2786.3(4)$ Å^3, $Z = 4$, and $R = 0.0672$ for 3969 observed reflections.

Single crystals of **7** and **8** were mounted on top of a glass fiber using perfluoropolyether oil and immediatly transferred to the diffractometer where the crystals were cooled to 173 K (**7**) and 183 K (**8**) by an Oxford cryo system. The determination of the unit cell parameters and the collection of intensity data were performed with an image plate detector system (Stoe IPDS diffractometer) using the Stoe IPDS software, Version No. 2.90 (1998).[34] The crystal of **7** showed relatively weak diffraction power; hence the irradiation time was augmented to 9 min per image. The crystal-to-image distance for crystal **7** could be set to 50 mm (resulting in $\theta_{max} = 30.3°$), whereas for crystal **8** the respective distance had to be set to 76 mm ($\theta_{max} = 24.6°$) due to a long cell axis and therefore prevent overlap of neighboring reflections. Lorentz and polarization corrections were done with INTEGRATE; numerical absorption corrections[35] were performed with XRED, using 13 (for **7**) and 14 (for **8**) measured and indexed crystal faces using a video camera installed at the IPDS diffractometer. Both structures were solved with direct methods using SHELXS-97.[36] The refinements were performed with SHELXL-97.[37]

In **7**, the hydride hydrogen was finally found by difference electron density calculations near the 2-axis. The *x* and *z* coordinates were shifted to the special position $x = 0.50$ and $z = 0.75$, resulting in a distance of about 2.0 Å from the tungsten atom. The *y* coordinate of the hydride approached the main residual electron density maximum near the tungsten atom during refinement stage, but the isotropic displacement parameter was freely refined, resulting in the acceptable value of 0.07(4) Å^2.

Table 3. Crystals Data and Structure Refinement Parameters for 7 and 8

	7	**8**
formula	$C_{22}H_{44}P_4W$	$C_{23}H_{44}O_2P_4W$
M_r	616.30	660.31
cryst habit	red plate single crystal	orange plate single crystal
cryst size (mm)	0.30 × 0.30 × 0.11	0.35 × 0.22 × 0.12
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/c$
a (Å)	12.8920(10)	9.1712(7)
b (Å)	12.5780(9)	8.9647(5)
c (Å)	16.9976(14)	33.982(3)
α (deg)	90	90
β (deg)	97.424(9)	94.231(10)
γ (deg)	90	90
V (Å^3)	2733.2(4)	2786.3(4)
ρ_{calc} (g cm^{-3})	1.498	1.574
Z	4	4
F(000)	1240	1328
temp (K)	173(2)	183(2)
μ (cm^{-1})	44.67	43.93
abs corr	numerical	numerical
T_{min}/T_{max} (°C)	0.3746/0.6393	0.3086/0.6207
θ range (deg)	3.16−30.32	2.23−24.63
hkl range	$-18 < h < 17$ $-17 < k < 17$ $-24 < l < 24$	$-10 < h < 10$ $-10 < k < 10$ $0 < l < 39$
no. of data measd	14 195	8847
no. of unique data	3831	4675
no. of data obsd[a]	3377	3969
no. of params	133	282
max. shift/esd	0.001	0.001
resd dens (e Å^{-3})	+4.302, −2.723	+1.881, −2.991
R1 (obs)	0.0463	0.0672
wR2 (obs)	0.1229	0.1527
GooF	1.121	1.446

[a] With $I_{obs} \geq 2\sigma(I)$.

The thermal ellipsoids in the ORTEP drawings of Figures 2 and 3 are drawn at the 30% probability level. Additional information on the data collection and refinement parameters for **7** and **8** are given in Table 3.

