Preparation of Di-*tert*-butoxytungsten(VI) Alkylidene Complexes by Protonation of Tri-*tert*-butoxytungsten(VI) Alkylidene Complexes[1]

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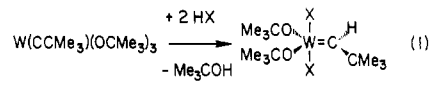
$W(CCMe_3)(OCMe_3)_3$ reacts with 2 equiv of HX (X = Cl, Br, $MeCO_2$, $PhCO_2$, OPh, OC_6F_5, O-*p*-C_6H_4Cl) to give trigonal-bipyramidal neopentylidene complexes of the type $W(CHCMe_3)(OCMe_3)_2X_2$. Octahedral complexes of the type $W(CHCMe_3)(OCMe_3)_2X_2(py)$ (X = Cl, Br, I, O_2CCF_3) in general are more stable than five-coordinate species. A six-coordinate propylidene complex, $W(CHEt)(OCMe_3)_2Cl_2(py)$, can be prepared but analogous five-coordinate species, $W(CHEt)(OCMe_3)_2X_2$ (X = phenoxide, Cl, Br), evidently are too unstable to isolate. Addition of carboxylic acids to $W(CEt)(OCMe_3)_3$ yields unstable complexes of the type $W(CHEt)(OCMe_3)_2(O_2CR')_2$ that rearrange to propylene complexes $W(propylene)(OCMe_3)_2(O_2CR')_2$ in a reaction that is second order in W. The rearrangement is relatively fast when catalyzed by added $R'CO_2H$. It is proposed that the α-carbon atom of the alkylidene ligand is protonated to give an alkyl ligand which subsequently loses a proton from the β-carbon atom to give the olefin. Addition of only 1 equiv of $R'CO_2H$ to $W(CR'')(OCMe_3)_3$ (R'' = Me, Et) yields relatively stable alkylidene complexes of the type $W(CHR'')(OCMe_3)_3(O_2CR')$.

Introduction

It is generally accepted that tungsten(VI) alkylidene complexes are the active species in systems that will catalytically metathesize olefins.[2] In spite of this fact, however, few types of tungsten(VI) alkylidene complexes have been identified, isolated, and characterized.[2,3] Consequently, the relative stability and reactivity of tungsten alkylidene complexes have not been examined systematically. This is unfortunate, since it is likely that only in this manner can one hope to learn how to control side reactions and achieve desirable goals such as the metathesis of functionalized olefins.[4] In this paper we show that some alkylidene complexes can be prepared by protonating alkylidyne complexes. Protonation has great potential as a general preparative route to a variety of alkylidene complexes, since many alkylidyne complexes, including those containing functional groups, are now available on a millimole scale or larger by the metathetical reaction between an acetylene and the W≡W bond in $W_2(OCMe_3)_6$.[5] Among other things we will show here that rearrangement of an alkylidene ligand containing a β-proton to an olefin is relatively facile and that this rearrangement is catalyzed by acids, at least in molecules where it is slow enough to follow.

Results

Isolation of Alkylidene Complexes. $W(CCMe_3)(OCMe_3)_3$ reacts with 2 equiv of gaseous HCl or HBr, carboxylic acids, or phenols to give *tert*-butyl alcohol and neopentylidene complexes of the type shown in eq 1. The



(1)

X = Cl, Br, $MeCO_2$, $PhCO_2$, OPh, OC_6F_5, O-p-C_6H_4Cl

halide complexes are analogous to complexes of the type $W(CHCMe_3)(OCH_2CMe_3)_2X_2$ reported by Osborn.[2c,d] $W(CHCMe_3)(OCMe_3)_2Cl_2$ and $W(CHCMe_3)(OCMe_3)_2Br_2$ are by far the least stable thermally of this class; they decompose over a period of 1–2 days in the solid state at 25 °C under nitrogen. The phenoxide derivatives are considerably more stable than the halide derivatives, while the carboxylate derivatives appear to be quite stable indeed. We propose that all have the basic structure shown in eq 1 since the neopentylidene ligand in $W(O)(CHCMe_3)(PEt_3)Cl_2$[2b] lies in the equatorial plane of the roughly trigonal-bipyramidal complex, the two *tert*-butoxide ligands are inequivalent in the $W(CHCMe_3)(OCMe_3)_2X_2$ species, and the carboxylate ligands are equivalent. The carboxylate ligands are almost certainly bidentate, a fact that contributes to the stability of the carboxylate complexes (cf. higher coordinate adducts of the halide complexes of the type $W(CHCMe_3)(OCMe_3)_2X_2(py)$ below). In each of these derivatives, and all the others we will be discussing later, the values for J_{CH_α} in the neopentylidene ligand are in the range of 130–140 Hz (see Table I), characteristic of an "undistorted" neopentylidene ligand in which C_α is approximately sp^2 hybridized, not one in which H_α is bridging between C_α and W and the W–C_α–C_β angle is large.[3d,f,6] Any of these reactions can be reversed by treating the neopentylidene complex with 2 equiv of lithium *tert*-butoxide (eq 2).

$$W(CHCMe_3)(OCMe_3)_2X_2 \xrightarrow[-2LiX,\ -Me_3COH]{+2LiOCMe_3} W(CCMe_3)(OCMe_3)_3 \quad (2)$$

Octahedral pyridine adducts can be prepared by adding pyridine to the five-coordinate complexes, or, alternatively,

(1) Multiple Metal–Carbon Bonds. 37. For part 36 see: Strutz, H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1600.

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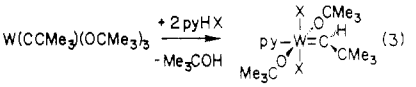
Table I. Chemical Shifts and Coupling Constants (Hz) for Alkylidene Ligands.

compound	$\delta(H_\alpha)$	$\delta(C_\alpha)$	J_{CH_α}	J_{HW}	J_{CW}
$W(CHCMe_3)(OCMe_3)_2Cl_2$	10.62	289.9	138	12.0	157
$W(CHCMe_3)(OCMe_3)_2Br_2$	10.99	297.1	133	12.2	154
$W(CHCMe_3)(OCMe_3)_2(OPh)_2$	9.24	236.6	133	5.6	183
$W(CHCMe_3)(OCMe_3)_2(OC_6H_4Cl)_2$	9.18	265.2	131	11.0	180
$W(CHCMe_3)(OCMe_3)_2(OC_6F_5)_2$	9.94	281.1	133	5.9	175
$W(CHCMe_3)(OCMe_3)_2Cl_2(py)$	10.76	302.3	130	8.4	
$W(CHCMe_3)(OCMe_3)_2Br_2(py)$	11.11	306.1	133	9.8	
$W(CHCMe_3)(OCMe_3)_2I_2(py)$	11.38	314.4	133		
$W(CHCMe_3)(OCMe_3)_2(O_2CCF_3)_2(py)$	11.46	305.1	130	8.1	171
$W(CHCH_2CH_3)(OCMe_3)_2Cl_2(py)$	11.30	304.0	141	7.8	
$W(CHC_6H_5)(OCMe_3)_2Cl_2(py)$	11.45	290.5	136		157
$W(CHCMe_3)(OCMe_3)_2(O_2CPh)_2$	11.21	294.8	135	11.0	178
$W(CHCMe_3)(OCMe_3)_2(O_2CMe)_2$	10.84	293.6	130	11.0	180
$W(CHCH_2CMe_3)(OCMe_3)_2(O_2CPh)_2$	11.82	288.8	138		178
$W(CHCH_3)(OCMe_3)_2(O_2CPh)_2$	11.56				
$W(CHCH_2CH_3)(OCMe_3)_2(O_2CPh)_2$	11.50				
$W(CHCH_3)(OCMe_3)_2(O_2CMe)_2$	11.23				
$W(CHCH_2CMe_3)_2(O_2CMe)_2$	11.15				
$W(CHCH_3)(OCMe_3)_2(O_2CPh)_2(py)$	11.64				
$W(CHCH_2CH_3)(OCMe_3)_2(O_2CPh)_2(py)$	11.53				
$W(CHCHMe_2)(OCMe_3)_2(O_2CPh)_2(py)$	11.38	298.2	139		175
$W(CHCH_2CMe_3)(OCMe_3)_2(O_2CPh)_2(py)$	11.81	288.9	136		178
$W(CHCH_3)(OCMe_3)_3(O_2CPh)$	10.07	263.4	136		186
$W(CHCH_2CH_3)(OCMe_3)_3(O_2CPh)$	9.99	271.0	135	4.9	174
$W(CHCH_3)(OCMe_3)_3(O_2CMe)$	9.95	263.6	137	4.9	186
$W(CHCH_2CH_3)(OCMe_3)_3(O_2CMe)$	9.85	272.7	136	4.3	183
$W(CHCD_3)(OCMe_3)_2(O_2CMe)(O_2CPh)$	11.39				

by protonating $W(CCMe_3)(OCMe_3)_3$ with a pyridinium salt (eq 3). They appear to be considerably more stable than



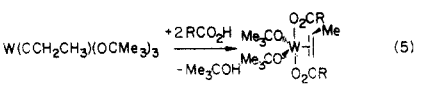
X = Cl, Br, I, CF_3CO_2

their base-free analogues. In all of them the *tert*-butoxide ligands are inequivalent. We favor the structure shown in eq 3.

