Reductive Cleavage of Aldehydes to Oxo−Alkylidene and Oxo−Alkylidyne Complexes in Their Reactions with $W_2(OCH_2{}^tBu)_6(py)_2$

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Aldehydes react with $W_2(OCH_2{}^tBu)_6(py)_2$ to give $W_2(\mu\text{-}CHR)(O)(OCH_2{}^tBu)_6(py)$ compounds, where R = alkyl or aryl, which, in the presence of excess pyridine, yield $W_2(\mu\text{-}CR)(\mu\text{-}O)(OCH_2{}^tBu)_5(py)_2$ compounds and neopentanol. A relative order of rates of reductive cleavage of the C═O bond is found to be aryl > alkyl, and for *p*-X-C_6H_4CHO, the rates follow the order X = CF_3 > H > F > Me > OMe. Four complexes have been structurally characterized by single-crystal X-ray crystallography: $W_2(\mu\text{-}CH^cC_3H_5)(O)(OCH_2{}^tBu)_6(py)$, **1**; $W_2(\mu\text{-}CH(tolyl))(O)(OCH_2{}^tBu)_6(py)$, **2**; $W_2(\mu\text{-}C^cC_3H_5)(\mu\text{-}O)(OCH_2{}^tBu)_5(py)_2$, **3**, and $W_2(\mu\text{-}C(p\text{-}MeOC_6H_4))(OCH_2{}^tBu)_5(py)_2$, **4**. Factors influencing the reductive cleavage of the C═O bond are discussed in light of earlier studies of related reactions, and most notably comparisons are made with the development of a molecular alternative to the McMurry reagent.

Introduction

The reductive coupling of aldehydes and ketones to olefins is a reaction that has stirred great interest in the organic chemical community and has found applications ranging from natural product[1] to polymer synthesis.[2] The general reaction is termed the McMurry reaction based on the extensive studies made by McMurry and co-workers involving reduced forms of titanium and aldehydes and ketones.[3] In general, the procedure involves two steps. (1) The first step is the formation of the reduced or active titanium. This can be achieved in a wide variety of ways typically starting from either $TiCl_4$ or $TiCl_3$ with reduction by any one of a large variety of reducing agents such as Li, Na, K, KC_8, $LiAlH_4$, Zn, Zn/Cu, Mg, or Mg/Hg. (2) The second step is the addition of the aldehyde or ketone followed by an appropriate workup. The two-step process is generally necessary since many of the reducing agents react independently with the aldehydes and ketones. The reactions are very sensitive to the conditions, and the details of the preparation of the active reduced titanium may be critical with respect to success or failure. Since the reaction is heterogeneous, there has been much speculation about the nature of the reduced titanium, and it seems clear that we are not dealing with a discrete entity since products and product distributions may be sensitive to the specific preparation (reducing agent, stoichiometry, etc.). There is considerable evidence that the olefination reaction proceeds by way of pinacolate intermediates, though in some instances a carbene pathway may be operative or may compete.[4] A number of excellent reviews on this reaction are available, including some that are very recent and ones that challenge the uniformity of the pinacolate pathway.[5]

At this point is it worth noting that the olefination reaction is not unique to reduced titanium species. Sharpless in 1972 reported that a reaction mixture formed from the reaction between WCl_6 and Li^nBu would reductively couple aldehydes and ketones to give olefins.[6] This reaction was, however, never developed further by Sharpless, and it too probably involved ill-defined reduced tungsten halide species and could well have been heterogeneous in nature. Cotton and Walton found that discrete ditungsten halide/ethoxide complexes would reductively couple aldehydes and ketones to give pinacolate compounds, but no O−C bond cleavage was observed in these $W_2^{IV,IV}$ to $W_2^{V,V}$ transformations.[7] Mayer observed the first discrete reactions involving lower valent tungsten halides and ketones to give oxo−alkylidenes, eq 1, where L = $PMePh_2$.

$$WCl_2L_4 + R_2C{=}O \rightarrow W(O)(CR_2)Cl_2L_2 + 2L \quad (1)$$

Studies of reaction 1 revealed that $PMePh_2$ dissociation was a necessary step prior to activation of the C═O bond. Most remarkably Mayer also observed the reduc-

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tive cleavage of CO_2 in its reaction with WCl_2L_4 to give $W(O)(CO)Cl_2L_2$ ($L = PMePh_2$).[8]

Work in this lab long ago showed[9] that $W_2(O^iPr)_6(py)_2$ and acetone reacted to yield $W_4(O)_2(O^iPr)_{12}(py)_x$ and $Me_2C{=}CMe_2$, and subsequently we started to investigate the two-step olefination reaction described by eq 2, where $[W_2]$ represents a $W_2(OR)_6$ compound.

$$[W_2](py)_2 + RR'C{=}O \rightarrow [W_2](\mu\text{-}CRR')(O)(py) + py \quad (2a)$$

$$[W_2](\mu\text{-}CRR')(O)(py) + R^2R^3C{=}O \rightarrow [W_2](O)_2 + RR'C{=}CR^2R^3 + py \quad (2b)$$

There is a potential advantage of this two-step process over the so-called McMurry reagents in that a selective cross coupling can be achieved. To press the advantage of this two-step process, eq 2, one must know of the limitations and efficiencies of each step. We have already noted some limitations with regard to steric factors and functional group tolerance.[10,11] In this paper we describe our studies of the first step of the reaction, eq 2a, between $W_2(OCH_2{}^tBu)_6(py)_2$ and aldehydes. Subsequently we shall describe studies of the second step. In this way we hope to determine what competitive advantages may be offered by our two-step reaction and also to elucidate the mechanistic aspects of the reaction pathway involving these discrete dinuclear complexes.

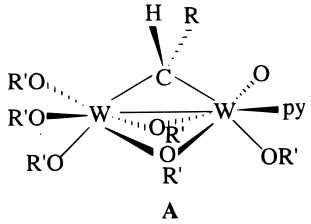
Results and Discussion

Alkylidene Formation. Alkyl and aryl aldehydes reacted in hydrocarbon solutions with $W_2(OCH_2{}^tBu)_6(py)_2$ at room temperature according to eq 3.

$$W_2(OCH_2{}^tBu)_6(py)_2 + RCH{=}O \xrightarrow[\text{hydrocarbon}]{25\ ^\circ C} W_2(\mu\text{-}CHR)(O)(OCH_2{}^tBu)_6(py) + py \quad (3)$$

In a typical benchtop reaction the preparation of the μ-alkylidene complex may well be complete within 30 min to 2 h, but the reaction mixture may be left for 12 h before cooling and concentrating the solution, from which crystals are obtained. Reactions in NMR tubes have been monitored by ^1H and ^{13}C NMR spectroscopy in toluene-d_8 and benzene-d_6. At 0 °C the NMR tube reaction 3 is sufficiently slow to be monitored with time conveniently, but at room temperature the reaction is complete within 5−10 min. The reaction may be followed readily by both ^1H and ^{13}C NMR spectroscopy as the R*CH*=O moiety is transformed to μ-*CH*R and oxo ligands. The aldehyde proton resonance is typically downfield of δ 9, whereas the μ-C*H*R resonances appear in the region δ 4.5−5.5. In the ^{13}C NMR spectrum the μ-^{13}CHR signal appears at $\delta \sim 170$ with coupling to ^{183}W, $I = 1/2$, 14.5% natural abundance. The latter signal is easily monitored for isotopically labeled aldehydes, $R^{13}CHO$. By NMR spectroscopy the conversion depicted by eq 3 is quantitative.

The NMR data for the μ-alkylidene complexes are consistent with the molecular structures determined for two representative compounds by single-crystal X-ray crystallography (vida infra) and indicate the molecule lacks any element of symmetry. Schematically, their structures can be represented by the drawing shown in **A** below. The appearance of six ^{t}Bu resonances and the diastereotopic CH_2 proton signals clearly imply a relatively rigid structure with the pyridine molecule being bound to the W_2 center.



A

Reactivity Order. We have studied the relative rates of cleavage of a series of para-substituted benzaldehydes in competition experiments. In these reactions, to a cooled solution of $W_2(OCH_2{}^tBu)_6(py)_2$ in toluene-d_8 at −78 °C was added 0.5 equiv of each of two para-substituted benzaldehydes in an NMR tube. This was then placed in a precooled probe of an NMR spectrometer at 0 °C, and the relative consumption of the two aldehydes and the respective formation of their μ-alkylidene complexes were monitored. In this way we determined the following order of reactivity for p-X-C_6H_4-CHO: X = CF_3 > H > F > Me > OMe. The faster reactivity of the p-CF_3 group was quite dramatic, as its conversion to the μ-$CHC_6H_4CF_3$ compound was essentially complete before the others had shown any reaction. We note that this order of reactivity correlates roughly with the electron-withdrawing properties of X and the Hammet σ constant: CF_3 (0.54), H (0.00), F (0.06), CH_3 (−0.17), OMe (−0.27). We also compared the rate of ^{t}BuCH_2CHO with p-$CF_3C_6H_4$CHO and found that the alkyl aldehyde reacted much more slowly. Indeed, ignoring steric factors, we can state that ArCHO > RCHO, where Ar = aryl and R = alkyl.