Preparation of W(CMes)(dme)Br$_3$ (5a). A methylene chloride solution (50 mL) containing the pentacarbonylmetal acylate complex **1** (2 g, 3.67 mmol) is cooled to −95 °C (CH_2Cl_2/liquid N_2), and a cold (−95 °C) solution of oxalyl bromide (0.41 mL, 4.40 mmol) is added. The solution is warmed to −20 °C and stirred at that temperature for 1 h, then cooled again at −70 °C. In succession, a 10-fold excess of DME and a cold CH_2Cl_2 solution (−70 °C) of an equivalent amount of bromine are added. The resulting deep orange-brown solution is then warmed to room temperature. The solvent is removed in vacuo, and the filtrate is redissolved in methylene chloride, filtered over a layer of Celite, and recrystallized in CH_2Cl_2/pentane to afford brown microcrystals of **5a** (2.20 mmol, yield: 60%). ^{1}H NMR (C_6D_6, 298 K): δ 6.62 (s, 2H, Mes), 2.80 (s, 6H, 2CH_3-Mes), 3.60 and 3.18 (s, 6H, *Me*OCH_2CH_2O*Me*), 3.00 and 2.89 (m, 4H, MeO*C*H_2*C*H_2OMe), 1.98 (s, 3H, CH_3-Mes). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 324.1 (m, CMes), 148.2 (s, *ipso*-Mes), 141.1 (s, *o*-Mes), 135.2 (s, *p*-Mes), 127.8 (s, *m*-Mes), 76.7 (s, MeO*C*H_2*C*H_2OMe), 75.5 (s, *Me*O*C*H_2*C*H_2OMe), 68.8 (s, MeO*C*H_2*C*H_2OMe), 58.7 (s, MeO*C*H_2*C*H_2O*Me*), 21.3 (s, 2CH_3-Mes), 20.1 (s, CH_3-Mes).

Preparation of *trans*-W(CMes)(dmpe)$_2$Cl (5). Compound **3** (3.0 g, 4.0 mmol) was dissolved in xylene (150 mL), and dmpe (1.5 mL, 8.79 mmol, 2.2 equiv) was added. The resulting mixture was refluxed at 140 °C for 4 days. The solution became red and was then cooled to room temperature. The solvent was

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(36) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(37) Sheldrick, G. M. *SHELX97*; University of Göttingen: Germany, 1997.

removed in vacuo and the resulting precipitate dissolved in *n*-hexane at 0 °C, then filtered through a layer of Celite. After removal of the solvent, drying under dynamic vacuum, and recrystallization in CH_2Cl_2/hexane, 2.21 g of **5** (3.4 mmol, 85%) was obtained as orange crystals.

Alternative method: to a stirred solution of **5a** (1.0 g, 1.59 mmol) in acetonitrile were added dmpe (0.60 mL, 3.5 mmol) and a large excess of zinc. After 24 h at 25 °C, the organic phase was decanted and reduced to dryness under vacuum. The remaining solid was extracted with CH_2Cl_2 and the extract filtered, concentrated, and recrystallized in CH_2Cl_2/hexane, giving **5b** (0.95 mmol, 60%). ^{1}H NMR (toluene-d_8, 298 K): δ 6.60 (s, 2H, Mes), 2.50 (s, 6H, $2CH_3$-Mes), 1.97 (s, 3H, CH_3-Mes), 1.55 (br, 4H, PCH_2), 1.47 (s br, 12H, PMe), 1.43 (s br, 12H, PMe′), 1.18 (br, 4H, PCH_2′). ^{31}P{^{1}H} NMR (toluene-d_8, 298 K): δ 23.12 (s, $^1J_{pw}$ = 282 Hz). ^{13}C{^{1}H} NMR (toluene-d_8, 298 K): δ 260.4 (q, $^2J_{cp}$ = 10 Hz, CMes), 147.9 (s, *ipso*-Mes), 136.1 (s, *o*-Mes), 132.2 (s, *p*-Mes), 128.0 (s, *m*-Mes), 33.7 (q, PCH_2), 23.1 (s, $2CH_3$-Mes), 22.4 (q, PMe), 21.3 (s, CH_3-Mes), 18.2 (q, PMe′). IR (THF, cm^{-1}): $\nu_{W\equiv C}$ 928 (m). MS (FAB, CH_2Cl_2): *m*/*e* 650 (M^+), 500 (M^+ − dmpe), 390 (M^+ − dmpe − Mes). Anal. Calcd for $WC_{22}H_{43}P_4Cl$ (650.18): W, 28.27; C, 40.60; H, 6.61. Found: W, 28.20; C, 40.74; H, 6.33.