Attempts to prepare alkylidene complexes that contain β-protons by protonating $W(CCH_2CH_3)(OCMe_3)_3$ with 2 equiv of a phenol or HX (X = Br, Cl) produces only intractable and as yet unidentified product mixtures. We assume that the five-coordinate propylidene complexes decompose, since by using pyridinium salts we can prepare stable six-coordinate molecules analogous to those shown in eq 3. An example is shown in eq 4. This compound shows little sign of decomposition even after heating a solution of it in C_6D_6 to 60 °C for 1 day.

$$W(CCH_2CH_3)(OCMe_3)_3 + 2pyHCl \xrightarrow{-Me_3COH} W(CHCH_2CH_3)(OCMe_3)_2Cl_2(py) \quad (4)$$

Reactions between $W(CCH_2CH_3)(OCMe_3)_3$ and two or more equivalents of a carboxylic acid proved to be much more interesting. The product contains two inequivalent *tert*-butoxide ligands, two inequivalent carboxylate ligands, and a propylene ligand on the basis of ^1H and ^{13}C NMR data. It is relatively stable in the presence of excess carboxylic acid (no change in 1 day). We favor the pseudotrigonal-bipyramidal structure shown in eq 5 in which the



R = Me, Ph

olefin does not rotate rapidly on the NMR time scale about the olefin–metal bond axis. An analogous reaction between $W(CCH_3)(OCMe_3)_3$ and 2 equiv of a carboxylic acid yields an analogous ethylene complex. A reaction between $W(CCHMe_2)(OCMe_3)_3$ and 2 equiv of a carboxylic acid yields an isobutylene complex in which the *tert*-butoxide ligands are equivalent but the carboxylate ligands are not. All of these data are consistent with molecular geometries analogous to that shown in eq 5. Interestingly, an analogous reaction between $W(CCH_2CMe_3)(OCMe_3)_3$ and 2 equiv of carboxylic acid gives a stable neohexylidene complex whose structure is believed to be analogous to that of the neopentylidene complex shown in eq 1. The neohexylidene ligand in $W(CHCH_2CMe_3)(OCMe_3)_2(O_2CR)_2$ does not rearrange to *tert*-butylethylene, an olefin that one might anticipate would be relatively weakly bound compared to the others we have mentioned. In view of this fact, and the fact that we could see alkylidene α-proton resonances in intermediates in several of the reactions above, we investigated the reactions between alkylidyne complexes and carboxylic acids in more detail.

Mechanism of Alkylidene to Olefin Rearrangement. Addition of only 1 equiv of benzoic acid to $W(CCH_3)(OR)_3$ (OR = $OCMe_3$ throughout) cleanly yields an ethylidene complex of composition $W(CHCH_3)(OR)_3(O_2CPh)$ (eq 6). It can be isolated as an oil. This

$$W(CCH_3)(OR)_3 + PhCO_2H \rightarrow W(CHCH_3)(OR)_3(O_2CPh) \quad (6)$$

mono(benzoate) species decomposes only relatively slowly in solution ($t_{1/2} \approx 1$ day) to give intractable products. We could see no evidence for formation of a stable ethylene complex. If between 1 and 2 equiv of benzoic acid are used, then a mixture of the relatively stable mono(benzoate) and the relatively unstable bis(benzoate) complex is formed (eq 7). The *tert*-butyl alcohol formed in this reaction can be

$$W(CCH_3)(OR)_3 + 1.XPhCO_2H \rightarrow (X = 0\text{–}9)\ 0.XW(CHCH_3)(OR)_2(O_2CPh)_2 + (1\text{–}0.X)W(CHCH_3)(OR)_3(O_2CPh) \quad (7)$$

removed in vacuo and the product mixture isolated as an orange oil. It is especially easy to follow the progress of decomposition of the bis(benzoate) complex in this mixture by ^1H NMR since the signals for the α-protons in the ethylidene ligands in the two complexes are separated by approximately 1 ppm (Figure 1; Table I).

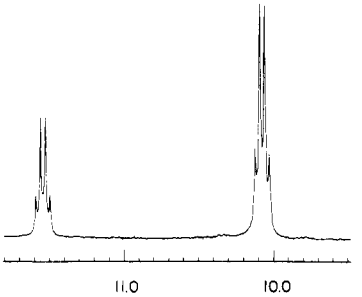
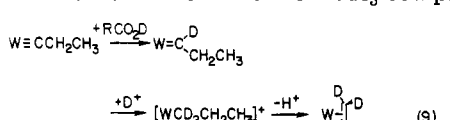


Figure 1. The ethylidene α-proton signals in $W(CHCH_3)(OCMe_3)_2(O_2CPh)_2$ (left) and $W(CHCH_3)(OCMe_3)_3(O_2CPh)$ (right).

It can be shown that rearrangement of the ethylidene ligand to an ethylene ligand in the bis(benzoate) complex is catalyzed by excess benzoic acid. If we add exactly 2 equiv of benzoic acid to $W(CCH_3)(OR)_3$ in ether and remove the solvent and *tert*-butyl alcohol in vacuo, we obtain fairly pure $W(CHCH_3)(OR)_2(O_2CPh)_2$ as an orange oil. If this product is divided into two parts and a few milligrams of benzoic acid added to one part, the rate of decomposition of the ethylidene complex to the ethylene complex is greatly accelerated ($t_{1/2} \approx 5$ min vs. 30 min). Other experiments involving reactions between $W(CCH_2CH_3)(OR)_3$ and an excess of CD_3CO_2D confirm that deuterium is incorporated into the propylene product (eq 8). The

$$W(CCH_2CH_3)(OR)_3 \xrightarrow{10CD_3CO_2D} 0.90W(CD_2CHCH_3)(OR)_2(O_2CCD_3)_2 + 0.10W(CHDCHCH_3)(OR)_2(O_2CCD_3)_2 \quad (8)$$

fact that no deuterium is observed in the C(2) position in the propylene ligand and that no deuterium is incorporated into propylene when $W(CH_2CHCH_3)(OR)_2(O_2CCH_3)_2$ is treated with excess CD_3CO_2D demonstrate that deuterium is incorporated prior to formation of the propylene ligand and that the alkylidene to olefin rearrangement is irreversible under the reaction conditions. A plausible explanation is that the initial α-deuterioethylidene complex is further deuterated at C_α to give an ethyl complex which then loses a proton from the β-carbon atom, as shown in eq 9. Formation of some $DHC{=}CHCH_3$ complex (1:1,



(9)

cis:trans) is the result of proton leakage into the acid pool. The result shown in eq 10 lends some support to the

$$W(CHCMe_3)(OR)_2(O_2CMe)_2 \xrightarrow{10MeCO_2D} W(CDCMe_3)(OR)_2(O_2CMe)_2 \quad (10)$$

proposal that the alkylidene α-carbon atom is protonated, although this result is not definitive. We cannot say at this point whether the intermediate alkyl complex is more likely to be cationic ($[W(alkyl)(OR)_2(O_2CPh)_2]^+$) or neutral ($W(alkyl)(OR)_2(O_2CPh)_3$).

In order to examine the rearrangement of $W(CHCH_3)(OR)_2(O_2CPh)_2$ in the absence of extraneous benzoic acid, we turned to mixtures of $W(CHCH_3)(OR)_2(O_2CPh)_2$ and $W(CHCH_3)(OR)_3(O_2CPh)$. We found that the amount of $W(CHCH_3)(OR)_3(O_2CPh)$ did not change significantly over the time period during which $W(CHCH_3)(OR)_2(O_2CPh)_2$ decomposed substantially to $W(CH_2CH_2)(OR)_2(O_2CPh)_2$. The rate of rearrangement of $W(CHCH_3)(OR)_2(O_2CPh)_2$ to $W(CH_2CH_2)(OR)_2(O_2CPh)_2$ was found to be second order in the concentration of $W(CHCH_3)(OR)_2(O_2CPh)_2$ at any given concentration between 0.01 and 0.11 M. In a typical kinetic run the rearrangement was followed by ^{1}NMR for approximately 2 half-lives. A typical second-order kinetic plot is shown in Figure 2. Necessarily, any intramolecular rearrangement of $W(CHCH_3)(OR)_2(O_2CPh)_2$ to $W(CH_2CH_2)(OR)_2(O_2CPh)_2$ must be relatively slow. The simplest explanation is that the rearrangement is still acid catalyzed; i.e., one molecule of $W(CHCH_3)(OR)_2(O_2CPh)_2$ is delivering a proton to the C_α of a second molecule of $W(CHCH_3)(OR)_2(O_2CPh)_2$ and probably receiving one in return from the β-carbon atom of the intermediate ethyl complex. Therefore, for now we can view $W(CHCH_3)(OR)_2(O_2CPh)_2$ as a source of benzoic acid, although according to the kinetic results $W(CHCH_3)(OR)_2(O_2CPh)_2$ cannot actually lose benzoic acid to give $W(CCH_3)(OR)_2(O_2CPh)$.

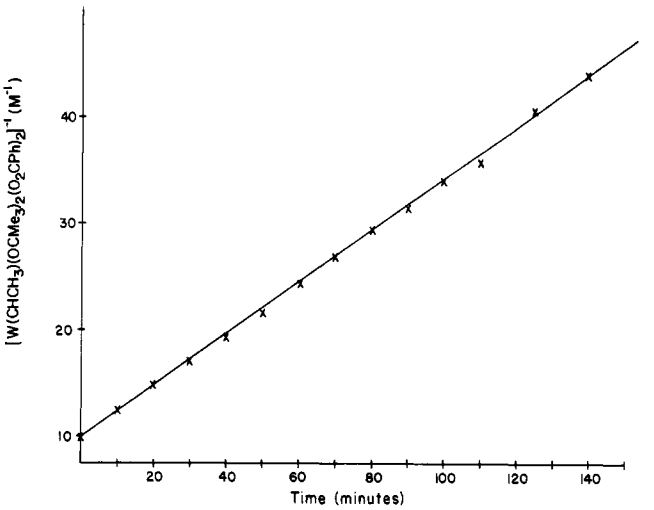


Figure 2. Second-order kinetic plot for rearrangement of $W(CHCH_3)(OCMe_3)_2(O_2CPh)_2$ to $W(CH_2CH_2)(OCMe_3)_2(O_2CPh)_2$. Starting concentrations are given in Table II, entry 1.

Table II. The Dependency of Rate of Rearrangement of the Ethylidene Ligand in $W(CHCH_3)(OCMe_3)_2(O_2CPh)_2$ upon W Concentration[a]

initial $[W(CHCH_3)(OR)_2(O_2CPh)_2]$,[b] M	$[W(CHCH_3)(OR)_3(O_2CPh)]$,[b] M	$10^3 k_{obsd}$, M^{-1} s^{-1}
0.207	0.026	4.1 (3)
0.179	0.054	2.2 (2)
0.126	0.107	0.8 (1)
0.104	0.013	4.3 (3)

[a] T = 296 K. [b] ±0.5%; OR = $OCMe_3$.