Steric factors are, however, important, as Bu^{t}CHO reacts only very slowly at room temperature and reaction 3 is not complete in 12 h. [Also dicyclopropyl ketone and ^{t}Bu(Me)C=O do not react, even though their olefins can be formed by a McMurry olefination.]

Functional Group Tolerance. We have previously noted that esters and amides do not enter into olefination reactions with $W_2(OR)_6(py)_2$ compounds. Furthermore, certain α,β-unsaturated aldehydes may yield products of 1,4- or 1,2-addition.[11] Here, ring closure, which may or may not be reversible, is evidently faster, and this facilitates the uptake of a second equivalent of substrate. C−C double bonds are, however, themselves inert and do not impede reactions 3, nor have we observed any olefin metathesis involving the μ-alkylidene complexes. Terminal alkynes and nitrile functionalities do compete for access to the $(W{\equiv}W)^{6+}$ center, as evidenced by our studies of the reactions involving

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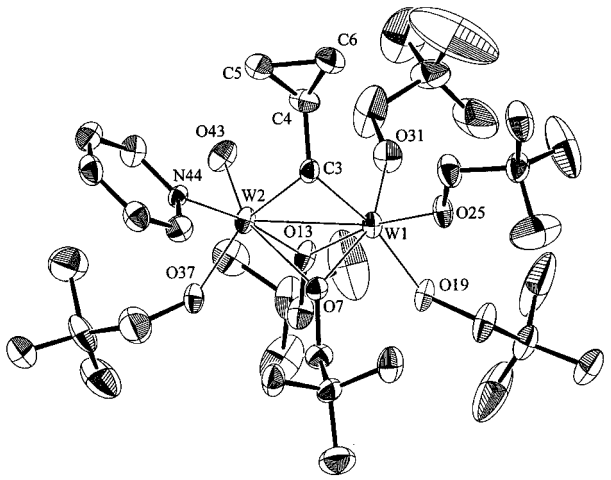

Figure 1. ORTEP drawing of $W_2(OCH_2{}^tBu)_6(\mu\text{-}CH^cC_3H_5)$-(O)(py), **1**, showing the atom-numbering scheme.

p-XC_6H_4CHO, where X = C≡CH and C≡N. For X = C≡CH, we find evidence for competitive cleavage of the C≡CH functionality, as evidenced by a ^{13}C signal at δ 348 ppm and an alkylidene at δ 165 (see Experimental Section). In the case of X = C≡N, we have obtained evidence that the CH═O bond is preferentially cleaved to give a μ-$CH(C_6H_4CN)$ complex [$\delta(\mu\text{-C}) = 165$, $\bar{\nu}$(C≡N) 2228 cm^{-1}], though a pure crystalline compound has not been obtained that has proved satisfactory for a single-crystal study. From other work we have shown that aryl nitriles undergo reductive cleavage faster than alkyl nitriles,[12] and so we propose that reaction 3 may well prove generally tolerant of nitrile functionalities but not terminal alkynes.

Solid-State Molecular Structures. $W_2(OCH_2{}^tBu)_6(\mu\text{-}CH^cC_3H_5)(O)(py)$. A view of the μ-cyclopropyl methylidene complex, **1**, is given in Figure 1. Selected bond distances and bond angles are given in Table 1. The central W_2O_7CN moiety may be viewed as a confacial bioctahedron, and the W−W distance of 2.66(1) Å is consistent with a d^1-d^1 metal−metal bonded $W_2{}^{10+}$ moiety. The W−O(oxo) distance is 1.71(1) Å, which implies some triple-bond character. With W(2) being in an octahedral geometry two of the t_{2g} type orbitals may be used in π-bonding to the oxo group and the remaining t_{2g} orbital can be used to form the W−W bond. There is therefore a mutual competition for the Wt_{2g} orbitals in the structure depicted by **A**, and that shown in Figure 1 for compound **1** reveals that the t_{2g} orbitals are satisfactorily employed in both M−M and metal−oxo bonding. The W−O terminal distances are, as expected, shorter than the W−O bridging distances for the RO ligands, and the W(1)−OR (terminal) distances are somewhat shorter than their W(2)−OR counterparts. The latter trend is understandable in that two t_{2g} orbitals on W(1) are available for π-bonding with the RO ligands and are not in competition with an oxo ligand as they are at W(2). Also of note is the asymmetry within the W−O−W bridging distances. The W−O distances to W(1) are shorter, and that to O(7), which is trans to the oxo ligand, is most pronounced: W(1)−O(7) = 2.045(5) versus W(2)−O(7) = 2.332(5) Å. The W−C distances of 2.16 and 2.17 Å are essentially identical and are least perturbed by the oxo group which is cis to the W(2)−C(3) bond, O(43)−W(2)−C(3) = 97.3°. Finally we note that the W−N(pyridine) bond of 2.18(1) Å is shorter than the W−N(py) distances in $W_2(OCH_2{}^tBu)_6(py)_2$, 2.27(1) Å (av).[13] This is consistent with it being bound more strongly to the $W_2{}^{10+}$ center.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $W_2(OCH_2{}^tBu)_6(py)(O)(\mu\text{-}CH^cC_3H_5)$ (1)

W(1)−W(2)	2.6586(6)	W(1)−O(7)	2.045(5)
W(1)−O(13)	2.111(5)	W(1)−O(19)	1.945(5)
W(1)−O(25)	1.919(5)	W(1)−O(31)	1.828(5)
W(1)−C(3)	2.171(8)	W(2)−O(7)	2.332(5)
W(2)−O(13)	2.049(5)	C(5)−C(6)	1.50(1)
W(2)−O(43)	1.713(5)	C(4)−C(5)	1.53(1)
W(2)−C(3)	2.156(8)	C(3)−C(4)	1.48(1)
W(2)−N(44)	2.177(6)	C(4)−C(6)	1.49(1)
W(2)−O(37)	1.967(5)		
W(2)−W(1)−O(7)	57.7(1)	W(2)−W(1)−O(13)	49.3(1)
W(2)−W(1)−O(19)	125.7(2)	W(2)−W(1)−O(25)	139.4(2)
W(2)−W(1)−O(31)	97.9(2)	W(2)−W(1)−C(3)	51.9(2)
W(1)−C(3)−W(2)	75.8(3)	W(1)−C(3)−C(4)	125.4(5)
W(2)−C(3)−C(4)	116.5(5)	C(3)−C(4)−C(5)	121.7(7)
C(3)−C(4)−C(6)	123.9(8)	C(5)−C(4)−C(6)	59.7(6)
C(4)−C(5)−C(6)	58.9(6)	C(4)−C(6)−C(5)	61.4(6)
O(7)−W(1)−O(13)	76.8(2)	O(7)−W(1)−O(19)	89.6(2)
O(7)−W(1)−O(25)	101.8(2)	O(7)−W(1)−O(31)	155.6(2)
O(7)−W(1)−C(3)	72.4(2)	O(13)−W(1)−O(19)	84.2(2)
O(13)−W(1)−O(25)	168.5(2)	O(13)−W(1)−O(31)	87.9(2)
O(13)−W(1)−C(3)	100.2(2)	O(19)−W(1)O(25)	84.4(2)
O(19)−W(1)−O(31)	107.9(2)	O(19)−W(1)−C(3)	159.8(3)
O(25)−W(1)−O(31)	96.9(2)	O(25)−W(1)−C(3)	90.1(3)
O(31)−W(1)−C(3)	92.1(3)	W(1)−W(2)−O(7)	47.8(1)
W(1)−W(2)−O(13)	51.3(1)	W(1)−W(2)−O(37)	121.0(2)
W(1)−W(2)−O(43)	108.4(2)	W(1)−W(2)−N(44)	130.6(2)
W(1)−W(2)−C(3)	52.4(2)	O(7)−W(2)−O(13)	71.9(2)
O(7)−W(2)−O(37)	83.0(2)	O(7)−W(2)−O(43)	156.1(2)
O(7)−W(2)−N(44)	103.4(2)	O(7)−W(2)−C(3)	67.4(2)
O(13)−W(2)−O(37)	88.4(2)	O(13)−W(2)−O(43)	95.2(2)
O(13)−W(2)−N(44)	171.7(2)	O(13)−W(2)−C(3)	102.7(2)
O(37)−W(2)−O(43)	117.4(3)	O(37)−W(2)−N(44)	84.2(2)
O(37)−W(2)−C(3)	142.6(3)	O(43)−W(2)−N(44)	91.6(3)
O(43)−W(2)−C(3)	97.3(3)	N(44)−W(2)−C(3)	81.2(3)
W(1)−O(7)−W(2)	74.5(2)	W(1)−O(13)−W(2)	79.5(2)

$W_2(\mu\text{-}CH(C_6H_4CH_3))(O)(OCH_2{}^tBu)_6(py)$, 2. The molecular structure of compound **2** that is derived from the reductive cleavage of tolualdehyde is shown in Figure 2, and selected bond distances and angles are given in Table 2. The structural refinement of **2** involved isotropic treatment of all nonmetal atoms, and therefore the quality of the structural data is not as good as for compound **1**. However, the salient features of the structure are without doubt, and an inspection of the view shown in Figure 2 reveals the similarity to that of **1** shown in Figure 1. Moreover, the metrical parameters reported in Table 2 reveal all the same trends that we described in detail for compound **1**.