Preparation of *trans*-W(CMes)(η^1-HBH$_3$)(dmpe)$_2$ (6). Compound **5** (2.0 g, 3.08 mmol) was dissolved in THF (50 mL) and $NaBH_4$ (0.35 g, 9.23 mmol) added. The resulting mixture was warmed to 55 °C and stirred at this temperature for 12 h; then the solvent was removed in vacuo, and the precipitate redissolved in benzene. After filtration over Celite, the solvent was again removed in vacuo, and the precipitate was washed with pentane (3 × 20 mL) and recrystallized in CH_2Cl_2/pentane to afford 1.9 g of **6** (3.02 mmol, 98%) as brown microcrystals. ^{1}H NMR (THF-d_8, 298 K): δ 6.70 (s, 2H, Mes), 2.52 (s, 6H, $2CH_3$-Mes), 1.99 (s, 3H, CH_3-Mes), 1.77 (br, 4H, PCH_2), 1.67 (s br, 12H, PMe), 1.38 (s br, 12H, PMe′), 1.20 (br, 4H, PCH_2′), −2.30 (d br, HBH_3). ^{31}P{^{1}H} NMR (THF-d_8, 298 K): δ 22.4 (s, $^1J_{PW}$ = 281 Hz). ^{13}C{^{1}H} NMR (THF-d_8, 298 K): δ 266.5 (q, $^2J_{CP}$ = 9 Hz, CMes), 148.0 (s, *ipso*-Mes), 136.2 (s, *o*-Mes), 133.3 (s, *p*-Mes), 128.2 (s, *m*-Mes), 34.0 (q, PCH_2), 23.4 (m, PMe), 22.8 (s, $2CH_3$-Mes), 21.3 (s, CH_3-Mes), 20.7 (q, PMe′). IR (THF, cm^{-1}): $\nu_{W\equiv C}$ 927 (m), ν_{B-Ht} 2352 (s), ν_{B-Hb} 2035 (s), ν_{W-Hb} 1740 (m br). MS (FAB, toluene): *m*/*e* 630 (M^+), 615 (M^+ − BH_4), 310 (M^+ − BH_4 − 2dmpe). Anal. Calcd for $WC_{22}H_{47}P_4B$ (629.54): C, 41.93; H, 7.47. Found: C, 42.30; H, 7.61.

Preparation of *trans*-W(CMes)(η^1-DBD$_3$)(dmpe)$_2$ (6a). Compound **6a** was prepared in an analogous fashion to compound **6**, utilizing 0.2 g (0.31 mmol) of compound **5**, 0.03 g (0.72 mmol) of $NaBD_4$, and 50 mL of THF. Recrystallization in CH_2Cl_2/pentane afforded 0.18 g of **6a** (0.28 mmol, 90%) as brown microcrystals. This compound closely resembles **6** in its spectroscopic properties. 2D NMR (toluene-d_8, 293 K): δ-2.65 (s br, DBD_3). ^{11}B NMR (toluene-d_8, 293 K): δ −2.3 (s br, DBD_3).

Preparation of *trans*-W(CMes)(dmpe)$_2$(H) (7). Compound **6** (1.0 g, 1.59 mmol) was dissolved in THF (30 mL), and quinuclidine (0.53 g, 4.76 mmol) was added. The resulting mixture was stirred 3 h at 30 °C and then 3 h at 45 °C. The solvent was removed in vacuo, and the precipitate redissolved in *n*-hexane. After filtration over Celite, the solvent and excess quinuclidine were removed in vacuo for 4 h at 50 °C, to afford after recrystallization in CH_2Cl_2/pentane 0.96 g of the hydride **7** (1.56 mmol, 98%) as red crystals.