As shown by the data in Table II, the rate of rearrangement of $W(CHCH_3)(OR)_2(O_2CPh)_2$ *also* depends upon the concentration of $W(CHCH_3)(OR)_3(O_2CPh)$, rearrangement being slowed at higher concentrations of $W(CHCH_3)(OR)_3(O_2CPh)$. In this range of concentrations the dependence on the concentration of $W(CHCH_3)(OR)_3(O_2CPh)$ is not straightforward. Exactly what is happening is not clear, but we might speculate that $W(CHCH_3)(OR)_3(O_2CPh)$ either interacts with $W(CHCH_3)(OR)_2(O_2CPh)_2$ to form some intermediate dimeric complex, thereby decreasing the rate of formation of the required intermediate ethyl ligands, or that it reacts with some intermediate in the decomposition reaction to reform $W(CHCH_3)(OR)_2(O_2CPh)_2$ at a rate that is competitive with formation of $W(CH_2CH_2)(OR)_2(O_2CPh)_2$. The details of the inhibition by $W(CHCH_3)(OR)_3(O_2CPh)$ would be interesting to clarify in future studies. However, as we shall see, there are other exchange reactions that

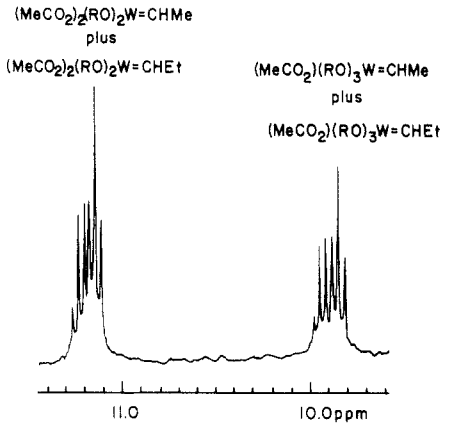


Figure 3. The alkylidene α-proton signals in the mixture of compounds generated in the reaction shown in Scheme I.

Scheme I

$W(CDEt)(OR)_2(OAc^*)_2$ (~60%)/$W(CDEt)(OR)_3(OAc^*)$ (~40%)

+

$W(CHMe)(OR)_2(OAc)_2$ (~60%)/$W(CHMe)(OR)_3(OAc)$ (~40%)

↓

$W(CHEt)(OR)_2(OAc)_2$, $W(CHMe)(OR)_2(OAc)_2$ } 1:1 $W(CHEt)(OR)_3(OAc)$, $W(CHMe)(OR)_3(OAc)$ } 1:1

$W(CDEt)(OR)_2(OAc)_2$, $W(CDMe)(OR)_2(OAc)_2$, $W(CDEt)(OR)_3(OAc)$, $W(CDMe)(OR)_3(OAc)$

OAc = O_2CMe; OAc^* = O_2CCD_3; *OAc* = either

almost certainly will complicate the issue.

In eq 11 we show a labelling experiment that confirms that mono- and bis(carboxylate) alkylidene complexes interconvert rapidly at 25 °C. After several hours both

$$W(CHCH_2CH_3)(OR)_2(O_2CPh)_2\ (10\%\ W(CHCH_2CH_3)(OR)_3(O_2CPh)) + W(CHCH_3)(OR)_3(O_2CPh)\ (5\%\ W(CCH_3)(OR)_3) \rightleftharpoons W(CHCH_3)(OR)_2(O_2CPh)_2 + W(CHCH_2CH_3)(OR)_3(O_2CPh) \quad (11)$$

$W(CH_2CH_2)(OR)_2(O_2CPh)_2$ and $W(CH_2CHCH_3)(OR)_2(O_2CPh)_2$ were observed in the ^1H NMR spectrum of the mixture.

The result of a more complex version of this type of experiment is shown in Scheme I. The mixture of all eight possible protio- or deuterio-, mono- or bis(carboxylate), and ethylidene or propylidene complexes was formed in minutes (Figure 3). The four protio alkylidene products could be identified by their characteristic alkylidene proton signals in the 10–12 ppm region. The methyl groups of the deuterio ethylidene complexes could be observed in the pattern for the methyl groups of the two protio ethylidene complexes near 5 ppm. This experiment proves that H_α and D_α in alkylidene ligands and carboxylate ligands exchange between mono- and bis(carboxylate) complexes at a much faster rate than the rate at which the alkylidene ligand in a bis(carboxylate) complex rearranges to an olefin. Rapid H_α and D_α exchange supports the conclusion drawn from the kinetic studies that one bis(carboxylate) alkylidene complex can act as a source of acid for another.

A clearer demonstration of carboxylate ligand exchange is shown in Scheme II; CD_3 ethylidene complexes were employed here in order to simplify the ^1H NMR spectra as shown in Figure 4. The signal for the ethylidene proton in $W(CHCD_3)(OR)_2(O_2CPh)(O_2CMe)$ must be the one of relative area 2 between the signal for the ethylidene α-proton in $W(CHCD_3)(OR)_2(O_2CPh)_2$ and the signal for the ethylidene α-proton in $W(CHCD_3)(OR)_2(O_2CMe)_2$.

Finally, the results in eq 12 confirm that alkylidene mono(carboxylate) complexes rapidly interconvert with

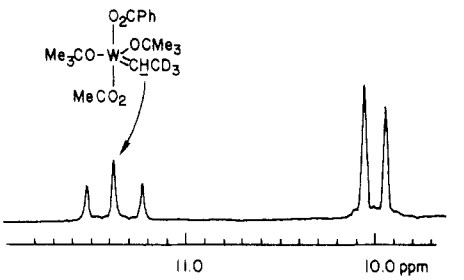


Figure 4. The ethylidene α-proton signals in the mixture of compounds generated in the reaction shown in Scheme II.

Scheme II

~2:3 $W(CHCD_3)(OR)_2(O_2CMe)_2$/$W(CHCD_3)(OR)_3(O_2CMe)$

+

~2:3 $W(CHCD_3)(OR)_2(O_2CPh)_2$/$W(CHCD_3)(OR)_3(O_2CPh)$

↓

1:2:1 { $W(CHCD_3)(OR)_2(O_2CPh)_2$, $W(CHCD_3)(OR)_2(O_2CPh)(O_2CMe)$, $W(CHCD_3)(OR)_2(O_2CMe)_2$ } + { $W(CHCD_3)(OR)_3(O_2CPh)$, $W(CHCD_3)(OR)_3(O_2CMe)$ } 1:1

alkylidyne complexes. Although we have not studied this reaction in any detail, we suspect that benzoic acid is transferred directly from one metal to another, i.e., $W(CHMe)(OR)_3(O_2CPh)$ is not in equilibrium with $W(CMe)(OR)_3$ and benzoic acid.

$$W(CHMe)(OR)_3(O_2CPh) + W(CEt)(OR)_3 \xrightleftharpoons{K_{eq} \approx 1} W(CMe)(OR)_3 + W(CHEt)(OR)_3(O_2CPh) \quad (12)$$

Since olefin complexes of the type $W(olefin)(OCMe_3)_2(O_2CR')_2$ are unusual examples of W(IV) olefin complexes, we became interested in knowing whether the olefin could be displaced readily. When $W(propylene)(OCMe_3)_2(O_2CPh)_2$ in toluene was treated with ethylene (40 psi) for 1 h at 25 °C, $W(C_2H_4)(OCMe_3)_2(O_2CPh)_2$ was formed quantitatively. Ethylene was not consumed and approximately 1 equiv of propylene was observed in a GC of the reaction mixture. We saw no evidence for formation of butenes or a propylene/ethylene codimer. Therefore we assume that propylene is simply displaced by ethylene. If a d^0 metallacyclopentane complex[7a] is an intermediate, it does not rearrange readily by a β-hydride elimination process to give olefin dimers, a process that is catalyzed by certain tantalum complexes.[7b]

In spite of the above result, we were still somewhat surprised to find that ethylene and propylene are easily displaced from complexes of the type $W(olefin)(OCMe_3)_2(O_2CR')_2$ by 2 equiv of PMe_3 at 25 °C. For example, $W(CH_2CHCH_3)(OCMe_3)_2(O_2CCH_3)_2$ was prepared as an oil and treated with ~5 equiv of PMe_3 in pentane. After 1 h the solution had turned blue. Large diamagnetic blue crystals of $W(OCMe_3)_2(O_2CMe)_2(PMe_3)_2$ could be isolated in ~50% yield. Blue-green prisms of $W(OCMe_3)_2(O_2CPh)_2(PMe_3)_2$ could be isolated in ~40% yield upon treating $W(C_2H_4)(OCMe_3)_2(O_2CPh)_2$ in ether with excess PMe_3 for 16 h. NMR spectra of these species show them to be highly symmetric, at least on the NMR time scale. An all-trans structure is a reasonable possibility.