In completing our description of the structures of the μ-CHR compounds it is worthy of mention that the μ-C-alkylidene atom is chiral. The two tungsten centers are different, and we observe two different values of $J^{183}{}_{W-}{}^{13}{}_C$. Also it is possible to have isomers where the oxo and the CR groups are arranged either syn or anti. In the two structures described, the cyclopropyl and tolyl groups are syn to the oxo ligand, i.e., on the same side of the molecule. Also in studies of reaction 3 by NMR spectroscopy, only in the case of *p*-NC−C_6H_4CHO have

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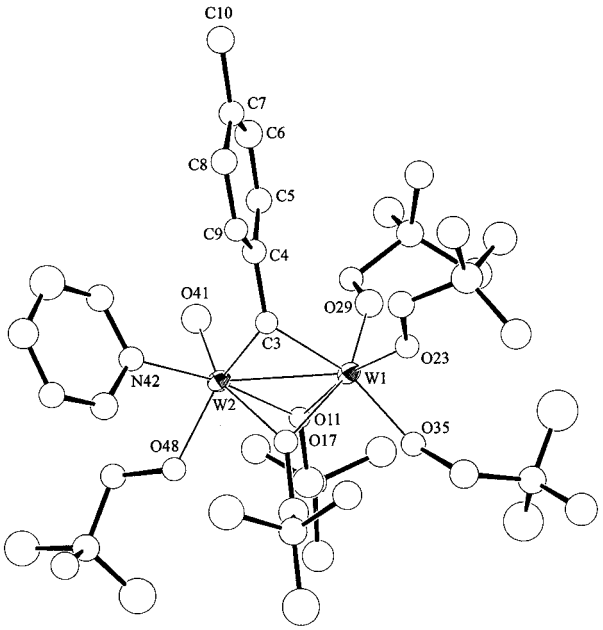


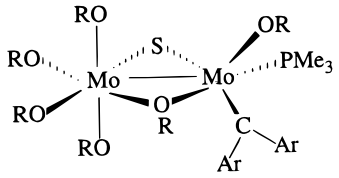
Figure 2. ORTEP drawing off $W_2(OCH_2{}^tBu)_6(\mu\text{-}CH(C_6H_4\text{-}CH_3))(O)(py)$, **2**, showing the atom-numbering scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $W_2(OCH_2{}^tBu)_6(py)(O)(\mu\text{-}CHC_6H_4CH_3)$ (2)

W(1)−W(2)	2.655(1)	W(2)−C(3)	2.15(2)
W(1)−O(17)	2.06(1)	W(2)−O(11)	2.08(1)
W(1)−O(23)	1.95(1)	C(3)−C(4)	1.47(3)
W(1)−O(29)	1.85(1)	C (4)−C(9)	1.41(3)
W(1)−C(3)	2.16(2)	C(5)−C(6)	1.38(3)
W(1)−O(11)	2.11(1)	C(6)C(7)	1.40(3)
W(2)−O(17)	2.30(1)	C(7)−C(8)	1.37(3)
W(2)−O(41)	1.73(1)	C(7)−C(10)	1.54(3)
W(2)−O(48)	1.97(1)	C(8)−C(9)	1.42(3)
W(2)−N(42)	2.19(2)		
W(2)−W(1)−O(11)	50.1(3)	W(2)−W(1)−O(17)	56.7(3)
W(2)−W(1)−O(23)	138.9(4)	W(2)−W(1)−O(29)	97.5(4)
W(2)−W(1)−O(35)	125.8(4)	W(2)−W(1)−C(3)	51.7(5)
W(1)−C(3)−W(2)	76.0(6)	W(1)−C(3)−C(4)	132.0(1)
W(2)−C(3)−C(4)	126.0(1)	C(3)−C(4)−C(5)	124.0(2)
C(3−C(4)−C(9)	121.0(2)	C(5)−C(4)−C(9)	115.0(2)
C(4)−C(5)−C(6)	122.0(2)	C(5)−C(6)−C(7)	122.0(2)
C(6)−C(6)−C(8)	118.0(2)	C(6)−C(7)−C(10)	124.0(2)
C(8)−C(7)−C(10)	118.0(2)	C(7)−C(8)−C(9)	121.0(2)
C(4)−C(9)−C(8)	123.0(2)	O(11)−W(1)−O(17)	76.7(5)
O(11)−W(1)−O(23)	168.9(5)	O(11)W(1)−O(29)	86.3(5)
O(11)−W(1)−O(35)	85.2(5)	O(11)−W(1)−C(3)	101.2(6)
O(17)−W(1)−O(23)	103.0(5)	O(17)−W(1)−O(29)	154.2(6)
O(17)−W(1)−O(35)	88.0(5)	O(17)−W(1)−C(3)	69.8(6)
O(23)−W(1)−O(29)	97.4(6)	O(23)−W(1)−O(35)	83.7(5)
O(23)−W(1)−C(3)	88.9(6)	O(29)−W(1)−O(35)	110.1(6)
O(29)−W(1)−C(3)	95.2(7)	O(35)−W(1)−C(3)	154.4(6)
W(1)−W(2)−O(11)	51.4(3)	W(1)−W(2)−O(17)	48.4(3)
W(1)−W(2)−O(41)	110.0(5)	W(1)−W(2)−O(48)	120.4(4)
W(1)−W(2)−N(42)	129.3(4)	W(1)−W(2)−C(3)	52.3(5)
O(11)−W(2)−O(17)	72.3(5)	O(11)−W(2)−O(41)	96.7(6)
O(11)−W(2)−O(48)	89.7(5)	O(11)−W(2)−N(42)	171.1(5)
O(11)−W(2)−C(3)	103.0(6)	O(17)−W(2)−O(41)	158.2(6)
O(17)−W(2)−O(48)	80.7(5)	O(17)−W(2)−N(42)	101.6(5)
O(17)−W(2)−C(3)	65.8(6)	O(41)−W(2)−O(48)	118.8(6)
O(41)−W(2)−N(42)	91.1(6)	O(41)−W(2)−C(3)	99.8(7)
O(48)−W(2)−N(42)	82.9(5)	O(48)−W(2)−C(3)	137.7(6)
N(42)−W(2)−C(3)	79.6(7)	W(1)−O(11)−W(2)	78.5(4)
W(1)−O(11)−C(12)	130.0(1)	W(2)−O(11)−C(12)	129.0(1)
W(1)−O(17)−W(2)	74.9(4)		

we ever seen evidence for the formation of more than one μ-*CH*R ligand, together with 12 ^{t}Bu signals. We are inclined to the view that we observe the thermodynamic product in most, if not all, cases by NMR spectroscopy.

Finally, it is worth noting that in the reductive cleavage of $Ar_2C{=}S$ in reactions with $Mo_2(OCH_2{}^tBu)_6$ we observed the formation of a bridging sulfido, terminal carbene structure as shown in **B**.[14] Here one Mo center



B

is in an octahedral environment and the other a trigonal bipyramid with the terminal Mo=CAr_2, a bridging Mo−S, and one terminal Mo−OR group in equatorial sites. The preference for the μ-sulfido and terminal carbene arrangement versus the μ-carbene, terminal oxo geometry with the fusing of six- and five-coordinate versus six- and six-coordinate metal centers reveals the flexible nature of bonding modes at $M_2{}^{10+}$ metal centers. In terms of metal−ligand bonding the preference for a sulfide to bridge over an oxide is rather typical in higher valent molybdenum and tungsten chemistry.

The Important Role of Pyridine. Pyridine serves many roles in reaction 3. (1) It serves as a labile ligand in solution, allowing, by its dissociation, the aldehyde access to the $W_2{}^{6+}$ center. Without py dissociation there is no reaction. (2) It serves to protect $W_2(OCH_2{}^tBu)_6$ from dimerization. However, this reaction is relatively slow so that one can study the direct reaction between $W_2(OCH_2{}^tBu)_6$ and RCHO. In these reactions in toluene-d_8 we observe facile substrate uptake at low temperatures with pinacolate formation. Here presumably the favorable cooperative binding of two aldehydes suppresses the reductive cleavage, and oxidation of the $W_2{}^{6+}$ centers occurs by an alternative route, cf. the results of Cotton and Walton noted earlier.[7] (3) Pyridine also plays an important role in stabilizing the μ-alkylidene complexes. (i) It slows down the next step in the reaction, eq 2**b**, wherein olefination occurs, and (ii) it suppresses association or dimerization reactions which might otherwise lead to loss of the discrete $[W_2]$ complex.

The μ-alkylidene complexes may be stored under an inert atmosphere at room temperature for seemingly indefinite periods without decomposition. However, in solution the complexes slowly decompose over a period of 7−9 days at room temperature. By use of the labeled μ-^{13}CHPh ligand (derived from commercially available Ph^{13}CHO) we have monitored the loss of the $W_2(\mu\text{-}^{13}CHPh)$ signal. With time this is replaced by a signal at δ 62, which shows coupling to two protons and one tungsten, indicative of the formation of a W-$^{13}CH_2Ph$ ligand by hydrogen atom abstraction.