An alternative method could be employed, using 1.0 g (1.59 mmol) of **6** in THF (30 mL) and 2.46 mL of PMe_3 (23.85 mmol, 15 equiv), instead of quinuclidine. The resulting mixture was stirred 3 days at room temperature. The solvent and the byproduct Me_3PBH_3 were removed by sublimation under dynamic vacuum at 50 °C for 2 h. The solid was dissolved in benzene and filtered over Celite. Removal of the solvent from the filtrate and then washing the solid with pentane (3 × 20 mL) afforded after recrystallization in CH_2Cl_2/pentane 0.94 g of the hydride **7** (1.53 mmol, 96%). ^{1}H NMR (C_6D_6, 298 K): δ 6.72 (s, 2H, Mes), 2.62 (s, 6H, $2CH_3$-Mes), 2.05 (s, 3H, CH_3-Mes), 1.67 (s br, 12H, PMe), 1.52 (m br, 4H, PCH_2), 1.46 (s br, 12H, PMe′), 1.42 (m br, 4H, PCH_2′), −6.58 (q, 1H, $^2J_{HP}$ = 32.10 Hz, $^1J_{HW}$ = 31.50 Hz, WH). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ 24.4 (s, $^1J_{PW}$ = 281 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 260.4 (q, $^2J_{CP}$ = 10 Hz, CMes), 151.5 (s, *ipso*-Mes), 137.4 (s, *o*-Mes), 135.4 (s, *p*-Mes), 130.8 (s, *m*-Mes), 34.0 (q, PCH_2), 27.8 (m, PMe), 25.4 (m, PMe′), 22.6 (s, $2CH_3$-Mes), 21.5 (s, CH_3-Mes). ^{183}W {^{1}H} NMR (toluene-d_8, 298 K: δ −1612 (pseudo-q, $^1J_{WP}$ = 281 Hz). MS (FAB, toluene): *m*/*e* 615 (M^+), 310 (M^+ − 2dmpe). Anal. Calcd for $WC_{22}H_{44}P_4$ (615.73): W, 29.86; C, 42.87; H, 7.15. Found: W, 29.26; C, 42.67; H, 7.28.

Preparation of *trans*-W(CMes)(dmpe)$_2$(D) (7a). Compound **7a** was prepared in analogous fashion to compound **7**, utilizing 0.1 g (0.16 mmol) of compound **6a**, 0.05 g (0.45 mmol) of quinuclidine, and 30 mL of THF. Recrystallization in CH_2Cl_2/pentane afforded 0.07 g of **7a** (0.11 mmol, 70%) as red crystals. 2D NMR (toluene-d_8, 183 K): δ −6.60 (m br, WD).

Preparation of *trans*-W(CMes)(η^1-OC(O)H)(dmpe)$_2$ (8). A red solution of the hydride **7** (50 mg, 0.08 mmol) in THF (15 mL) was stirred under 1 bar of carbon dioxide for 30 min at −25 °C. The solution became immediately bright orange. The resulting mixture was then allowed to warm to room temperature, and the solvent and excess CO_2 were rapidly removed under high vacuum. The residue was washed three times with pentane (3 × 10 mL) to afford after recrystallization in diethyl ether 53.6 mg of the η^1-formate complex **8** (0.068 mmol, 85%) as orange crystals. ^{1}H NMR (toluene-d_8, 298 K): δ 8.25 (s, 1H, OC(O)H), 6.56 (s, 2H, Mes), 2.50 (s, 6H, $2CH_3$-Mes), 1.96 (s, 3H, CH_3-Mes), 1.60 (s br, 12H, PMe), 1.43 (m br, 4H, PCH_2), 1.30 (s br, 12H, PMe′), 1.27 (m br, 4H, PCH_2′). ^{31}P{^{1}H} NMR (toluene-d_8, 298 K): δ 31.3 (s, $^1J_{PW}$ = 286 Hz). ^{13}C{^{1}H} NMR (toluene-d_8, 298 K): δ 263.4 (q, $^2J_{CP}$ = 9 Hz, CMes), 165.9 (s, OC(O)H), 147.8 (s, *ipso*-Mes), 137.4 (s, *o*-Mes), 135.2 (s, *p*-Mes), 131.5 (s, *m*-Mes), 33.4 (m, PCH_2), 30.1 (m, PMe), 25.0 (s, $2CH_3$-Mes), 22.7 (m, PMe′), 21.1 (s, CH_3-Mes). IR (THF, cm^{-1}): $\nu_{W\equiv C}$ 921 (m); $\nu_{(OCO)}$ 1962, 1621. MS (FAB, CH_2Cl_2): *m*/*e* 660 (M^+), 615 (M^+ − CO_2H), 510 (M^+ − dmpe). Anal. Calcd for $WC_{23}H_{44}P_4O_2$ (659.73): C, 41.83; H, 6.67. Found: C, 41.83; H, 6.75.