Discussion

There is some evidence in the literature that tungsten alkylidyne complexes can be protonated to give alkylidene complexes. For example, $[W(CCMe_3)Cl_4]^-$ and W-

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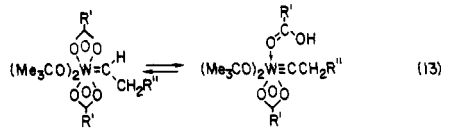
$(CCMe_3)Cl_3(dme)$ react with water or amines in the presence of base and phosphine ligands to give octahedral complexes of the type $W(X)(CHCMe_3)Cl_2L_2$ (X = O[3c] or NR[3f]; L = a phosphine).[3e] $W(CCMe_3)(CH_2CMe_3)_3$ is known to react with water to give $[W(O)(CH_2CMe_3)_3]_2(\mu\text{-}O)$ in high yield,[8] and $W(CCMe_3)(OCMe_3)_3$ reacts with water in the presence of NEt_4OH to give $[NEt_4][WO_3(CH_2CMe_3)]$.[9] Protonation of the neopentylidyne α-carbon atom in d^0 tungsten neopentylidyne complexes to give products that contain good π-bonding ligands (O or NR) is not altogether surprising in view of the fact that d^0 neopentylidene and (rare) neopentylidyne complexes of Nb and Ta are formed by what is most consistently a deprotonation of neopentyl and neopentylidene α-carbon atoms, respectively, by either an internal base (e.g., an alkyl ligand) or an external base.[10] $Mo(CCMe_3)(CH_2CMe_3)_3$[11] and $W(CCMe_3)(CH_2CMe_3)_3$[12] presumably are formed in a series of α-deprotonation reactions related to those better documented for Nb and Ta systems. It is interesting to note that complexes of the type $W(CCH_2R'')(OCMe_3)_3$ do not react with water to give $[WO_3(CH_2CH_2R'')]^-$ complexes.[9] There are several possible reasons, one of the most attractive of which is that the intermediate $W{=}CHCH_2R''$ complex rearranges to an olefin complex.

There is only one report in the literature that clearly documents alkylidene ligand rearrangement; $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CHCHMe_2)]^+$ rearranges to $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CH_2CMe_2)]^+$ in a reaction that is first order in Re with $\Delta H^{\ddagger} = 20.4$ (14) kcal mol^{-1} and $\Delta S^{\ddagger} = -2.7$ (3) eu.[12] The only report of alkylidene rearrangement in a "high oxidation state" complex came from studies of reactions between Nb and Ta neopentylidene complexes and internal olefins.[14] Complexes such as $Ta(CHCMe_3)(OCMe_3)_2Cl(PMe_3)$ will metathesize *cis*-2-pentene relatively efficiently ($\sim$50 turnovers to metathesis products), the reaction being limited by "rearrangement" of intermediate ethylidene and propylidene complexes to ethylene and propylene. Intermediate alkylidene complexes could not be observed. The rearrangements reported here are the first documented in a "high oxidation state" (d^0) alkylidene complex.

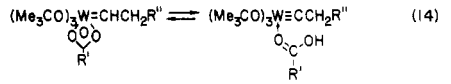
The most surprising feature of the alkylidene ligand rearrangement is that it is catalyzed by acid, either free acid or acid "sequestered" in the alkylidene complex itself. Intramolecular rearrangement, most reasonably via a vinyl hydride intermediate, is relatively slow. Note that we cannot exclude bimolecular decomposition of $W(CHCH_2R'')(OCMe_3)_2(O_2CPh)_2$ via transfer of a β-proton in an alkylidene ligand directly to the α-carbon atom of another alkylidene ligand nor by direct transfer of H_α in one complex to the α-carbon atom in another, although steric factors would appear to prevent such reactions. An interesting possibility that is less likely to be limited by steric factors is that an alkylidene complex is in equilibrium with an alkylidyne complex containing coordinated carboxylic acid (eq 13). The coordinated carboxylic acid



(13)

could then catalyze the alkylidene ligand rearrangement in a reaction that is bimolecular in tungsten. The carboxylic acid cannot be lost to the bulk solution, since then a reaction order of 3/2 would be expected. This α-deprotonation reaction (eq 13), along with transfer of carboxylate and *tert*-butoxide ligands between metals in a bimetallic intermediate could account for all the observed labeling results.

Two of the more interesting questions this study generates are why complexes of the type $W(CHCH_2R'')(OCMe_3)_3(O_2CR')$ are relatively stable vs. $W(CHCH_2R'')(OCMe_3)_2(O_2CR')_2$ complexes toward rearrangement of the alkylidene ligand to an olefin and why $W(CHCH_2CMe_3)(OCMe_3)_2(O_2CR')_2$ and $W(CHMe_2)(OCMe_3)_2(O_2CR')_2$ are more stable than $W(CHCH_2Me)(OCMe_3)_2(O_2CR')_2$ and $W(CHCH_3)(OCMe_3)_2(O_2CR')_2$ in the absence of excess acid. Although we can only speculate, it is worth considering the possibility that the hypothetical equilibrium shown in eq 14 lies further to the left than that



(14)

shown in eq 13. A practically opposite point of view is that the higher overall electron count in $W(CHR'')(OCMe_3)_2(O_2CR')_2$ complexes (16e vs. 14e in $W(CHR'')(OCMe_3)_3(O_2CR')$ complexes) makes the alkylidene α-carbon atom more nucleophilic and formation of the olefin complex by an acid-catalyzed route therefore easier. The answer to the second question is almost certainly related to the increased steric crowding about the alkylidene α- and β-carbon atoms; in more crowded circumstances both the intermolecular delivery of a proton to the alkylidene ligand's α-carbon atom and removal of a proton from the β-carbon atom in the incipient alkyl complex should be slowed down.

The most interesting question is the most difficult to answer. Is the acid-catalyzed or bimolecular arrangement of an alkylidene ligand in high oxidation state systems a general phenomenon, or will an intramolecular rearrangement, perhaps via a vinyl hydride intermediate, also operate in some circumstances? We will be looking for other clear-cut examples of rearrangement in high oxidation state alkylidene complexes to provide the answer.

Experimental Section

General procedures can be found elsewhere.[12] $W(CCMe_3)(OCMe_3)_3$ was prepared according to the reported method.[12] Other $W(CR)(OCMe_3)_3$ complexes were prepared by the reaction between $W_2(OCMe_3)_6$ and the appropriate nitrile[4b] as described below. Chemical shifts (^1H and ^{13}C NMR) are relative to Me_4Si, and coupling constants are in hertz. Routine coupling constants, multiplicities, and intensities usually are not noted individually. Chemical shifts and coupling constants (when available) for alkylidene complexes are collected in Table I. The NMR solvent was C_6D_6 unless otherwise noted.

Preparations. $W(CCHMe_2)(OCMe_3)_3$. $W_2(OCMe_3)_6$ (4.00 g, 4.96 mmol) was dissolved in pentane (50 mL), and 1 equiv of Me_2CHCN (451 μL, 4.96 mmol) was added. The solution turned from dark red to amber over the period of several minutes. During this time $[W(N)(OCMe_3)_3]_x$ precipitated from solution. The solution was filtered, and the solvent was removed in vacuo. The crude product was purified by sublimation at 40 °C (0.01 μm) to give large colorless prisms (2.01 g, 89%): ^1H NMR δ 4.03 (hept, J = 5.8 Hz, $CCHMe_2$), 1.44 ($OCMe_3$), 1.23 (d, J = 5.8 Hz, $CCHMe_2$); ^{13}C NMR δ 268.3 ($CCHMe_2$), 79.2 ($OCMe_3$), 46.1

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($CCHMe_2$), 32.7 ($OCMe_3$), 26.5 ($CCHMe_2$). Anal. Calcd for $WC_{16}H_{34}O_3$: C, 41.93; H, 7.48. Found: C, 41.80; H, 7.36.

$W(CCH_2CMe_3)(OCMe_3)_3$. $W_2(OCMe_3)_6$ (4.00 g, 4.96 mmol) was dissolved in pentane (50 mL), and 1 equiv of Me_3CCH_2CN (0.48 g, 4.9 mmol) was added. Over the period of 3 h the solution turned from dark red to amber and $[W(N)(OCMe_3)_3]_x$ precipitated. The solvent was removed in vacuo and the residue sublimed (60 °C, 0.01 μm) to give a colorless crystalline solid (1.65 g, 68%): ^1H NMR δ 4.16 (J_{HW} = 7.3 Hz, CCH_2CMe_3), 1.46 ($OCMe_3$), 1.13 (CCH_2CMe_3); ^{13}C NMR δ 274.5 (CCH_2CMe_3), 76.5 ($OCMe_3$), 56.4 (J_{CW} = 45 Hz, CCH_2CMe_3), 27.5 (CCH_2CMe_3), 25.0 ($OCMe_3$), 22.2 (CCH_2CMe_3). Anal. Calcd for $WC_{18}H_{38}O_3$: C, 44.45; H, 7.88. Found: C, 44.23; H, 7.60.

$W(CHCMe_3)(OCMe_3)_2X_2$. X = Cl. Two equivalents of HCl gas (0.42 mmol, 9.5 mL) were added via syringe to a solution of $W(CCMe_3)(OCMe_3)_3$ (0.10 g, 0.21 mmol) in toluene (10 mL) at −78 °C. The solution turned orange-red immediately. Upon warming to room temperature the solution became yellow. The solvent was removed in vacuo leaving yellow crystals of product that was essentially pure by NMR. The compound decomposes over several days at room temperature in the solid state: ^1H NMR δ 10.62 ($CHCMe_3$), 1.44 (CMe_3), 1.40 (CMe_3), 1.13 (CMe_3); ^{13}C NMR δ 289.9 ($CHCMe_3$), 92.0 ($OCMe_3$), 90.4 ($OCMe_3$), 42.5 ($CHCMe_3$), 32.7 (CMe_3), 29.8 (CMe_3), 29.7 (CMe_3).

X = Br. The same procedure as above was followed: ^1H NMR δ 10.99 ($CHCMe_3$), 1.47 (CMe_3), 1.44 (CMe_3), 1.40 (CMe_3); ^{13}C NMR δ 297.1 ($CHCMe_3$), 93.0 ($OCMe_3$), 91.5 ($OCMe_3$), 43.2 ($CHCMe_3$), 32.0 (CMe_3), 29.7 (CMe_3), 29.5 (CMe_3).