In an attempt to "stabilize" solutions of the $W_2(\mu\text{-}CHR)$-containing complexes, we monitored the fate of toluene-d_8 solutions of $W_2(\mu\text{-}^{13}CHPh)(O)(OCH_2{}^tBu)_6(py)$ in the presence of excess (ca. 100 equiv) added pyridine. Here we noted a different decomposition mode, namely, the formation of μ-alkylidyne oxo complexes with the elimination of neopentanol. This type of reaction ap-

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pears general for this class of compounds and is represented by the stoichiometric reaction shown in eq 4

$$W_2(\mu\text{-CHR})(O)(OCH_2{}^tBu)_6(py) + py \xrightarrow[\text{toluene}]{25\ ^\circ C,\ 2-3\ \text{days}} W_2(\mu\text{-CR})(O)(OCH_2{}^tBu)_5(py)_2 + {}^tBuCH_2OH \quad (4)$$

.

The transformation of the μ-CHR to μ-CR ligand is readily followed by NMR spectroscopy, and the μ-^{13}CR carbon is found at ca. δ 340 with coupling to two equivalent tungsten-183 nuclei. This is a rare example of the conversion of an alkylidene to an alkylidyne with the loss of a W−O bond. Of course, alkylidene to alkylidyne transformations are well-known in organometallic chemistry and may be brought about by deprotonation of a μ-CHR ligand by a strong base[15] or by H atom transfer[16] to a good leaving group such as in the liberation of an alkane. The reverse reaction, protonation of an alkylidyne to give an alkylidene,[17] is also known, but in the present case we find no evidence for the reverse reaction shown in eq 4. For *p*-X-C_6H_4CH ligands we observed that eq 4 proceeds more rapidly when X = CF_3 than when X = OMe.

The exact role of pyridine in reaction 4 is not entirely understood since the addition of Et_3N, NH_3, or quinuclidine does not bring about this alkylidene to alkylidyne transformation. Moreover, the addition of alkoxide ion (1 equiv) as $KOCH_2{}^tBu$ in the presence of 18-crown-6 yields, by NMR spectroscopy, adduct formation, i.e., an anion of the type $[W_2(\mu\text{-}^{13}CHPh)(O)(OCH_2{}^tBu)_7]^-$. In the presence of 10 equiv of added $KOCH_2{}^tBu$ the compound is destroyed and the fate of the μ-^{13}CHPh ligand appears to be $Ph^{13}CH_2OH$, as deduced by ^{13}C NMR spectroscopy. This would be a rare example of C−O bond re-formation, though not entirely without precedent.[18] Although the latter finding is of some interest in itself, we have not pursued it further at this time because it is not germane to the central theme of this work, namely, the study of the reductive cleavage, reaction 3.

Alkylidyne Oxo Structures. $W_2(\mu\text{-}C^cC_3H_5)(\mu\text{-}O)(OCH_2{}^tBu)_5(py)_2$, 3. An ORTEP view of the μ-cyclopropyl methylidyne complex is given in Figure 3, and selected bond distances and bond angles are listed in Table 3. There is a central $W_2O_6CN_2$ unit wherein two six-coordinate octahedral metal centers share a common face formed by the μ-CR, the μ-oxo, and one μ-$OCH_2{}^tBu$ ligand. Of note in comparison with the structure of **1** are (i) the shortening of the W−C distances from 2.16 to 1.97 Å and (ii) the decrease in the W−W distance from 2.66 to 2.44 Å. There is no oxidation state change, and each tungsten atom is six-coordinate and in a pseudo-octahedral geometry in both structures. This reduction by 0.2 Å of the W−C and W−W distances is a result of mixing of Wd_π−Cp_π and Wd_π−Wd_π bonding, as has been noted once before by us.[19] It is also interesting to note that the two W−N(pyridine) bonds are trans to the

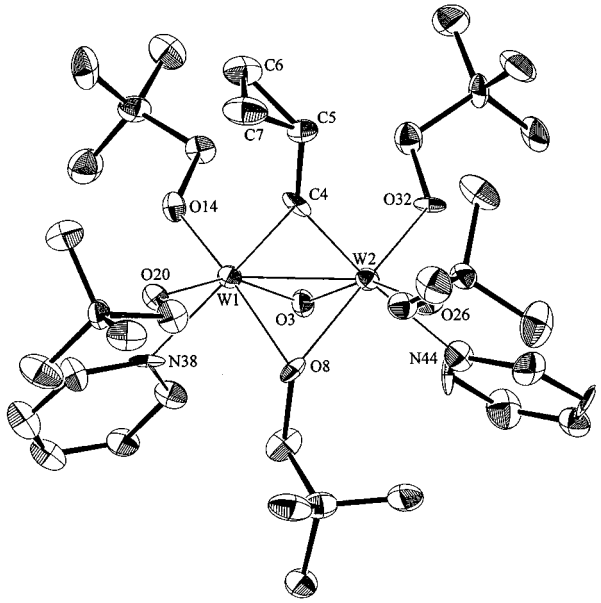

Figure 3. ORTEP drawing of $W_2(OCH_2{}^tBu)_5(\mu\text{-}C^cC_3H_5)(O)(py)_2$, **3**, showing the atom-numbering scheme.

Table 3. Selected Bond Distances (Å) and Angles for $W_2(OCH_2{}^tBu)_5(O)(py)_2(\mu\text{-}C^cC_3H_5)$ (3)

W(1)−W(2)	2.4456(7)	W(2)−O(26)	1.924(8)
W(1)−O(3)	1.969(9)	W(2)−O(32)	1.910(8)
W(1)−O(8)	2.143(8)	W(2)−N(44)	2.35(1)
W(1)−O(14)	1.894(9)	W(2)−C(4)	1.98(1)
W(1)−O(20)	1.936(8)	C(4)−C(5)	1.47(2)
W(1)−N(38)	2.39(1)	C(5)−C(6)	1.52(2)
W(1)−C(4)	1.96(1)	C(5)−C(7)	1.48(2)
W(2)−O(3)	1.961(9)	C(6)−C(7)	1.43(2)
W(2)−O(8)	2.178(9)		

W(2)−W(1)−O(3)	51.4(2)	W(2)−W(1)−O(8)	56.2(2)
W(2)−W(1)−O(14)	123.7(3)	W(2)−W(1)−O(20)	128.5(3)
W(2)−W(1)−N(38)	128.1(3)	W(2)−W(1)−C(4)	51.9(4)
W(1)−C(4)−W(2)	76.9(5)	W(1)−C(4)−C(5)	146.0(1)
W(2)−C(4)−C(5)	137.0(1)	C(4)−C(5)−C(6)	120.0(1)
C(4)−C(5)−C(7)	120.0(1)	C(6)−C(5)−C(7)	57.0(1)
C(5)−C(6)−C(7)	60.0(1)	C(5)−C(7)−C(6)	63.0(1)
O(3)−W(1)−O(8)	75.1(3)	O(3)−W(1)−O(14)	95.4(4)
O(3)−W(1)−O(20)	155.7(4)	O(3)−W(1)−N(38)	83.6(4)
O(3)−W(1)−C(4)	94.6(5)	O(8)−W(1)−O(14)	167.6(3)
O(8)−W(1)−O(20)	86.3(3)	O(8)−W(1)−N(38)	91.9(3)
O(8)−W(1)−C(4)	90.7(5)	O(14)−W(1)−O(20)	100.4(4)
O(14)−W(1)−N(38)	79.0(4)	O(14)−W(1)−C(4)	98.0(5)
O(20)−W(1)−N(38)	81.4(4)	O(20)−W(1)−C(4)	101.3(5)
N(38)−W(1)−C(4)	176.4(4)	W(1)−W(2)−O(3)	51.7(3)
W(1)−W(2)−O(8)	54.9(2)	W(1)W(2)−O(26)	127.3(3)
W(1)−W(2)−O(32)	122.8(3)	W(1)−W(2)−N(44)	132.3(3)
W(1)−W(2)−C(4)	51.2(4)	O(3) −W(2) −O(8)	74.4(3)
O(3)−W(2)−O(26)	154.9(4)	O(3)−W(2)−O(32)	98.1(4)
O(3)−W(2)−N(44)	86.0(4)	O(3)−W(2)−C(4)	94.2(5)
O(8)−W(2)−O(26)	86.1(4)	O(8)−W(2)−O(32)	172.0(4)
O(8)−W(2)−N(44)	97.6(4)	O(8)−W(2)−C(4)	89.2(4)
O(26)−W(2)−O(32)	100.2(4)	O(26)−W(2)−N(44)	81.0(4)
O(26)−W(2)−C(4)	101.3(5)	O(32)−W(2)−N(44)	78.7(4)
O(32)−W(2)−C(4)	94.3(4)	N(44)−W(2)−C(4)	172.9(5)
W(1)−O(3)−W(2)	77.0(3)	W(1)−O(8)−W(2)	68.9(3)

W−μ-alkylidyne bonds and the W−N distances are long, 2.35(1) and 2.39(1) Å, when compared to that in **1**. Presumably this arises because of the high trans-influence of the W−C multiple bond. Also because W−OR bonds are stronger than W−py bonds, the py ligands occupy the site trans to the ligand of highest trans-influence.