Preparation of *trans*-W(CMes)(η^1-OPr)(dmpe)$_2$ (9). Compound **7** (30 mg, 0.0487 mmol) was dissolved in toluene (5 mL) and propionaldehyde (3.54 μL, 0.0487 mmol) added by microsyringe at room temperature. The red solution became immediately orange. After a few minutes, the solvent was removed in vacuo and the precipitate recrystallized in CH_2Cl_2/pentane at −30 °C to afford **9**. Yield: 27 mg (90%). ^{1}H NMR (toluene-d_8, 298 K): δ 6.74 (s, 2H, Mes), 3.21 (t, 2H, O−CH_2), 2.62 (s, $2CH_3$-Mes), 2.07 (s, CH_3-Mes), 1.54 (s br, 12H, PMe), 1.48 (m br, 4H, PCH_2), 1.37 (s br, 12H, PMe′), 1.33 (m br, 4H, PCH_2′). ^{31}P{^{1}H} NMR (toluene-d_8, 298 K): δ 25.3 (s, $^1J_{PW}$ = 288 Hz). ^{13}C{^{1}H} NMR (toluene-d_8, 298 K): δ 247.6 (q, $^2J_{CP}$ = 9 Hz, CMes), 149.2 (s, *ipso*-Mes), 136.0 (s, *o*-Mes), 130.4 (s, *p*-Mes), 128.0 (s, *m*-Mes), 73.2 (s br, O−CH_2), 33.5 (q, PCH_2), 23.0 (s, $2CH_3$-Mes), 22.5 (m, PMe), 21.2 (s, CH_3-Mes), 18.1 (m, PMe′). MS (EI): *m*/*e* 674 (M^+), 616 (M^+ − OPr), 523 (M^+ − dmpe). Anal. Calcd for $WC_{25}H_{50}P_4O$ (673.73): C, 44.53; H, 7.42. Found: C, 44.48; H, 7.03.

Preparation of *trans*-W(CMes)(η^1-OBn)(dmpe)$_2$ (10). Compound **7** (30 mg, 0.0487 mmol) was dissolved in toluene (5 mL) and benzaldehyde (5.0 μL, 0.0487 mmol) added by microsyringe at room temperature. An immediate color change from red to orange was observed. After a few minutes, the solvent was removed in vacuo and the precipitate recrystallized in CH_2Cl_2/pentane at −30 °C to afford **10**. Yield: 29 mg (97%). ^{1}H NMR (toluene-d_8, 298 K): δ 7.39 (d, 2H, *o*-benzal.), 7.13 (d, 1H, *p*-benzal.), 6.96 (m, 2H, *m*-benzal.), 6.60 (s, 2H, Mes), 4.23 (s, 2H, CH_2O), 2.52 (s, 6H, $2CH_3$-Mes), 1.98 (s, 3H, CH_3-Mes), 1.46 (s br, 12H, PMe), 1.42 (m br, 4H, PCH_2), 1.34 (s br, 12H, PMe′), 1.25 (m br, 4H, PCH_2′). ^{31}P{^{1}H} NMR