$W(CHCMe_3)(OCMe_3)_2(OR')_2$ (OR' = OC_6H_5, p-OC_6H_4Cl, OC_6F_5). OR' = OC_6H_5. $W(CCMe_3)(OCMe_3)_3$ (0.75 g, 1.6 mmol) was added to a solution of phenol (0.30 g, 3.2 mmol) in dichloromethane (10 mL). After 5 min the solvent was removed in vacuo leaving an orange crystalline powder. Recrystallization from pentane at −30 °C gave large orange crystals (two crops, 0.68 g, 73%): ^1H NMR δ 9.24 (J_{HW} = 5.6 Hz, $CHCMe_3$), 7.33, 7.17, 6.91 (H_m, H_o, H_p, respectively), 1.31 (s, 18, $OCMe_3$), 1.09 ($CHCMe_3$); ^{13}C NMR δ 263.6 (J_{CW} = 183 Hz, $CHCMe_3$), 166.6, 129.2, 119.4, 119.3 (C_{ipso}, C_m, C_o, C_p, respectively), 87.0 ($OCMe_3$), 41.4 ($CHCMe_3$), 35.2 ($CHCMe_3$), 30.7 ($OCMe_3$). Anal. Calcd for $WC_{25}H_{38}O_4$: C, 51.20; H, 6.53. Folund: C, 50.75; H, 6.66.

OR' = p-OC_6H_4Cl. The procedure was essentially the same as above starting with $W(CCMe_3)(OCMe_3)_3$ (0.50 g, 1.1 mmol) and p-chlorophenol (0.27 g, 2.1 mmol) in dichloromethane (10 mL). Recrystallization from pentane at −30 °C gave yellow prisms (0.53 g, 77%): ^1H NMR δ 9.18 (J_{HW} = 11.0 Hz, $CHCMe_3$), 7.25, 6.86 (H_o and H_m), 1.21 (br s, 18, $OCMe_3$), 0.97 ($CHCMe_3$); ^{13}C NMR δ 265.2 (J_{CW} = 180 Hz, $CHCMe_3$), 165.0, 129.1. 123.9, 120.4 (C_{ipso}, C_m, C_p, C_o, respectively), 87.5 ($OCMe_3$), 41.6 ($CHCMe_3$), 34.9 ($CHCMe_3$), 30.6 ($OCMe_3$).

OR' = OC_6F_5. The procedure was essentially the same as in the first starting with $W(CCMe_3)(OCMe_3)_3$ (0.50 g, 1.1 mmol) and pentafluorophenol (0.39 g, 2.1 mmol) in dichloromethane (10 mL). The crude product crystallized from pentane at −30 °C as a yellow solid (0.53 g, 65%): ^1H NMR δ 9.94 ($CHCMe_3$), 1.36 (br s, 9, $OCMe_3$), 1.24 (br s, 9, $OCMe_3$), 0.81 ($CHCMe_3$); ^{13}C NMR δ 281.1 ($CHCMe_3$), 141.5, 138.5, 134.2 ($J_{CF} \approx$ 235–245 Hz, OC_6F_5), 42.5 ($CHCMe_3$), 33.4 ($CHCMe_3$), 30.4 ($OCMe_3$); C_{ipso} and $OCMe_3$ signals were not found. This compound decomposes readily in solution to unidentified products.

$W(CHCMe_3)(OCMe_3)_2X_2(py)$ (X = Cl, Br, I, O_2CCF_3). The general procedure was to add $W(CCMe_3)(OCMe_3)_3$ to 2 equiv of pyH^+X^- in dichloromethane (25 mL/g of W). After 10 min the solvent was removed in vacuo and the residue was recrystallized from pentane.

X = Cl. A 1.00-g sample of $W(CCMe_3)(OCMe_3)_3$ (2.12 mmol) and 0.49 g of pyHCl (4.2 mmol) yield 0.92 g of orange crystals (79%): ^1H NMR δ 10.76 ($CHCMe_3$), 9.44, 6.96, 6.74 (H_o, H_p, H_m, respectively), 1.41 (CMe_3), 1.26 (CMe_3), 1.21 (CMe_3); ^{13}C NMR δ 302.3 ($CHCMe_3$), 149.9, 137.2, 123.9 (C_o, C_p, C_m, respectively), 89.8 ($OCMe_3$), 88.9 ($OCMe_3$), 43.1 ($CHCMe_3$), 34.0 (CMe_3), 30.1 (CMe_3), 29.0 (CMe_3).

X = Br. A 0.30-g sample of $W(CCMe_3)(OCMe_3)_3$ (0.64 mmol) and 0.20 g of pyHBr (1.3 mmol) yield 0.31 g of orange powder (76%): ^1H NMR δ 11.11 ($CHCMe_3$), 9.54, 6.96, 6.68 (H_o, H_p, H_m, respectively), 1.39 (CMe_3), 1.28 (CMe_3), 1.24 (CMe_3); ^{13}C NMR δ 306.1 ($CHCMe_3$), 150.7, 136.6, 123.8 (C_o, C_p, C_m, respectively), 91.4 ($OCMe_3$), 90.3 ($OCMe_3$), 43.9 ($CHCMe_3$), 32.9 (CMe_3), 29.9 (CMe_3), 29.1 (CMe_3). Anal. Calcd for $WC_{18}H_{33}NO_2Br_2$: C, 33.82; H, 5.20. Found: C, 33.85; H, 5.19.

X = I. A 0.30-g sample of $W(CCMe_3)(OCMe_3)_3$ (0.64 mmol) and 0.26 g of pyHI (1.3 mmol) yield 0.30 g of red powder (64%): ^1H NMR δ 11.38 ($CHCMe_3$), 9.49, 6.93, 6.64 (H_o, H_p, H_m, respectively), 1.38 (CMe_3), 1.33 (CMe_3), 1.29 ($OCMe_3$); ^{13}C NMR δ 314.4 ($CHCMe_3$), 151.9, 136.7, 123.9 (C_o, C_p, C_m, respectively), 92.4 ($OCMe_3$), 91.1 ($OCMe_3$), 45.0 ($CHCMe_3$), 32.1 (CMe_3), 29.7 (CMe_3), 28.8 (CMe_3).

X = O_2CCF_3. A 0.50-g sample of $W(CCMe_3)(OCMe_3)_3$ (1.1 mmol) and 0.41 g of $pyHO_2CCF_3$ (2.1 mmol) yield 0.55 g of yellow crystals (73%): ^1H NMR δ 11.46 (J_{HW} = 8.1 Hz, $CHCMe_3$), 8.96, 6.82, 6.55 (H_o, H_p, H_m, respectively), 1.43 (CMe_3), 0.98 (CMe_3), 0.93 (CMe_3); ^{13}C NMR δ 305.1 ($CHCMe_3$), 159.2 (J_{CF} = 38 Hz, O_2CCF_3), 148.1, 138.3, 124.7 (C_o, C_p, C_m, respectively), 117.1 (J_{CF} = 285 Hz, O_2CCF_3), 88.9 ($OCMe_3$), 44.0 ($CHCMe_3$), 35.0 (CMe_3), 30.1 (CMe_3), 28.5 (CMe_3). Anal. Calcd for $WC_{22}H_{33}F_6NO_6$: C, 37.46; H, 4.72. Found: C, 37.06; H, 4.64.

$W(CHCH_2CH_3)(OCMe_3)_2Cl_2(py)$. $W(CCH_2CH_3)(OCMe_3)_3$ (0.30 g, 0.68 mmol) was added to a solution of pyHCl (0.16 g, 1.4 mmol) in dichloromethane (10 mL). The color of the solution changed to orange immediately. The solvent was removed in vacuo and the residue recrystallized from toluene/pentane (1:1) to give the large orange crystals of product (0.27 g, 77%): ^1H NMR δ 11.30 (t, 1, J = 7.8 Hz, $CHCH_2CH_3$), 9.75, 6.89, 6.64 (H_o, H_p, H_m, respectively), 5.56 (quin, 2, J = 7.8 Hz, $CHCH_2CH_3$), 1.19 (br s, 18, $OCMe_3$), 1.13 (t, 3, J = 7.5 Hz, $CHCH_2CH_3$); ^{13}C NMR δ 304.0 ($CHCH_2CH_3$), 150.2, 137.5, 123.8 (C_o, C_p, C_m, respectively), 87.9 ($OCMe_3$), 38.4 ($CHCH_2CH_3$), 29.9 ($OCMe_3$), 29.2 ($OCMe_3$), 18.8 ($CHCH_2CH_3$). Anal. Calcd for $WC_{16}H_{29}Cl_2NO_2$: C, 36.80; H, 5.60. Found: C, 36.59; H, 5.63.

$W(CHC_6H_5)(OCMe_3)_2Cl_2(py)$. $W(CC_6H_5)(OCMe_3)_3$ (1.00 g, 2.03 mmol) was added to a solution of pyHCl (0.47 g, 4.1 mmol) in dichloromethane (10 mL). The color changed to red immediately. The solvent was removed in vacuo, and the residue was recrystallized from toluene/pentane at −30 °C (two crops, 0.96 g, 83%): ^1H NMR δ 11.45 (CHC_6H_5), 9.72 (br d, 2, py-H_o), 7.33 (m, 4, C_6H_5-H_o and H_m), 6.90 (t, 1, py-H_p), 6.66 (m, 3, C_6H_5-H_p and py-H_m), 1.23 ($OCMe_3$), 1.06 ($OCMe_3$); ^{13}C NMR δ 290.5 (CHC_6H_5), 150.3 (py-C_o), 144.0 (C_6H_5-C_{ipso}), 137.8 (py-C_p), 132.4, 129.9, 126.9 (C_6H_5-C_o, C_m, C_p), 123.9 (py-C_m), 89.5 ($OCMe_3$), 88.7 ($OCMe_3$), 29.4 ($OCMe_3$), 29.3 ($OCMe_3$).

$W(CHR'')(OCMe_3)_2(O_2CR')_2$. R'' = CMe_3; R' = C_6H_5. Two equivalents of benzoic acid (0.52 g, 4.3 mmol) were added to a solution of $W(CCMe_3)(OCMe_3)_3$ (1.00 g, 2.12 mmol) in ether (25 mL). After 1 min the solvent was removed in vacuo and the residue was recrystallized from ether/pentane at −40 °C to yield yellow crystals of product (two crops, 1.15 g, 85%): ^1H NMR δ 11.21 ($CHCMe_3$), 8.45 (H_o), 7.17 (H_m and H_p), 1.49 (CMe_3), 1.37 (CMe_3), 1.31 (CMe_3); ^{13}C NMR δ 294.8 ($CHCMe_3$), 173.2 (O_2CPh), 134.6 (C_{ipso}), 132.1, 130.2, 128.5 (C_p, C_o (or C_m), C_m (or C_o)), 89.1 ($OCMe_3$), 88.3 ($OCMe_3$), 43.0 ($CHCMe_3$), 34.9 (CMe_3), 30.3 (CMe_3), 29.8 (CMe_3). Anal. Calcd for $WC_{27}H_{38}O_6$: C, 50.48; H, 5.96. Found: C, 50.52; H, 5.97.

