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light. The absorption bands at 274–287 and 235–257 nm are assigned as charge transfer bands $(\epsilon \sim 4 \times 10^4)$. An additional band at 209–222 nm $(\epsilon \sim 4 \times 10^4)$ is observed in all complexes containing a coordinated iodide ligand regardless of the nature of the counterion. The large value of the extinction coefficient tends to rule out the possibility of an iodide impurity in these compounds. The iodohexakis(aryl isocyanide) complexes show a set of bands that are red shifted from the positions of their alkyl analogues (Table I).

Table I also summarizes the ^1H NMR spectral data and major CN infrared stretching frequencies. The chemical shifts agree reasonably well with previously published data in the case of known compounds and are consistent with their fluxionality in solution.[5b,c] The chemical shift of the protons of coordinated *tert*-butyl isocyanide is quite insensitive to its coordination environment. The chemical shift of protons on the carbon atom α to the isocyanide nitrogen atom is somewhat more sensitive to the coordination environment; however, only a few examples have been characterized. The infrared spectral properties of the known compounds are consistent with the values reported in the literature.

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Registry No. $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$, 78656-70-9; $[Mo(CN\text{-}t\text{-}C_4H_9)_6Cl]Cl$, 66652-50-4; $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]I$, 66700-89-8; $[Mo(CN\text{-}t\text{-}C_4H_9)_6I](PF_6)$, 79516-88-4; $[Mo(CNCH_3)_6I](BF_4)$, 79466-85-6; $[Mo(CN\text{-}c\text{-}C_6H_{11})_6I]I$, 79466-86-7; $[Mo(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$, 41982-05-2; $[Mo(CN\text{-}c\text{-}C_6H_{11})_7](PF_6)_2$, 72155-82-9; $[W(CN\text{-}t\text{-}C_4H_9)_6CN](H_2PO_4)$, 79466-88-9; $[W(CN\text{-}t\text{-}C_4H_9)_6I]I$, 66652-48-0; $[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$, 66687-57-8; $[Mo(CNC_6H_4\text{-}p\text{-}Cl)_6I]I$, 79466-89-0; $[Mo(CNC_6H_4\text{-}p\text{-}Cl)_6I](PF_6)$, 79466-91-4; $[Mo(CNC_6H_4\text{-}p\text{-}CH_3)_6I](PF_6)$, 79466-93-6; $[Mo(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2]$, 79466-94-7; $[Mo(CN\text{-}t\text{-}C_4H_9)_5(CO)I]I$, 79466-95-8; $[W(CN\text{-}t\text{-}C_4H_9)_4(CO)I_2]$, 79466-96-9; $[Mo(CN\text{-}t\text{-}C_4H_9)_6SnCl_3](PF_6)$, 79466-98-1; $[Mo(CN\text{-}t\text{-}C_4H_9)_7](BPh_4)_2$, 76945-59-0; $[Mo(CN\text{-}c\text{-}C_6H_{11})_7]I_2$, 79466-99-2; $Mo(CNCH_3)_3(CO)_3$, 79516-89-5; $Mo(CO)_6$, 13939-06-5; $Mo(CN\text{-}t\text{-}C_4H_9)_3(CO)_3$, 79516-90-8; $W(CN\text{-}t\text{-}C_4H_9)_3(CO)_3$, 70095-01-1; $Mo(CNC_6H_4\text{-}p\text{-}Cl)_3(CO)_3$, 79516-91-9; $Mo(CNC_6H_4\text{-}p\text{-}CH_3)_3(CO)_3$, 79516-92-0; $Mo(CN\text{-}c\text{-}C_6H_{11})_3(CO)_3$, 31473-80-0; $W(CO)_6$, 14040-11-0.

Synthesis and Characterization of Tungsten Oxo Neopentylidene Complexes[1]

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Tantalum complexes of the type $Ta(CHCMe_3)X_3(PR_3)_2$ (X = Cl or Br) react with $W(O)(OCMe_3)_4$ to give $[Ta(OCMe_3)_4X]_2$ and $W(O)(CHCMe_3)X_2(PR_3)_2$. In $W(O)(CHCMe_3)X_2(PR_3)_2$ the phosphine ligands are trans and the oxo and neopentylidene ligands are cis to one another. Five-coordinate complexes can be prepared by scavenging one phosphine ligand with $PdCl_2(PhCN)_2$. Addition of 1 or 2 equiv of $AlCl_3$ to $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ in dichloromethane yields mono- and dicationic complexes, respectively. If $AlMe_3$ is added to $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ unstable $[W(O)(CHCMe_3)(CH_3)(PEt_3)_2]^+(AlMe_2Cl_2^-)$ is formed, which on treatment with TMEDA yields $W(O)(CHCMe_3)(CH_3)(Cl)(TMEDA)$. Attempts to prepare cationic complexes with BF_4^- or PF_6^- counterions yielded fluoride complexes. Complexes containing *tert*-butoxide ligands in place of halides have been prepared by several routes. *tert*-Butoxide complexes containing phosphine ligands are relatively unstable toward decomposition to give phosphine oxide. Phosphine-free, unstable $[W(O)(CHCMe_3)(OCMe_3)_2]_2$ and other phosphine-free complexes such as $W(O)(CHCMe_3)Cl_2(TMEDA)$ and $W(O)(CHCMe_3)(S_2CNMe_2)_2$ have also been prepared. In none of these complexes is the $W{=}C_\alpha{-}C_\beta$ angle in the neopentylidene ligand large, as judged by the relatively high values for J_{CH_α} (115–130 Hz).