(toluene-d_8, 298 K): δ 25.3 (s, $^1J_{PW}$ = 288 Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K): δ 263.1 (q, $^2J_{CP}$ = 10 Hz, CMes), 150.5 (s, *ipso*-Mes), 136.4 (s, *ipso*-Bn), 133.8 (s, *p*-Bn), 129.6 (s, *o*-Mes), 128.9 (s, *o*-Bn), 128.1 (s, *m*-Bn), 127.8 (s, *p*-Mes), 126.5 (s, *m*-Mes), 74.0 (pseudo-q, W−O−C), 33.6 (q, PCH_2), 23.0 (s, $2CH_3$-Mes), 22.6 (m, PMe), 21.2 (s, CH_3-Mes), 18.4 (m, PMe′). Anal. Calcd for $WC_{29}H_{50}P_4O$ (721.73): C, 48.21; H, 6.93. Found: C, 48.02; H, 6.57.

Preparation of *trans*-W(CMes)(η^1-O*i*Pr)(dmpe)$_2$ (11). Compound **7** (30 mg, 0.0487 mmol) was dissolved in toluene (5 mL) and acetone (5.66 mg, 0.0974 mmol) added at room temperature. The solution was then allowed to warm to 60 °C. The compound **11** is spectroscopically observable by ^{31}P NMR after a few minutes, but the reaction was complete only after 2 days at 60 °C. The solvent was then removed in vacuo and the precipitate recrystallized in diethyl ether to afford **11** as orange crystals. Yield: 28 mg (93%). ^1H NMR (toluene-d_8, 298 K): δ 6.71 (s, 2H, Mes), 3.56 (sp, 1H, O-CHMe$_2$), 2.64 (s, $2CH_3$-Mes), 2.07 (s, CH_3-Mes), 1.52 (s br, 12H, PMe), 1.47 (m br, 4H, PCH_2), 1.41 (s br, 12H, PMe′), 1.34 (m br, 4H, PCH_2′). $^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K): δ 23.4 (s, $^1J_{PW}$ = 288 Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K): δ 248.5 (q, $^2J_{CP}$ = 9 Hz, CMes), 151.2 (s, *ipso*-Mes), 136.5 (s, *o*-Mes), 130.2 (s, *p*-Mes), 128.4 (s, *m*-Mes), 78.7 (s br, O−CHMe$_2$), 33.6 (q, PCH_2), 23.0 (s, $2CH_3$-Mes), 22.5 (m, PMe), 21.2 (s, CH_3-Mes), 18.9 (m, PMe′). MS (FAB, toluene): *m*/*e* 674 (M^+), 615 (M^+ − O*i*Pr), 524 (M^+ − dmpe), 465 (M^+ − dmpe − O*i*Pr).