R'' = CH_2CMe_3; R' = C_6H_5., Two equivalents of benzoic acid (0.15 g, 1.2 mmol) were added to a solution of $W(CCH_2CMe_3)(OCMe_3)_3$ (0.30 g, 0.62 mmol) in ether (10 mL). The solvent was removed in vacuo leaving a yellow oil which was essentially pure by NMR: ^1H NMR δ 11.82 (t, 1, J = 8.5 Hz, $CHCH_2CMe_3$), 8.46 (H_o), 7.16 (H_m and H_p), 5.45 (d, 2, J = 8.5 Hz, $CHCH_2CMe_3$), 1.31 (CMe_3), 1.29 (CMe_3), 1.07 (CMe_3); ^{13}C NMR δ 288.8 ($CHCH_2CMe_3$), 174.1 (O_2CPh), 134.3 (C_{ipso}), 132.2 (C_p), 130.2 (C_o or C_m), 128.5 (C_m or C_o), 88.1 ($OCMe_3$), 87.7 ($OCMe_3$), 58.1 ($CHCH_2CMe_3$), 38.0 ($CHCH_2CMe_3$), 30.2 ($CHCH_2CMe_3$), 29.6 (br q, $OCMe_3$).

R'' = CMe_3; R' = CH_3. Two equivalents of acetic acid (120 μL, 2.1 mmol) were added to a solution of $W(CCMe_3)(OCMe_3)_3$ (0.50 g, 1.1 mmol) in ether (10 mL). The solvent was removed in vacuo to give highly pentane-soluble, oily, yellow crystals that were pure by ^1H NMR: ^1H NMR δ 10.84 ($CHCMe_3$), 1.98 (O_2CCH_3), 1.37 (CMe_3), 1.35 (CMe_3), 1.34 (CMe_3); ^{13}C NMR δ 293.6 ($CHCMe_3$), 177.9 (O_2CCH_3), 88.6 ($OCMe_3$), 87.8 ($OCMe_3$), 42.6 ($CHCMe_3$), 34.7 (CMe_3), 30.1 (CMe_3), 29.6 (CMe_3), 23.2 (O_2CCH_3).

The following bis(carboxylate) alkylidene complexes were prepared in situ by adding slightly less than 2 equiv of carboxylic

acid (usually 1.8–1.9 equiv) to an ethereal solution of the appropriate $W(CR'')(OCMe_3)_3$ complex. The deficiency of acid allowed the resulting $W(CHR'')(OCMe_3)_2(O_2CR')_2$ complex to be observed conveniently by slowing down the rearrangement of the alkylidene ligand to an olefin. ^1H NMR samples were contaminated with $W(CHR'')(OCMe_3)_3(O_2CR')$ as well as the corresponding olefin complex. Only ^1H NMR resonances characteristic of the alkylidene ligand in $W(CHR'')(OCMe_3)_2(O_2CR')$ are given below. Carboxylate and *tert*-butoxide resonances were not assigned.

R'' = CH_3; R' = C_6H_5: ^1H NMR δ 11.56 (q, 1, J = 7.9 Hz, C*H*CH_3), 5.28 (d, 3, J = 7.9 Hz, CHC*H*$_3$).

R'' = CH_2CH_3; R' = C_6H_5: ^1H NMR δ 11.50 (t, 1, J = 7.5 Hz, C*H*CH_2CH_3), 5.51 (quintet, 2, J = 7.5 Hz, CHC*H*$_2$$CH_3$).

R'' = CH_3; R' = CH_3: ^1H NMR δ 11.23 (q, 1, J = 7.9 Hz, C*H*CH_3), 5.10 (d, 3, J = 7.9 Hz, CHC*H*$_3$).

R'' = CH_2CH_3; R' = CH_3: ^1H NMR δ 11.15 (t, 1, J = 7.9 Hz, C*H*CH_2CH_3), 5.30 (quintet, 2, J = 7.5 Hz, CHC*H*$_2$$CH_3$).

W(CHR'')(OCMe$_3$)$_2$(O$_2$CC$_6$H$_5$)$_2$(py). R'' = CH_3. $W(CCH_3)(OCMe_3)_3$ (0.50 g, 1.2 mmol) was dissolved in ether (10 mL) and 2 equiv of pyridine were added (190 μL, 2.3 mmol) followed by two equivalents of benzoic acid (0.28 g, 2.3 mmol). The solvent was removed immediately in vacuo from the solution, and the residue was recrystallized from ether/pentane at −40 °C to give fine yellow needles (two crops, 0.62 g, 78%). The product is too unstable in solution to obtain a reliable ^{13}C NMR spectrum and decomposes substantially in the solid state after 1 day at room temperature: ^1H NMR δ 11.64 (q, 1, J = 8.0 Hz, C*H*CH_3), 8.76 (py-H_o), 8.51 (C_6H_5-H_o), 7.21 (C_6H_5-H_m and H_p), 7.01 (py-H_p), 6.70 (py-H_m), 5.43 (d, 3, J = 8.0 Hz, CHC*H*$_3$), 1.22 (s, 18, $OCMe_3$).

R'' = CH_2CH_3. The same procedure as that above was followed for R = CH_3 starting with $W(CCH_2CH_3)(OCMe_3)_3$ (0.50 g, 1.1 mmol). The product was isolated as yellow needles from ether/pentane at −40 °C (two crops, 0.40 g, 51%). This compound is unstable in solution and in the solid state: ^1H NMR δ 11.53 (t, 1, J = 8.1 Hz, C*H*CH_2CH_3), 8.76 (py-H_o), 8.50 (C_6H_5-H_o), 7.19 (C_6H_5-H_m and H_p), 6.99 (py-H_p), 6.68 (py-H_m), 5.64 (quintet, 2, J = 7.6 Hz, CHC*H*$_2$$CH_3$), 1.24 (s, 18, $OCMe_3$), 1.17 (t, 3, J = 7.8 Hz, $CHCH_2CH_3$).

R'' = $CHMe_2$. The above procedure was repeated starting with $W(CCHMe_2)(OCMe_3)_3$ (0.30 g, 0.66 mmol). The product was isolated as yellow crystals (0.39 g, 85%). This compound was sufficiently stable in solution to obtain a ^{13}C NMR spectrum but it decomposed substantially in the solid state in 1 day at room temperature: ^1H NMR δ 11.38 (d, J = 9.7 Hz, C*H*$CHMe_2$), 8.74 (py-H_o), 8.49 (C_6H_5-H_o), 7.20 (C_6H_5-H_m and H_p), 6.99 (py-H_p), 6.68 (py-H_m), 5.27 (m, CHC*H*Me_2), 1.33 (d, 6, J = 6.4 Hz, CHCH*Me*$_2$), 1.26 ($OCMe_3$), 1.25 ($OCMe_3$); ^{13}C NMR δ 298.2 (*C*HCHMe$_2$), 172.3 ($O_2CC_6H_5$), 149.8 (py-C_o), 136.2 (py-Cp), 135.0 (C_6H_5-C_{ipso}), 131.9 (C_6H_5-Cp), 130.2 (C_6H_5-C_m or C_o), 128.5 (C_6H_5-C_m or C_o), 123.8 (py-C_m), 87.2 ($OCMe_3$), 43.7 (*C*HCHMe$_2$), 30.2 ($OCMe_3$), 29.5 ($OCMe_3$), 28.6 (CHCH*Me*$_2$).

R'' = CH_2CMe_3. The above procedure was repeated beginning with $W(CCH_2CMe_3)(OCMe_3)_3$ (0.30 g, 0.62 mmol). The product was obtained as orange prisms (two crops, 0.38 g, 84%) from ether/pentane at −40 °C: ^1H NMR δ 11.81 (t, 1, J = 8.3 Hz, C*H*CH_2CMe_3), 8.74 (py-H_o), 8.48 (C_6H_5-H_o), 7.20 (C_6H_5-H_m and H_p), 7.01 (py-H_p), 6.69 (py-H_m), 5.60 (d, 2, J = 8.3 Hz, $CHCH_2CMe_3$), 1.28 ($OCMe_3$), 1.26 ($OCMe_3$), 1.06 ($CHCH_2CMe_3$); ^{13}C NMR δ 288.9 (*C*HCH_2CMe_3), 173.4 ($O_2CC_6H_5$), 150.1 (py-C_o), 135.7 (py-C_p), 134.8 (C_6H_5-C_{ipso}), 132.1 (C_6H_5-C_p), 130.2 (C_6H_5-C_m or C_o), 128.5 (C_6H_5-C_m or C_o), 123.6 (py-C_m), 87.8 ($OCMe_3$), 87.6 ($OCMe_3$), 58.0 (*C*HCH_2CMe_3), 37.9 ($CHCH_2CMe_3$), 30.4 ($CHCH_2CMe_3$), 29.7 ($OCMe_3$). Anal. Calcd for $WC_{33}H_{45}O_6N$: C, 53.88; H, 6.17. Found: C, 53.67; H, 6.11.

W(CHR'')(OCMe$_3$)$_3$(O$_2$CR'). All of these compounds were prepared in the same way. One equivalent of carboxylic acid was added to a solution of $W(CR'')(OCMe_3)_3$ in ether (10 mL ether per 100 mg W). The solution was then stripped in vacuo to give a dark yellow oil. ^1H NMR showed these products to be 90–95% pure $W(CHR'')(OCMe_3)_3(O_2CR')$.