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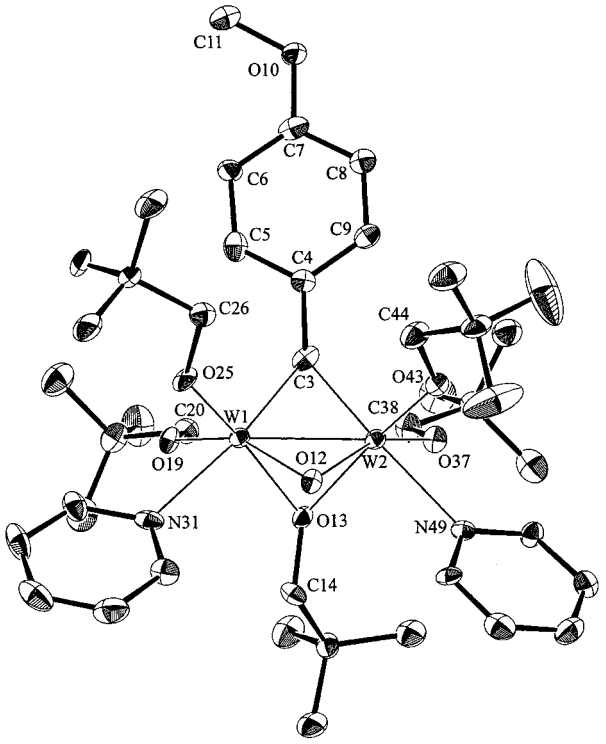

Figure 4. ORTEP drawing of $W_2(OCH_2{}^tBu)_5(\mu\text{-}CC_6H_4\text{-}OMe)(O)(py)_2$, **4**, showing the atom-numbering scheme.

The orientation of the cyclopropyl ring in **3** is turned roughly 90° from the orientation found in **1**. We suspected that there might be some significance to this in that the C_3 ring orbitals could interact with the W_2C orbitals of the bridging alkylidene moiety. However, a simple EHMO calculation revealed no significant interactions involving the cyclopropyl ring and the alkylidyne carbon. Any electronic interaction is at best very weak, and we attach little significance to this difference between the structures of **1** and **3**.

$W_2(\mu\text{-}C\text{-}C_6H_4\text{-}p\text{-}OMe)(\mu\text{-}O)(OCH_2{}^tBu)_5(py)_2$, 4. The molecular structure of the *p*-methoxybenzylidyne complex **4** is shown in Figure 4, and selected bond distances and bond angles are given in Table 4. The structure is seen to be very closely related to that of **3**, with W−W = 2.45(1) Å and W−C for the bridging benzylidyne = 1.97(1) and 1.99(1) Å. The pyridine ligands are again trans to the W−C alkylidyne bonds, and the W−N distances are long, 2.36(1) Å. The alignment of the C_6 ring does allow some interaction between the aromatic π-orbitals and the $Wd_\pi-Cp_\pi-Wd_\pi$ orbitals of the central core. This is akin to the type of interaction seen for Ar−CO_2^- ligands at M_2^{4+} centers, where M = Mo and W.[20]

Concluding Remarks

The reaction between an aldehyde and $W_2(OCH_2{}^tBu)_6$ in a hydrocarbon solvent proceeds with only a few exceptions to yield $W_2(\mu\text{-}CHR)(O)(OCH_2{}^tBu)_6(py)$ compounds. The exceptions arise from the presence of certain functional groups such as terminal ethyne moieties or the presence of an unhindered C=C bond in the β-position. The ability of the latter to give 1,4-addition products shows that the energy of activation for C=O reductive cleavage must be greater than ring closure, which is favored by the chelate effect. The relative rates of the reductive cleavage of aldehydes show that electronic factors are important. The rates of cleavage are roughly inversely proportional to the nucleophilicity of the carbonyl oxygen and correlate with the ease of reduction of the carbonyl group. In the reactions between $Mo_2(OCH_2{}^tBu)_6$ and $(p\text{-}X\text{-}C_6H_4)_2C{=}S$ it was also noted that X = CF_3 yielded a rate enhancement over X = H.[14] However, in this reaction, electron donors such as X = Me_2N and Me were also more reactive relative to X = H and F. In the present instance it seems that the lower in energy the C−O π^*-orbital, the faster the reductive cleavage. The fact that no reaction is observed between $Mo_2(OCH_2{}^tBu)_6$ and aldehydes leads us to believe that there is a greater kinetic barrier for M = Mo since the Mo−Mo π-orbitals are roughly 0.5 eV lower in energy[21] thus disfavoring the M_2 π to C=O π^* donation. That cyclopropane carboxaldehyde enters into the reductive cleavage reaction, eq 3, without opening the C_3 ring indicates that neither radical nor significant carbonium character can be imparted to the ketonic carbon during the cleavage process.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $W_2(OCH_2{}^tBu)_5(py)_2(\mu\text{-}O)(\mu\text{-}CC_5H_4OCH_3)$ (4)

W(1)−W(2)	2.4507(6)	W(2)−N(49)	2.360(6)
W(1)−O(12)	1.981(5)	W(2)−C(3)	1.990(7)
W(1)−O(13)	2.161(5)	O(10)−C(7)	1.372(9)
W(1)−O(19)	1.927(5)	C(3)−C(4)	1.45(1)
W(1)−O(25)	1.914(5)	C(4)−C(5)	1.39(1)
W(1)−N(31)	2.362(6)	C(4)C(9)	1.41(1)
W(1)−C(3)	1.971(7)	C(5)−C(6)	1.40(1)
W(2)−O(12)	1.976(5)	C(6)−C(7)	1.38(1)
W(2)−O(13)	2.156(5)	C(7)−C(8)	1.40(1)
W(2)−O(37)	1.930(5)	C(8)−C(9)	1.38(1)
W(2)−O(43)	1.898(5)		

W(2)−W(1)−O(12)	51.6(1)	W(2)−W(1)−O(25)	124.0(2)
W(2)−W(1)−O(13)	55.3(1)	W(2)−W(1)−N(31)	134.2(2)
W(2)−W(1)−O(19)	126.8(1)	W(2)−W(1)−C(3)	52.1(2)
W(1)−C(3)−W(2)	76.5(3)	W(1)−C(3)−C(4)	140.3(5)
W(2)−C(3)−C(4)	142.8(6)	C(3)−C(4)−C(5)	120.4(7)
C(3)−C(4)−C(9)	122.9(7)	C(5)−C(4)−C(9)	116.6(7)
C(4)−C(5)−C(6)	122.4(7)	C(5)−C(6)−C(7)	119.2(7)
O(10)−C(7)−C(6)	123.9(7)	O(10)−C(7)−C(8)	116.2(7)
C(6)−C(7)−C(8)	119.9(7)	C(7)−C(8)−C(9)	119.9(7)
C(4)−C(9)−C(8)	121.9(7)	C(7)−O(10)−C(11)	117.7(6)
O(12)−W(1)−O(13)	74.0(2)	O(12)−W(1)−O(19)	154.7(2)
O(12)−W(1)−O(25)	97.9(2)	O(12)−W(1)−N(31)	88.0(2)
O(12)−W(1)−C(3)	95.4(3)	O(13)−W(1)−O(19)	85.8(2)
O(13)−W(1)−O(25)	170.1(2)	O(13)−W(1)−N(31)	97.6(2)
O(13)−W(1)−C(3)	90.3(2)	O(19)−W(1)−O(25)	100.4(2)
O(19)−W(1)−N(31)	79.5(2)	O(19)−W(1)−C(3)	100.0(2)
O(25)−W(1)−N(31)	76.2(2)	O(25)−W(1)−C(3)	96.2(2)
N(31)−W(1)−C(3)	172.0(2)	W(1)−W(2)−O(12)	51.8(1)
W(1)−W(2)−O(13)	55.5(1)	W(1)−W(2)−O(37)	127.0(1)
W(1)−W(2)−O(43)	122.0(1)	W(1)W(2)−N(49)	130.8(1)
W(1)−W(2)−C(3)	51.4(2)	O(12)−W(2)−O(13)	74.2(2)
O(12)−W(2)−O(37)	156.9(2)	O(12)−W(2)−O(43)	95.0(2)
O(12)−W(2)−N(49)	85.4(2)	O(12)−W(2)−C(3)	94.9(2)
O(13)−W(2)−O(37)	87.3(2)	O(13)−W(2)−O(43)	167.8(2)
O(13)−W(2)−N(49)	94.1(2)	O(13)−W(2)−C(3)	89.9(2)
O(37)−W(2)−O(43)	101.7(2)	O(37)−W(2)−N(49)	82.2(2)
O(37)−W(2)−C(3)	98.9(2)	O(43)−W(2)−N(49)	79.2(2)
O(43)−W(2)−C(3)	96.8(3)	N(49)−W(2)−C(3)	175.9(2)
W(1)−O(12)−W(2)	76.5(2)	W(1)−O(13)−W(2)	69.2(1)
W(1)−O(13)−C(14)	119.2(4)	W(2)−O(13)−C(14)	128.4(4)
W(1)−O(19)−C(20)	126.9(4)	W(1)−O(25)−C(26)	133.8(4)
W(2)−O(37)−C(38)	126.4(4)	W(2)−O(43)−C(44)	128.7(4)