Preparation of *trans*-W(CMes)(η^1-1-phenylethoxy)(dmpe)$_2$ (12). Compound **7** (30 mg, 0.0487 mmol) was dissolved in toluene (5 mL) and acetophenone (6.16 μL, 0.0487 mmol) added by microsyringe at room temperature. The solution was then allowed to warm to 60 °C. The compound **12** is spectroscopically observable after a few minutes, but the reaction was complete only after 2 days at 60 °C. The solvent was then removed in vacuo and the precipitate recrystallized in diethyl ether to afford **12** as orange crystals. Yield: 28 mg (93%). ^1H NMR (toluene-d_8, 298 K): δ 7.64 (d, *o*-1-phenylethoxy), 7.10 (t, *p*-1-phenylethoxy), 6.96 (m, *m*-1-phenylethoxy), 6.61 (s, 2H, Mes), 4.17 (q, 1H, OC*H*MePh, $^3J_{HH}$ = 6.3 Hz), 2.58 (s, 6H, $2CH_3$-Mes), 1.97 (s, 3H, CH_3-Mes), 1.52 (m br, 4H, PCH_2), 1.43 (s br, 12H, PMe), 1.39 (s br, 12H, PMe′), 1.29 (m br, 4H, PCH_2′), 1.02 (d, 3H, OCHC*H*$_3$Ph, $^3J_{HH}$ = 6 Hz). $^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K): δ 23.6 (m, 18 Hz wide, $^1J_{PW}$ = 292 Hz), 23.0 (m, 18 Hz wide, $^1J_{PW}$ = 292 Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K): δ 248.2 (pseudo-q, $^2J_{CP}$ = 10 Hz, CMes), 155.4 (s, *ipso*-Ph), 148.5 (s, *ipso*-Mes), 136.2 (s, *o*-Mes), 132.8 (s, *p*-Mes), 131.1 (s, *p*-Ph), 128.7 (s, *m*-Mes), 127.9 (s, *o*-Ph), 126.6 (s, *m*-Ph), 77.7 (s, W-O*C*MePh), 33.3 (q, PCH_2), 31.5 (s, W-OC*C*H$_3$Ph), 22.8 (m, PMe), 22.7 (s, $2CH_3$-Mes), 21.1 (s, CH_3-Mes), 19.0 (m, PMe′). Anal. Calcd for $WC_{30}H_{52}P_4O$ (735.88): C, 48.92; H, 7.07. Found: C, 49.15; H, 7.25.

Preparation of *trans*-W(CMes)(η^1-diphenylmethoxy)(dmpe)$_2$ (13). Compound **7** (30 mg, 0.0487 mmol) was dissolved in toluene (5 mL) and benzophenone (18 mg, 0.0974 mmol) added at room temperature. The solution was then allowed to warm to 60 °C. The compound **13** is spectroscopically observable by ^{31}P NMR after a few minutes, but the reaction was complete only after 36 h at 60 °C. The solvent was then removed in vacuo and the precipitate recrystallized in diethyl ether to afford **13** as orange crystals. Yield: 27 mg (91%). ^1H NMR (toluene-d_8, 298 K): δ 7.60 (m, 4H, *o*-diphenylmethoxy), 7.24 (m, 2H, *p*-diphenylmethoxy), 7.00 (m, 4H, *m*-diphenylmethoxy), 6.59 (s, 2H, Mes), 5.08 (s br, OC*H*Ph$_2$), 2.59 (s, 6H, $2CH_3$-Mes), 1.96 (s, 3H, CH_3-Mes), 1.49 (s br, 12H, PMe), 1.45 (m br, 4H, PCH_2), 1.35 (s br, 12H, PMe′), 1.30 (m br, 4H, PCH_2′). $^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K): δ 24.2 (s, $^1J_{PW}$ = 286 Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K): δ 250.0 (q, $^2J_{CP}$ = 10 Hz, CMes), 154.2 (s, *ipso*-Mes), 138.5 (s, *ipso*-diphenylmethoxy), 136.5 (s, *o*-Mes), 132.2 (s, *p*-diphenylmethoxy), 131.5 (s, *p*-Mes), 130.4 (s, *o*-diphenylmethoxy), 127.1 (s, *m*-Mes), 126.9 (s, *m*-diphenylmethoxy), 86.7 (pseudo-q, O*C*HPh2), 33.0 (q, PCH_2), 23.4 (m, PMe), 22.4 (s, $2CH_3$-Mes), 21.1 (s, CH_3-Mes), 18.3 (m, PMe′). MS (FAB, toluene): *m*/*e* 797 (M^+), 665 (M^+ − Mes), 647 (M^+ − dmpe), 615 (M^+ − diphenylmethoxy), 497 (M^+ − 2dmpe), 460 (M^+ − dmpe − diphenylmethoxy), 307 (M^+ − 2dmpe − diphenylmethoxy). Anal. Calcd for $WC_{35}H_{54}P_4O$ (797.95): C, 52.63; H, 6.77. Found: C, 51.89; H, 6.41%