R'' = CH_3; R' = C_6H_5: ^1H NMR δ 10.07 (q, 1, J = 7.9 Hz, C*H*CH_3), 8.39 (H_o), 7.13 (H_m and H_p), 5.03 (d, 3, $^3J_{HH}$ = 7.9 Hz, CHC*H*$_3$), 1.42 (s, 9, $OCMe_3$), 1.28 (br s, 18, eq $OCMe_3$); ^{13}C NMR δ 263.4 (*C*HCH_3), 179.6 ($O_2CC_6H_5$), 135.3 (C_{ipso}), 132.2 (C_p), 129.7 (C_m or C_o), 128.6 (C_m or C_o), 84.8 (eq $OCMe_3$), 77.0 (ax $OCMe_3$), 31.8 ($OCMe_3$), 30.2 (br q, $OCMe_3$), 28.6 ($CHCH_3$).

R'' = CH_2CH_3; R' = C_6H_5: ^1H NMR δ 9.99 (t, 1, J = 7.9 Hz, C*H*CH_2CH_3), 8.38 (H_o), 7.18 (H_p and H_m), 5.25 (quin, 2, J = 7.6 Hz, CHC*H*$_2$$CH_3$), 1.47 (s, 9, ax $OCMe_3$), 1.30 (s, 18, eq $OCMe_3$), 1.10 (t, 3, J = 7.4 Hz, $CHCH_2CH_3$); ^{13}C NMR δ 271.0 (*C*HCH_2CH_3), 179.6 ($O_2CC_6H_5$), 135.0 (C_{ipso}), 132.2 (C_p), 129.7 (C_m or C_o), 128.4 (C_m or C_o), 84.7 (br s, eq $OCMe_3$), 76.4 (s, ax $OCMe_3$), 36.8 ($CHCH_2CH_3$), 31.7 (q, ax $OCMe_3$), 30.1 (br q, eq $OCMe_3$), 21.6 ($CHCH_2CH_3$).

R'' = CH_3; R' = CH_3: ^1H NMR δ 9.95 (q, 1, J = 7.9 Hz, C*H*CH_3), 4.98 (d, J = 7.9 Hz, CHC*H*$_3$), 1.88 (O_2CCH_3), 1.38 (s, 9, ax $OCMe_3$), 1.31 (s, 18, eq $OCMe_3$); ^{13}C NMR δ 263.6 (*C*HCH_3), 184.6 (O_2CCH_3), 84.5 (eq $OCMe_3$), 76.8 (ax $OCMe_3$), 31.8 (ax $OCMe_3$), 30.1 (br q, eq $OCMe_3$), 28.4 ($CHCH_3$), 24.1 (O_2CCH_3).

R'' = CH_2CH_3; R' = CH_3: ^1H NMR δ 9.85 (t, 1, J = 8.0 Hz, C*H*CH_2CH_3), 5.12 (quin, 2, J = 7.6, CHC*H*$_2$$CH_3$), 1.87 ($O_2CCH_3$), 1.39 (s, 9, ax $OCMe_3$), 1.31 (s, 18, eq $OCMe_3$), 1.02 (t, 3, J = 7.4 Hz, $CHCH_2CH_3$); ^{13}C NMR 272.7 (*C*HCH_2CH_3), 184.7 (O_2CCH_3), 84.6 (eq $OCMe_3$), 76.3 (ax $OCMe_3$), 36.7 ($CHCH_2CH_3$), 31.7 (ax $OCMe_3$), 30.1 (br q, eq $OCMe_3$), 24.1 (O_2CCH_3), 21.6 ($CHCH_2CH_3$).

W(olefin)(OCMe$_3$)$_2$(O$_2$CR')$_2$. Olefin = CH_2=CH_2; R' = C_6H_5. A slight excess of benzoic acid (1.07 g, 8.76 mmol) was added to a solution of $W(CCH_3)(OCMe_3)_3$ (1.80 g, 4.18 mmol) in ether (25 mL). The solution was stirred for 3 h, and then the solvent was removed in vacuo. The residue was recrystallized from ether/pentane (~1:1) at −40 °C. Large orange cubes were obtained (1.81 g, 72%): ^1H NMR δ 8.51 (H_o), 7.17 (H_m and H_p), 3.22 (s, J_{HW} = 6.1 Hz, C_2H_4), 1.03 (s, 18, $OCMe_3$); ^{13}C NMR δ 184.1 ($O_2CC_6H_5$), 134.7 (C_{ipso}), 133.0 (C_p), 130.2 (C_m or C_o), 128.6 (C_m or C_o), 83.9 ($OCMe_3$), 49.6 (t, J_{CH} = 158 Hz, J_{CW} = 27 Hz, C_2H_4), 20.9 ($OCMe_3$).

Olefin = CH_3CH=CH_2; R' = C_6H_5. Two equivalents of benzoic acid (83 mg, 0.68 mmol) were added to a solution of $W(CCH_2CH_3)(OCMe_3)_3$ (0.15 g, 0.34 mmol) in ether (10 mL). The solvent and *tert*-butyl alcohol (1 equiv) were removed in vacuo to give an orange oil. The oil was redissolved in ether (10 mL), and the solution was left stirring overnight. The solvent was removed in vacuo leaving a red oil. By ^1H NMR this oil was essentially pure product: ^1H NMR δ 8.55 (H_o), 8.43 (H_o), 7.16 (H_m and H_p), 3.94 (CH_3CH=CH_2), 3.72 (dd, J = 6.8 Hz, J = 11.7 Hz, CH_3CH=C*H*$_A$H$_B$), 3.16 (d, J = 6.3 Hz, C*H*$_3$CH=CH_2), 2.87 (dd, J = 6.8 Hz, J = 12.6 Hz, CH_3CH=CH$_A$*H*$_B$), 1.07 ($OCMe_3$), 1.01 ($OCMe_3$); ^{13}C NMR δ 183.36 ($O_2CC_6H_5$), 176.3 ($O_2CC_6H_5$), 135.3 (C_{ipso}), 133.7 (C_{ipso}), 133.0 (C_p), 131.9 (C_p), 130.2 (C_m or C_o), 129.9 (C_o or C_m), 128.6 (C_o or C_m), 128.4 (C_o or C_m), 87.3 ($OCMe_3$), 87.2 ($OCMe_3$), 71.0 (d, J_{CW} = 29 Hz, J_{CH} = 152 Hz, CH_3CH=CH_2), 58.3 (t, J_{CW} = 27 Hz, J_{CH} = 158 Hz, CH_3CH=CH_2), 29.4 ($OCMe_3$), 28.9 ($OCMe_3$), 24.8 (C*H*$_3$CH=CH_2).

Olefin = Me_2C=CH_2; R' = C_6H_5. Slightly more than 2 equiv of benzoic acid (0.50 g, 4.1 mmol) were added to a solution of $W(CCHMe_2)(OCMe_3)_3$ (0.90 g, 2.0 mmol) in ether (20 mL). Ether and *tert*-butyl alcohol were removed in vacuo to give an orange oil. The oil was redissolved in ether (20 mL). After 24 h the ether was removed in vacuo leaving an orange-red oil. This oil was dissolved in ~15 mL of pentane. Small orange crystals slowly formed in the solution at room temperature (two crops, 0.99 g, 80%): ^1H NMR δ 8.65 (H_o), 8.40 (H_o), 7.3–7.1 (H_p and H_m), 3.36 (s, 2, J_{HW} = 6.8 Hz, Me_2C=C*H*$_2$), 3.04 (*Me*$_2$C=CH_2), 1.09 ($OCMe_3$); ^{13}C NMR δ 186.6 ($O_2CC_6H_5$), 172.3 ($O_2CC_6H_5$), 136.5 (C_{ipso}), 133.6 (Cp), 133.1 (C_{ipso}), 131.1 (C_p), 130.4 (C_o or C_m), 129.8 (C_o or C_m), 128.8 (C_o or C_m), 128.2 (C_o or C_m), 87.5 ($OCMe_3$), 85.1 (Me_2C=CH_2), 61.7 (t, J_{CW} = 27 Hz, J_{CH} = 156 Hz, Me_2C=C*H*$_2$), 34.7 (*Me*$_2$C=CH_2), 29.4 ($OCMe_3$). Anal. Calcd for $WC_{26}H_{36}O_6$: C, 49.69; H, 5.77. Found: C, 49.81; H, 5.80.

Olefin = CH_2=CH_2; R' = CH_3. Two equivalents of acetic acid (53 μL, 0.93 mmol) were added to a solution of $W(CCH_3)(OCMe_3)_3$ (0.20 g, 0.46 mmol) in ether (10 mL). Ether and *tert*-butyl alcohol were removed in vacuo to give an orange oil. The oil was redissolved in ether (10 mL), and the solution was stirred overnight. The solvent was then removed in vacuo leaving a red oil of essentially pure product: ^1H NMR δ 2.93 (s, 4, CH_2=CH_2), 2.03 (s, 6, O_2CCH_3), 1.04 (s, 18, $OCMe_3$): ^{13}C NMR δ 184.9 (O_2CCH_3), 86.6 ($OCMe_3$), 55.0 (*t*, J_{CH} = 156 Hz, CH_2=CH_2), 28.8 ($OCMe_3$), 23.8 (O_2CCH_3).

Olefin = CH_3CH=CH_2; R' = CH_3. This compound was produced in the same manner as $W(CH_2$=$CH_2)(OCMe_3)_2(O_2CCH_3)_2$ above. It was isolated as a red oil which was essentially pure by

^{1}H NMR: ^{1}H NMR δ 3.70 (m, $CH_3CH{=}CH_2$), 3.46 (dd, J = 6.9 Hz, J = 11.7 Hz, $CH_3CH{=}CH_AH_B$), 3.05 (d, J = 6.2 Hz, $CH_3CH{=}CH_2$), 2.58 (dd, J = 6.9 Hz, J = 12.6 Hz, $CH_3CH{=}CH_AH_B$), 2.15 (O_2CCH_3), 1.96 (O_2CCH_3), 1.10 ($OCMe_3$), 1.04 ($OCMe_3$); ^{13}C NMR δ 189.6 (O_2CCH_3), 179.6 (O_2CCH_3), 86.7 ($OCMe_3$), 86.6 $OCMe_3$), 70.6 (d, J_{CH} = 153 Hz, J_{CW} = 28 Hz, $CH_3CH{=}CH_2$), 57.0 (t, J_{CH} = 156 Hz, J_{CW} = 26 Hz, $CH_3CH{=}CH_2$), 29.2 ($OCMe_3$), 28.7 ($OCMe_3$), 24.7 ($CH_3CH{=}CH_2$), 24.0 (O_2CCH_3), 23.8 (O_2CCH_3).