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The reaction shown in eq 4, which is promoted by excess py is sufficiently slow that in the initial reaction, eq 3, the μ-alkylidene oxo compounds are readily isolated and may be stored indefinitely. The second reaction with an aldehyde or ketone, reaction 2b, which presumably requires initial dissociation of py, is notably slower than the reductive cleavage, eq 2a, and reaction 3, which forms the basis of this stepwise selective olefination reaction. Finally we note that the combination of reactions 3 and 4, which may be represented by reaction 5, is a totally new reaction for an aldehyde.

$$W_2(OCH_2{}^tBu)_6(py)_2 + RCHO \xrightarrow[\text{hydrocarbons}]{25\ ^\circ C} W_2(\mu\text{-}CR)(\mu\text{-}O)(OCH_2{}^tBu)_5(py)_2 + {}^tBuCH_2OH \quad (5)$$

Experimental Section

All preparations were carried out in an inert atmosphere using standard Schlenk and drybox techniques. Hydrocarbon solvents, ether, and THF were dried and distilled from sodium diphenyl ketyl and stored over 4 Å molecular sieves. Dichloromethane was dried and distilled from calcium hydride and stored over 4 Å molecular sieves. Pyridine was washed with a sodium hydroxide solution, dried and distilled from calcium oxide, and stored over 4 Å molecular sieves. Benzaldehyde was washed with 1 N sodium hydroxide solution and saturated sodium sulfate solution, dried with calcium sulfate, distilled, and stored over 4 Å molecular sieves. Tolualdehyde, *p*-fluorobenzaldehyde, *p*-anisaldehyde, and α,α,α-trifluoro-*p*-tolualdehyde were dried over BaO, distilled, and stored over 4 Å molecular sieves. Cyclopropanecarboxaldehyde, 3,3-dimethylbutyraldehyde, and pivaldehyde were degassed with dry nitrogen and stored over 4 Å molecular sieves. NMR solvents (benzene-d_6, toluene-d_8, pyridine-d_5, and THF-d_8) were dried over molecular sieves and degassed with dry nitrogen. Neopentanol, magnesium sulfate, butyllithium, ethyl acetate, dimethylformamide, *p*-cyanobenzaldehyde, *p*-bromobenzaldehyde, triphenylphosphine, 18-crown-6, and carbon tetrabromide were purchased from Aldrich and used without further purification. α-^{13}C-benzaldehyde was purchased from Isotec and used without further purification. The preparations of $W_2(OCH_2{}^tBu)_6(py)_2$, $W_2(OCD_2{}^tBu)_6(py)_2$,[22] and KONp[23] have been previously described.

^{1}H NMR spectra were recorded on a Gemini-300 300 MHz spectrometer or on a UNITYplus-400 400 MHz spectrometer in dry and oxygen-free benzene-d_6 and toluene-d_8. ^{13}C NMR spectra were recorded on the Gemini-300 300 MHz spectrometer or on the UNITYplus-400 400 MHz spectrometer at 75 or 100 MHz, respectively. ^{19}F NMR spectra were recorded on the Gemini-300 300 MHz spectrometer or on the UNITYplus-400 400 MHz spectrometer at 282 or 376 MHz, respectively. All ^{1}H NMR chemical shifts are in parts per million relative to the C_6D_5H singlet of benzene-d_6 set at δ 7.15 or the methyl protio impurity in toluene-d_8 set at δ 2.09. ^{13}C NMR chemical shifts are in parts per million relative to the C_6D_6 triplet of benzene-d_6 set at δ 128.0 or the methyl septet of toluene-d_8 set at δ 20.4. ^{19}F NMR chemical shifts are in parts per million relative to the ^{19}F signal of the external reference CF_3CO_2H set at δ −78.9. IR spectra were collected on a Nicolet 510P FT-IR spectrophotometer as KBr pellets. Mass spectral analyses were performed on a Kratos MS80 RFQQ spectrometer using the FAB ionization method. Elemental analyses were performed on all the compounds reported herein. In all cases low C, H, and N data were obtained, a finding we attribute to the lability of the py ligands under a dynamic vacuum and in solution.

General Preparation of $W_2(\mu\text{-}CHR)(O)(py)(OCH_2{}^tBu)_6$ Complexes. This is typified by the preparation that follows. A solution of $W_2(OCD_2{}^tBu)_6(py)_2$ (500 mg, 0.477 mmol) in hexanes (20 mL) was treated with 1 equiv of benzaldehyde (48 μL, 0.477 mmol). The solution was allowed to stir at room temperature for 12 h. The solvent volume was reduced, and the flask was cooled to −20 °C. Red crystals of $W_2(\mu$-CHPh)$(OCD_2{}^tBu)_6(py)(O)$ were collected (324 mg, 0.301 mmol, 63.1% yield). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ = 8.53 (d, J_{HH} = 5.1 Hz, py, 2H), 7.03 (m, aryl, 3H), 6.68 (m, aryl, 3H), 6.38 (m, py, 2H), 5.47 (s, μ-C*H*Ph, 1H), 1.49 (s, $OCD_2{}^tBu$, 9H), 1.29 (s, $OCD_2{}^tBu$, 9H), 1.10 (s, $OCD_2{}^tBu$, 9H), 0.97 (s, $OCD_2{}^tBu$, 9H), 0.88 (s, $OCD_2{}^tBu$, 9H), 0.87 (s, $OCD_2{}^tBu$, 9H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 20 °C): δ = 169.95 (μ-*C*HPh, $J^{183}_{W-^{13}C}$ = 82.96 Hz, 76.93 Hz, I = 23.6%), 149.96, 133.08, 126.64, 124.37, 27.77, 27.35, 27.28, 26.94, 26.72, 26.16. IR (cm^{-1}, KBr): 2953 (s), 2903 (s), 2861 (s), 2703 (sh), 1609 (w), 1480 (m), 1449 (m), 1393 (m), 1362 (m), 1262 (w), 1219 (m), 1051 (s), 961 (m), 855 (w), 756 (m), 666 (m), 455 (w). M$^+$ *m*/*z* calcd (found): 1075.8 (1076.0).

General Preparation of $W_2(\mu\text{-}CR)(\mu\text{-}O)(py)_2(OCH_2{}^tBu)_5$ Complexes. This is exemplified by the following. A solution of $W_2(\mu$-CHPh)(O)(py)$(OCH_2{}^tBu)_6$ (482.1 mg, 0.4484 mmol) in hexanes (100 mL) was treated with pyridine (10 mL, 46.2 mmol). The solution was allowed to stir at room temperature for 48 h. The solution was stripped, the residue was redissolved in hexanes, and the flask was cooled at −20 °C in a refrigerator. $W_2(\mu$-CPh)$(OCD_2{}^tBu)_5(py)_2(O)$ was obtained as a red-orange powder (220.4 mg, 0.2066 mmol, 46.1% yield). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ = 8.82 (b, py, 4H), 7.31 (m, aryl, 2H), 7.08 (m, aryl, 2H), 6.91 (m, aryl, 3H), 6.67 (m, py, 4H), 4.55 (s, $OCH_2{}^tBu$, 8H), 4.09 (s, $OCH_2{}^tBu$, 2H), 1.06 (s, $OCH_2{}^tBu$, 36H), 0.92 (s, $OCH_2{}^tBu$, 9H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6/C_5D_5N, 20 °C): δ =341.04 (μ-*C*Ph, $J^{183}_{W-^{13}C}$ = 161.4 Hz, I = 28.7%), 192.52, 150.21, 135.48, 123.51, 34.33, 26.94, 26.50. IR (cm^{-1}, KBr): 2951 (s), 2903 (s), 2865 (s), 1606 (w), 1479 (m), 1462 (m), 1447 (m), 1392 (m), 1361 (m), 1218 (m), 1061 (s), 1022 (s), 950 (w), 851 (m), 755 (m), 697 (sh), 660 (s), 450 (w). M$^+$ *m*/*z* calcd (found): 1066.8 (1066.4).