Preparation of *trans*-W(CMes)(η^1-methoxypyridine)(dmpe)$_2$ (14). Compound **7** (30 mg, 0.0487 mmol) was dissolved in toluene (5 mL) and pyridine-2-carbaldehyde (4.63 μL, 0.0487 mmol) added by microsyringe at −40 °C. The compound **14** is spectroscopically observable by ^{31}P NMR after a few minutes at −40 °C. **14** decomposes within minutes at room temperature and could not be isolated. ^1H NMR (toluene-d_8, 233 K): aromatic hydrogens of the pyridine ring: δ 8.2 (6-CH, dd), 7.35 (5-CH, d), 6.55 (3-CH, dd), 6.40 (4-CH, ddd), 6.65 (s, 2H, Mes), 2.59 (s, 6H, $2CH_3$-Mes), 2.04 (s, 3H, CH_3-Mes), 1.47 (s br, 12H, PMe), 1.43 (m br, 4H, PCH_2), 1.39 (m br, 4H, PCH_2′), 1.35 (s br, 12H, PMe′), 1.30 (m br, 4H, PCH_2′). $^{31}P\{^1H\}$ NMR (toluene-d_8, 233 K): δ 25.5 (s, $^1J_{PW}$ = 287 Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, 233 K): δ 249.5 (pseudo-q, $^2J_{CP}$ = 9 Hz, CMes), 154.3 (s, *ipso*-Mes), 136.5 (s, *o*-Mes), 131.5 (s, *p*-Mes), 127.1 (s, *m*-Mes), 75.5 (pseudo-q, −O*C*H-), 33.0 (q, PCH_2), 23.4 (m, PMe), 22.4 (s, $2CH_3$-Mes), 21.1 (s, CH_3-Mes), 18.3 (m, PMe′).

Preparation of *trans*-W(CMes)(η^1-4-formylphenoxy)(dmpe)$_2$ (15). Compound **7** (30 mg, 0.0487 mmol) was dissolved in toluene (5 mL) and 4-hydroxybenzaldehyde (5.94 mg, 0.0487 mmol) added at room temperature. The reaction was complete within minutes and the solvent removed in vacuo. After recrystallization from toluene/pentane at −30 °C, **15** was obtained as orange crystals. Yield: 28 mg (93%). ^1H NMR (toluene-d_8, 298 K): δ 9.76 (s, 1H, aryl-C(O)H), 7.60 (s br, 2H, aryl H's), 6.62 (s, 2H, Mes), 5.98 (d, 2H, 8.7 Hz, aryl H's), 2.48 (s, 6H, $2CH_3$-Mes), 2.01 (s, 3H, CH_3-Mes), 1.48 (s br, 12H, PMe), 1.36 (m br, 8H, PCH_2), 1.24 (s br, 12H, PMe′). $^{31}P\{^1H\}$ NMR (toluene-d_8, 298 K): δ 29.4 (s, $^1J_{PW}$ = 285 Hz). $^{13}C\{^1H\}$ NMR (toluene-d_8, 298 K): δ 261.7 (pseudo-q, $^2J_{CP}$ = 10 Hz, CMes), 188.0 (s, aryl-*C*(O)H), 174.7 (s, W−O-*C*), 147.5 (s, *ipso*-Mes), 135.8 (s, *o*-Mes), 132.2 (s, *p*-Mes), 129.2 (s, *m*-Mes), 124.0 (s, *m*-4-formylphenoxy), 120.0 (s, *o*-4-formylphenoxy), 33.4 (q, PCH_2), 22.9 (s, $2CH_3$-Mes), 22.6 (m, PMe), 21.2 (s, CH_3-Mes), 18.9 (m, PMe′). Anal. Calcd for $WC_{29}H_{48}P_4O_2$ (735.85): C, 47.29; H, 6.52. Found: C, 47.56; H, 6.48.

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Supporting Information Available: Tables of positional and thermal parameters and complete lists of bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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