$W(OCMe_3)_2(O_2CC_6H_5)_2(PMe_3)_2$. An excess of trimethylphosphine (210 μL, 2.06 mmol) was added to a solution of $W(C_2H_4)(OCMe_3)_2(O_2CC_6H_5)_2$ (0.25 g, 0.42 mmol) in ether (25 mL). After 24 h the solvent was removed in vacuo. The resdue was recrystallized from toluene at −40 °C to give large blue-green prisms (0.12 g, 40%): ^{1}H NMR δ 8.83 (H_o), 7.34 (H_m), 7.22 (H_p), 1.47 (d, 18, J = 8.4 Hz, PMe_3), 1.20 ($OCMe_3$); ^{13}C NMR δ 173.3 ($O_2CC_6H_5$), 138.0 (C_{ipso}), 130.8 (C_m or C_o), 130.4 (C_p), 128.0 (C_m or C_o), 85.2 ($OCMe_3$), 30.3 ($OCMe_3$), 24.8 (PMe_3); ^{31}P NMR δ −31.6 (J_{PW} = 439 Hz). Anal. Calcd for $WC_{28}H_{46}O_6P_2$: C, 46.42; H, 6.40. Found: C, 46.72; H, 6.26.

$W(OCMe_3)_2(O_2CCH_3)_2(PMe_3)_2$. A solution of $W(CCH_2CH_3)(OMe_3)_3$ (0.75 g, 1.7 mmol) in ether (10 mL) was treated with ~2.2 equiv of acetic acid (210 μL, 3.7 mmol). After 30 min the solvent and *tert*-butyl alcohol (1 equiv) were removed in vacuo giving $W(CH_2{=}CHCH_3)(OCMe_3)_2(O_2CCH_3)_2$ as an oil. The oil was dissolved in pentane (20 mL) and an excess of trimethylphosphine (800 μL, 7.9 mmol) added. After 1 h the solution was dark blue. The solvent and excess PMe_3 were removed in vacuo, and the residue was recrystallized from pentane at −40 °C to give large blue crystals (0.49 g, 49%): ^{1}H NMR δ 2.39 (O_2CCH_3), 1.39 (PMe_3), 1.27 ($OCMe_3$); ^{13}C NMR δ 178.1 (O_2CCH_3), 84.7 ($OCMe_3$), 30.1 ($OCMe_3$), 24.7 (PMe_3), 24.7 (O_2CCH_3). Anal. Calcd for $WC_{18}H_{42}O_6P_2$: C, 36.01; H, 7.05. Found: C, 35.98; H, 6.92.

Rearrangement of $W(CHMe)(OCMe_3)_2(O_2CPh)_2$. Mixtures of $W(CHMe)(OCMe_3)_2(O_2CPh)_2$ and $W(CHMe)(OCMe_3)_3(O_2CPh)$ were prepared for kinetic study by adding the desired amount of benzoic acid (~1.6–1.9 equiv) to a solution of $W(CMe)(OCMe_3)_3$ (0.200 g, 0.465 mmol) in ether (10 mL). The solvent and *tert*-butyl alcohol were removed in vacuo. The resulting yellow oil was diluted to 2.00 mL in a volumetric flask with C_6D_6 ($[W]_{Tot}$ = 0.233 M). The solution was then divided between several NMR tubes and frozen at −78 °C until needed. The reaction was monitored by ^{1}H NMR at 296 K for approximately 2 half-lives. The data were obtained by integrating the $W(CHCH_3)(OCMe_3)_2(O_2CPh)_2$ doublet vs. the combined phenyl meta and para resonances of both starting alkylidenes and the product $[W(CH_2CH_2)(OCMe_3)_2(O_2CPh)_2]$. The concentration of $W(CHMe)(OCMe_3)_3(O_2CPh)$ could be derived similarly by integrating the $W(CHMe)(OCMe_3)_3(O_2CPh)$ doublet vs. the combined meta and para resonances. The concentration of $W(CHMe)(OCMe_3)_3(O_2CPh)$ did not vary significantly over the reaction time. Plots of $[W(CHMe)(OCMe_3)_2(O_2CPh)_2]^{-1}$ vs. time were linear (see Figure 2). Correlation coefficients to the linear least-squares best-fit line were >0.999. The rate constants obtained are listed in Table II.

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Registry No. $W(CHCMe_3)(OCMe_3)_2Cl_2$, 91230-62-5; $W(CHCMe_3)(OCMe_3)_2Br_2$, 98268-59-8; $W(CHCMe_3)(OCMe_3)_2(OPh)_2$, 98268-60-1; $W(CHCMe_3)(OCMe_3)_2(OC_6H_4$-*p*-Cl), 98268-61-2; $W(CHCMe_3)(OCMe_3)_2(OC_6F_5)_2$, 98268-62-3; $W(CHCMe_3)(OCMe_3)_2Cl_2(Py)$, 98268-43-0; $W(CHCMe_3)(OCMe_3)_2Br_2(py)$, 98268-44-1; $W(CHCMe_3)(OCMe_3)_2I_2(py)$, 98268-45-2; $W(CHCNe_3)(OCMe_3)_2(O_2CCF_3)_2(py)$, 98303-55-0; $W(CHCH_2CH_3)(OCMe_3)_2Cl_2(py)$, 98268-46-3; $W(CHC_6H_5)(OCMe_3)_2Cl_2(py)$, 98268-47-4; $W(CHCMe_3)(OCMe_3)_2(O_2CPh)_2$, 98268-63-4; $W(CHCMe_3)(OCMe_3)_2(O_2CMe)_2$, 98268-64-5; $W(CHCH_2CMe_3)(OCMe_3)_2(O_2CPh)_2$, 98268-65-6; $W(CHCH_3)(OCMe_3)_2(O_2CPh)_2$, 98268-66-7; $W(CHCH_2CH_3)(OCMe_3)_2(O_2CPh)_2$, 98268-67-8; $W(CHCH_3)(OCMe_3)_2(O_2CMe)_2$, 98268-68-9; $W(CHCH_2CMe_3)(OCMe_3)_2(O_2CMe)_2$, 98268-69-0; $W(CHCH_3)(OCMe_3)_2(O_2CPh)_2(py)$, 98268-48-5; $W(CHCH_2CH_3)(OCMe_3)_2(O_2CPh)_2(py)$, 98268-49-6; $W(CHCHMe_2)(OCMe_3)_2(O_2CPh)_2(py)$, 98268-50-9; $W(CHCH_2CMe_3)(OCMe_3)_2(O_2CPh)_2(py)$, 98268-51-0; $W(CHCH_3)(OCMe_3)_3(O_2CPh)$, 98268-70-3; $W(CHCH_2CH_3)(OCMe_3)_3(O_2CPh)$, 98268-71-4; $W(CHCH_3)(OCMe_3)_3(O_2CMe)$, 98268-72-5; $W(CHCH_2CH_3)(OCMe_3)_3(O_2CMe)$, 98268-73-6; $W(CHC_3)(O_2CMe)_2(O_2CPh)$, 98268-74-7; $W_2(OCMe_3)_6$, 57125-20-9; $W(N)(OCMe_3)_3$, 82209-24-3; $W(CCHMe_2)(OCMe_3)_3$, 98268-75-8; $W(CCH_2CMe_3)(OCMe_3)_3$, 98268-76-9; $W(CCMe_3)(OCMe_3)_3$, 78234-36-3; $W(CC_6H_5)(OCMe_3)_3$, 82228-87-3; $W(CMe)(OCMe_3)_3$, 82209-23-2; $W(CEt)(OCMe_3)_3$, 82228-88-4; $W(CHCH_2CH_3)(OCMe_3)_2(O_2CCH_3)_2$, 98268-77-0; $W(CH_2{=}CH_2)(OCMe_3)_2(O_2CC_6H_5)_2$, 98268-52-1; $W(CH_3CH{=}CH_2)(OCMe_3)_2(O_2CC_6H_5)_2$, 98268-53-2; $W(Me_2C{=}CH_2)(OCMe_3)_2(O_2CC_6H_5)_2$, 98268-54-3; $W(CH_2{=}CH_2)(OCMe_3)_2(O_2CCH_3)_2$, 98268-55-4; $W(CH_3CH{=}CH_2)(OCMe_3)_2(O_2CCH_3)_2$, 98268-56-5; $W(OCMe_3)_2(O_2CC_6H_5)_2(PMe_3)_2$, 98268-57-6; $W(OCMe_3)_2(O_2CCH_3)_2(PMe_3)_2$, 98268-58-7; $W(CHCD_3)(OCMe_3)_2(O_2CMe)_2$, 98268-78-1; $W(CHCD_3)(OCMe_3)_3(O_2CMe)$, 98268-79-2; $W(CHCD_3)(OCMe_3)_2(O_2CPh)_2$, 98268-80-5; $W(CHCD_3)(OCMe_3)_3(O_2CPh)$, 98268-81-6; $W(CHCD_3)(OCMe_3)_2(O_2CPh)(O_2CMe)$, 98268-82-7; Me_2CHCN, 78-82-0; Me_3CCH_2CN, 3302-16-7; HOC_6H_5, 108-95-2; *p*-HOC_6H_4Cl, 106-48-9; HOC_6F_5, 771-61-9; pyHCl, 628-13-7; pyHBr, 18820-82-1; pyHI, 18820-83-2; $pyHO_2CCF_3$, 464-05-1; HO_2CCH_3, 64-19-7.