Preparation of $W_2[(\mu\text{-}CH^cC_3H_5)](OCH_2{}^tBu)_6(py)(O)$ (1). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ = 8.90 (s, py, 2H), 6.82 (t, J_{HH} = 7.5 Hz, py, 1H), 6.48 (t, J_{HH} = 6.6 Hz, py, 2H), 5.73 (d, J_{HH} = 10 Hz, $OCH_2{}^tBu$, 1H), 5.53 (d, J_{HH} = 11.1 Hz, $OCH_2{}^tBu$, 1H), 5.20 (d, J_{HH} = 10.5 Hz, $OCH_2{}^tBu$, 1H), 5.04 (d, J_{HH} = 11.1 Hz, $OCH_2{}^tBu$, 1H), 4.58 (d, J_{HH} = 10.8 Hz, $OCH_2{}^tBu$, 1H), 4.49 (d, J_{HH} = 10.2 Hz, $OCH_2{}^tBu$, 2H), 4.44 (d, J_{HH} = 10.8 Hz, μ-C*H*-*c*-C_3H_5, 1H), 4.26 (d, J_{HH} = 11.7 Hz, $OCH_2{}^tBu$, 1H), 4.04 (d, J_{HH} = 12 Hz, $OCH_2{}^tBu$, 1H), 3.82 (d, J_{HH} = 10.2 Hz, $OCH_2{}^tBu$, 1H), 3.53 (d, J_{HH} = 10.2 Hz, $OCH_2{}^tBu$, 1H), 3.36 (d, J_{HH} = 9.9 Hz, $OCH_2{}^tBu$, 1H), 2.45 (m, -*c*-C*H*$(CH_2)_2$, 1H), 1.47 (s, $OCH_2{}^tBu$, 9H), 1.35 (s, $OCH_2{}^tBu$, 9H), 1.31 (s, $OCH_2{}^tBu$, 9H), 0.93 (s, $OCH_2{}^tBu$, 9H), 0.90 (s, $OCH_2{}^tBu$, 9H), 0.84 (s, $OCH_2{}^tBu$, 9H). The remaining proton resonances from the cyclopropyl group are obscured by the *tert*-butyl signals. ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 20 °C): δ = 174.44 (μ-CH-*c*-C_3H_5), 150.63, 137.91, 124.51, 93.26, 86.30, 81.54, 79.60, 77.92, 77.29, 36.13, 35.32, 35.21, 35.00, 34.18, 33.97, 28.44, 28.17, 28.04, 27.87, 27.67, 26.85, 15.20, 12.93. IR (cm^{-1}, KBr): 2955 (s), 2901 (s), 2866 (s), 1728 (w), 1607 (w), 1479 (m), 1449 (m), 1393 (m), 1362 (m), 1289 (w), 1261 (w), 1219 (m), 1055 (s), 1022 (s), 965 (m), 852 (s), 756 (m), 664 (s), 456 (w). M$^+$ *m*/*z* calcd (found): 1039.7 (1039.5).

Preparation of $W_2[(\mu\text{-}C^cC_3H_5)](OCH_2{}^tBu)_5(py)_2(O)$ (3). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ = 8.85 (s, py, 4H), 6.97 (t, J_{HH} = 7.5 Hz, py, 2H), 6.71 (m, py, 4H), 4.64 (m, -*c*-C*H*$(CH_2)_2$, 1H), 4.38 (s, $OCH_2{}^tBu$, 2H), 3.87 (s, $OCH_2{}^tBu$, 8H), 1.36 (m, -*c*-CH(C*H*$_2)_2$, 2H), 1.25 (m, -*c*-CH(C*H*$_2)_2$, 2H), 0.91 (s, $OCH_2{}^tBu$, 18H), 0.82 (s, $OCH_2{}^tBu$, 27H). The connectivity of the protons

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in the cyclopropyl ring was corroborated by a COSY spectrum. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 20 °C): δ = 357.85 (μ-*C*-*c*-C_3H_5), 150.25, 135.64, 123.94, 87.62, 86.64, 73.03, 35.48, 34.76, 33.09, 27.16, 26.99, 26.63, 15.79. IR (cm^{-1}, KBr): 2957 (s), 2903 (s), 2866 (s), 1726 (w), 1608 (w), 1479 (m), 1448 (m), 1393 (m), 1363 (m), 1311 (w), 1261 (w), 1220 (m), 1049 (s), 953 (s), 848 (s), 758 (m), 679 (s), 446 (w).

Reactions between $W_2(OCH_2{}^tBu)_6(py)_2$ and *p*-NCC_6H_4CHO. These reactions were performed according to the general procedure described above. The ^1H and $^{13}C\{^1H\}$ NMR spectra of an NMR-tube scale reaction were consistent with two competing reactions (^{13}C resonances at 165.2 and 162.7 ppm), but the material isolated from the bulk reaction displayed only one benzylidene resonance in the $^{13}C\{^1H\}$ NMR, a typical ^1H signal for the methine proton, and also a C≡N resonance in the IR spectrum. These data suggest that while the reaction is not clean, the compound that precipitates from solution is the carbonyl cleavage product. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ = 5.16 (s, μ-C*H*C_6H_4CN). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 20 °C): δ = 165.41 (μ-*C*HC_6H_4CN). IR (cm^{-1}, KBr): 2953 (s), 2903 (s), 2867 (s), 2228 (w), 1605 (m), 1480 (m), 1447 (m), 1393 (m), 1362 (m), 1289 (w), 1262 (w), 1219 (m), 1055 (s), 1019 (s), 965 (m), 851 (s), 756 (m), 662 (s), 457 (m). The treatment of the isolated material with an excess of pyridine resulted in a benzylidyne-type ^{13}C resonance and a C≡N resonance in the IR spectrum. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6/C_5D_5N, 20 °C): δ = 332.44 (μ-*C*C_6H_4CN). IR (cm^{-1}, KBr): 2952 (s), 2897 (s), 2862 (s), 2225 (w), 1608 (w), 1476 (m) 1390 (m), 1359 (m), 1223 (w), 1056 (s), 1021 (m), 843 (s), 750 (m), 678 (m).

Preparation of *p*-(1,1-Dibromoethenyl)bromobenzene. Triphenylphosphine (5.74 g, 21.9 mmol) was dissolved in CH_2Cl_2 (100 mL) and cooled to 0 °C. A solution of CBr_4 (3.47 g, 10.5 mmol) in CH_2Cl_2 (20 mL) was added slowly via addition funnel. The orange solution was allowed to stir at 0 °C for 2 h, at which time the temperature of the solution was decreased to −78 °C. A solution of *p*-bromobenzaldehyde (1.00 g, 5.40 mmol) in CH_2Cl_2 (20 mL) was added slowly via addition funnel. The solution was stirred for 2 h, allowed to warm slowly to room temperature, and quenched with water (5 mL). The organic layer was extracted with water (3 × 20 mL), dried over $MgSO_4$, and filtered, and the remaining solvent was removed to give a white powder residue. This residue was chromatographed on silica using a 20% ethyl acetate/hexane solution. Light yellow crystals of *p*-(1,1-dibromoethenyl)bromobenzene were collected (720 mg, 2.11 mmol, 39.1% yield). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ = 7.10 (d, J_{HH} = 8.7 Hz, 2H), 6.88 (s, 1h), 6.80 (d, J_{HH} = 8.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 20 °C): δ = 136.44, 134.57, 132.02, 130.46, 123.16, 91.07.

Preparation of *p*-Ethynylbenzaldehyde. A solution of *p*-(1,1-dibromoethenyl)bromobenzene (710 mg, 2.08 mmol) in ether (50 mL) was cooled to −78 °C. Four equivalents of butyllithium were added slowly via syringe to give a yellow solution. The bath was allowed to warm to −40 °C, at which time 2 mL of THF was added to give a bright red-orange solution. This solution was stirred for 5 min, recooled to −78 °C, and treated with 1 equiv of dimethylformamide. The solution was stirred for 30 min, then allowed to warm to room temperature and quenched carefully with water (5 mL). The ether layer was washed with water (4 × 15 mL), dried over $MgSO_4$, and filtered. The residue from the evaporation of the ether was run through a plug of silica (2:1 CH_2Cl_2/hexanes) to give *p*-ethynylbenzaldehyde (140 mg, 1.08 mmol, 51.7% yield). ^1H NMR (400 MHz, C_6D_6, 20 °C): δ = 9.46 (s, 1H), 7.23 (m, 4H), 2.74 (s, 1H). $^{13}C\{^1H\}$ NMR 100 MHz, C_6D_6, 20 °C): δ = 190.79, 133.00, 132.31, 129.76, 128.95, 81.52, 63.26. IR (cm^{-1}, KBr): 3220 (m), 2963 (s), 2930 (sh), 2859 (w), 2741 (w), 2363 (w), 2338 (w), 2100 (m), 1701 (m), 1605 (w), 1561 (w), 1304 (w), 1262 (s), 1208 (m), 1165 (sh), 1098 (s), 1020 (s), 801 (s), 737 (w), 685 (w), 529 (m).

Reactions between $W_2(OCH_2{}^tBu)_6(py)_2$ and *p*-Ethynylbenzaldehyde. These reactions were performed according to the general procedure described above. The ^1H and $^{13}C\{^1H\}$ NMR spectra of an NMR-tube scale reaction were consistent with two competing reactions (12 ^{t}Bu signals in the ^1H NMR and a ^{13}C resonance at 348.1 ppm). The material isolated from the bulk preparation displayed only one benzylidene resonance in the $^{13}C\{^1H\}$ NMR as well as a typical ^1H signal for the methine proton; however, a C≡CH resonance in the IR was notably absent. These data suggest that this reaction leads to more than one product, one possibly cleavage of the acetylenic functionality. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ = 5.27 (s, μ-C*H*C_4H_6CCH, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 20 °C): δ = 163.17 (μ-*C*HC_4H_6CCH). The treatment of the isolated material with an excess of pyridine resulted in a benzylidyne-type ^{13}C resonance. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6/C_5D_5N, 20 °C): δ = 338.65 (μ-*C*C_6H_4CCH).

$W_2(OCD_2{}^tBu)_6(py)(O)(\mu$-^{13}CHPh) + KONp (1 equiv). A Rototite NMR tube was charged with 10.3 mg (9.71×10^{-6} mol) of $W_2(OCD_2{}^tBu)_6(py)_2$, which was dissolved in 55 μL of a solution of $Ph^{13}CHO$ in C_6D_6 (0.177 M $Ph^{13}CHO$, 9.7×10^{-6} mol). More benzene-d_6 was added, the NMR tube was capped, and its $^{13}C\{^1H\}$ NMR spectrum measured to ensure the formation of $W_2(OCD_2{}^tBu)_6(py)(O)(\mu$-^{13}CHPh). To this solution was added KONp (1.5 mg, 1.2×10^{-5} mol), 18-crown-6 (5.2 mg, 2.0×10^{-5} mol), and two drops of THF-d_8 to increase the solubility of the crown ether in benzene. By $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C, 75 MHz), the disappearance of the μ-^{13}CHPh resonance from the $W_2(OCD_2{}^tBu)_6(py)(O)(\mu$-^{13}CHPh) complex (170.3 ppm) and concomitant appearance of a different μ-^{13}CHPh resonance at 157.5 ppm was observed. Both resonances containing the ^{13}C label show coupling to two inequivalent ^{183}W atoms (I = 1/2, 14% abundance) and to one proton, although the values of the coupling constants differ slightly. For the original μ-^{13}CHPh ligand, the values are $J_{^{183}W-^{13}C}$ = 82.5 Hz, 76.5 Hz and $J_{^{13}C-^1H}$ = 133.2 Hz. For the new μ-^{13}CHPh peak, the values are $J_{^{183}W-^{13}C}$ = 93.4 Hz, 71.0 Hz and $J_{^{13}C-^1H}$ = 131.7 Hz. The ^1H NMR (C_6D_6, 300 MHz, 20 °C) suggest the formation of a complex of the type $[W_2(OCD_2{}^tBu)_6(OCH_2{}^tBu)(py)(O)(\mu$-^{13}CHPh)]$^-$, as evidenced by the presence of seven equivalent ^{t}Bu signals and one $OCH_2{}^tBu$ resonance. However, the spectra have not been fully assigned, and the high solubility of the complex has prevented us from elucidating its identity by the acquisition of a crystal structure.

$W_2(OCD_2{}^tBu)_6(py)(O)(\mu$-^{13}CHPh) + KONp (10 equiv). To a Rototite NMR tube was added 9.5 mg (9.0×10^{-6} mol) of $W_2(OCD_2{}^tBu)_6(py)_2$ and 50 μL of a solution of $Ph^{13}CHO$ in C_6D_6 (0.177 M $Ph^{13}CHO$, 8.9×10^{-6} mol). More benzene-d_6 was added to the sample, and its $^{13}C\{^1H\}$ spectrum was recorded to ensure the complete formation of $W_2(OCD_2{}^tBu)_6(py)(O)(\mu$-^{13}CHPh). To this solution was added KONp (22.4 mg, 1.8×10^{-4} mol), 18-crown-6 (48.9 mg, 1.9×10^{-4} mol), and two drops of THF-d_8 to increase the solubility of the crown ether in benzene. A $^{13}C\{^1H\}$ spectrum (C_6D_6, 20 °C, 75 MHz) of this solution showed that the resonance of the ^{13}C label had changed to 70.9 ppm and that it was no longer bound to tungsten, as evidenced by the absence of ^{183}W satellites. The ^{13}C label showed coupling to two protons with a $J_{^{13}C-^1H}$ of 140 Hz. As we thought this might be an organic product, all volatile components were separated from the metal-containing byproducts by vacuum transfer. Inspection of the ^1H and $^{13}C\{^1H\}$ NMR spectra of the transferred material identified benzyl alcohol as the compound that contained the ^{13}C label.

Aldehyde Competition Experiments. In a typical experiment, 25.0 mg of $W_2(OCH_2{}^tBu)_6(py)_2$ was loaded into an NMR tube and dissolved in toluene-d_8. A few drops of $Si(CH_3)_4$ were added, and the NMR tube was fitted with a septum cap. The sample was then cooled to −78 °C in an acetone/CO_2 bath, and half an equivalent of each of two aldehydes was added by microsyringe. The tube was inverted to mix the reagents and placed in an NMR probe that had been precooled to 0 °C, and the ensuing reaction was monitored. Reaction preference was established by observing the disappearance of the RC*H*O

Table 5. Summary of Crystallographic Data[a]

	1	2	3	4
fw	1039.74	1089.80	1030.6	1096.75
cryst size, mm	0.12 × 0.14 × 0.40	0.08 × 0.12 × 0.16	0.10 × 0.20 × 0.24	0.12 × 0.16 × 0.16
cryst color	red	red/orange	orange	red
temp, °C	−170	−155	−169	−169
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	12.606(2)	12.014(2)	11.316(2)	14.834(3)
b, Å	19.923(4)	19.972(6)	9.685(2)	15.388(4)
c, Å	10.583(2)	11.496(3)	40.471(8)	12.344(3)
α, deg	104.52(1)	105.16(1)	90.0	112.48(1)
β, deg	112.21(1)	115.79(1)	94.19(1)	112.27(1)
γ, deg	95.16(1)	89.26(1)	90.0	81.77(1)
V, Å^3	2330.9(8)	2381.1(1)	4423.6(1)	2409.4(1)
Z	2	2	4	2
D_{calc}, g cm^{-3}	1.481	1.520	1.548	1.512
linear abs coeff, cm^{-1}	50.766	49.734	53.485	49.161
takeoff angle, deg	2.0	2.0	2.0	2.0
scan speed, deg/min	6.0	6.0	6.0	6.0
scan width, deg	2.0	1.8	1.2	1.8
2*θ* range, deg	6−45	6−45	6−45	6−45
no. of params refined	443	244	443	488
no. of data collected	8930	6518	7625	8299
no. of unique data	6124	6227	5748	6318
no. of unique data with $F > 3\sigma(F)$	5372	3829	4787	5595
$R(F)$	0.036	0.0571	0.0549	0.0341
$R_w(F)$	0.0372	0.0574	0.0511	0.0350
goodness of fit	1.255	1.474	1.345	1.051
max Δ/*σ*	0.44	0.0165	0.58	0.12

[a] **1**, $W_2(OCH_2{}^tBu)_6(py)(O)(\mu\text{-}CH^cC_3H_5)$; **2**, $W_2(OCH_2{}^tBu)_6(py)(O)(\mu\text{-}CHC_6H_4CH_3)$; **3**, $W_2(OCH_2{}^tBu)_5(py)_2(\mu\text{-}O)(\mu\text{-}C^cC_3H_5)$; **4**, $W_2(OCH_2{}^tBu)_5(py)_2(\mu\text{-}O)(\mu\text{-}CC_6H_4OCH_3)$.

signals of the reagents and the appearance of the μ-C*H*R signals with the intensities measured relative to the internal standard. The locations (^{1}H NMR, 400 MHz, 20 °C, toluene-d_8) of the peaks observed are denoted as "R (RC*H*O signal, μ-C*H*R signal)" and are as follows: *p*-$F_3CC_6H_4$ (9.34, 5.26); *p*-FC_6H_4 (9.39, 5.24); C_6H_4 (9.56, 5.40); *p*-$H_3CC_6H_4$ (9.61, 5.43); *p*-$H_3COC_6H_4$ (9.62, 5.00); ^{t}BuCH_2 (9.57, 5.62); ^{t}Bu (9.16, 4.82). To monitor the relative rates of alkylidene to alkylidyne conversion, two separate experiments were monitored. In each, 25.0 mg of $W_2(OCH_2{}^tBu)_6(py)_2$ was dissolved in 500 μL of C_6D_6. One equivalent of *p*-anisaldehyde was added to one sample, and 1 equiv of α,α,α-trifluoro-*p*-tolualdehyde was added to the other sample. A few drops of $Si(CH_3)_4$ were added to each sample, and the tubes were capped with a Rototite fitting. The samples were inverted several times to achieve thorough mixing. To each sample was added 100 μL of pyridine-d_5, and the reaction was monitored by NMR over several days. The extent of the reaction was measured by monitoring the disappearance of the μ-C*H*R peaks relative to the internal standards. Additionally, the alkylidene/alkylidyne ratio was simultaneously monitored by integration of the $-OCH_3$ and $-CF_3$ resonances of both species by ^{1}H and ^{19}F NMR, respectively. These signals (^{1}H NMR, 400 MHz; ^{19}F NMR, 376 MHz, 20 °C, C_6D_6) denoted as "R (alkylidene signal, alkylidyne signal)" were found at *p*-$H_3COC_6H_4$ (3.39, 3.46) in the ^{1}H NMR and *p*-$F_3CC_6H_4$ (−63.1, −63.5) in the ^{19}F NMR. Both NMR handles indicated the faster conversion of the μ-$CHC_6H_4CF_3$ ligand to its alkylidyne product relative to the analogous reaction with the μ-$CHPC_6H_4CH_3$ ligand.

Crystallographic Studies. General operating facilities and listings of programs have been given previously. [21] A summary of crystal data for the four compounds studied in this work are given in Table 5. Full details have been submitted as CIF files to the Cambridge Crystallographic Database.

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Supporting Information Available: Tables of complete bond distances, bond angles, positional coordinates, and anisotropic thermal parameters for the compounds **1**, **2**, **3**, and **4**, as well as ^{1}H NMR spectra of compounds **1**, **3**, $W_2(OCH_2{}^tBu)_6(py)(O)(\mu\text{-}CHC_6H_5)$, and $W_2(OCH_2{}^tBu)_5(py)_2(\mu\text{-}O)(\mu\text{-}CC_6H_5)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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