Introduction

Neopentylidene complexes of niobium and tantalum of several different types can be made readily by α hydrogen atom abstraction.[2] We had evidence that these principles extend to tungsten,[3] but, unfortunately, the necessary tungsten(VI) alkyl complexes are rare.[4] Therefore we had to turn to alternative methods to make tungsten(VI) neopentylidene complexes. We chose to attempt to transfer a neopentylidene ligand from tantalum to tungsten since tantalum alkylidene complexes are related to phosphorus ylides[2] and since we had been able to transfer a benzylidene or ethylidene ligand from phosphorus to tantalum.[5] The result was a route to what may be the most important type of group 6 alkylidene complex, that containing a second π-type ligand, in this case, an oxo ligand. Oxo alkylidene complexes are probably an important type of olefin metathesis catalyst,[6,7] and they have also led directly to the discovery of tungsten alkylidyne complexes which will metathesize acetylenes.[8] Here we

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Table I. Some Pertinent NMR and IR Data for Oxo Alkylidene Complexes[a]

compound	H_α, ppm	J_{CH_α}, Hz	C_α, ppm	J_{CW}, Hz	$\nu_{W=O}$, cm^{-1}
$W(O)(CHCMe_3)Cl_2(PMe_3)_2$	11.89	121	319		971
$W(O)(CHCMe_3)Cl_2(PEt_3)_2$	12.04	126	313	148	969
$W(O)(CHCMe_3)Cl_2(PMe_2Ph)_2$	12.23	117	320		970
$W(O)(CHCMe_3)Br_2(PEt_3)_2$	12.10	125	312		
$W(O)(CHCMe_3)Cl_2(PEt_3)$	9.87	115	295	176	979
$W(O)(CHCMe_3)Cl_2(PMe_3)(PhCN)$	10.02	121	297		
$W(O)(CHCMe_3)Cl_2(PMe_3)(THF)$	10.67	121	300		
$W(O)(CHCMe_3)Cl_2(TMEDA)$	11.02	127	300	174	
$[W(O)(CHCMe_3)Cl(PEt_3)_2]^+(AlCl_4^-)$	10.60[b]	127	313[c]	156	985
$[W(O)(CHCMe_3)(PEt_3)_2]^{2+}(AlCl_4^-)_2$	10.47[b,d]	125	317[c]		985
$[W(O)(CHCMe_3)(Me)(PEt_3)_2]^+(AlMe_2Cl_2^-)$	9.50[b]	108	314[c]		
$W(O)(CHCMe_3)(Me)(Cl)(TMEDA)$	10.42	119	286	186	960
$[W(O)(CHCMe_3)Cl(PEt_3)]^+(AlCl_4^-)$	9.10[b]	129	302[b]	162	946
$W(O)(CHCMe_3)(Cl)(F)(PEt_3)_2$	11.56		310		
$W(O)(CHCMe_3)(S_2CNMe_2)_2$	12.00	127	303		950
$W(O)(CHCMe_3)(OCMe_3)_2(PMe_3)$	9.64[e]		267[e]		
$W(O)(CHCMe_3)(OCMe_3)_2(PEt_3)$	9.71[e]	119	268[e]		
$W(O)(CHCMe_3)(OCMe_3)_2(PMe_2Ph)$	9.77[e,d]	123	269[e]	186	949
$[W(O)(CHCMe_3)(OCMe_3)_2]_2$	10.68[f]	135	290[e]	156	940

[a] Solvent = C_6D_6 unless otherwise noted. [b] Solvent = $CDCl_3$. [c] Solvent = CD_2Cl_2. [d] J_{HW} = 9 Hz. [e] Solvent = toluene-d_8. [f] J_{HW} = 12 Hz.

report the synthesis and characterization of a number of tungsten oxo neopentylidene complexes. Some of this work has been reported in preliminary form.[6a,7]

Results

Bis(phosphine) Complexes. Tantalum complexes of the type $Ta(CHCMe_3)X_3L_2$ (L = a phosphine ligand; X = Cl or Br) react readily with $W(O)(OCMe_3)_4$ in pentane as shown in eq 1. After 3 h yellow $W(O)(CHCMe_3)X_2L_2$

$$Ta(CHCMe_3)X_3L_2 + W(O)(OCMe_3)_4 \rightarrow 0.5[Ta(OCMe_3)_4X]_2 + W(O)(CHCMe_3)X_2L_2 \quad (1)$$

crystallizes out in about 70% yield. The tantalum product, which has been reported previously,[9] is more soluble in pentane. Many intermediates in this reaction can be observed by ^{31}P NMR, but after 3 h only the signal due to the oxo neopentylidene complex remains. Most commonly we prepare complexes in which X = Cl and L = PMe_3 or PEt_3. Complexes in which X = Cl and L = PMe_2Ph or X = Br and L = PEt_3 can also be prepared easily. The results when L is not a tertiary phosphine ligand will be described later.

In the $W(O)(CHCMe_3)X_2L_2$ complexes the ^{13}C NMR shift of the neopentylidene α-carbon atom is from 310 to 320 ppm. In $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ J_{CH_α} = 126 Hz, characteristic of a "normal" neopentylidene ligand, one which is not distorted by interaction of the CH_α electron pair and/or H_α with the metal.[10] The signal for H_α is found at ~12 ppm in the ^1H NMR spectrum. The phosphine ligands are equivalent, and, unlike those in $Ta(CHCMe_3)X_3L_2$ complexes,[11] not exchangeable on the NMR time scale. It is important to note that the W=O stretching frequency (~970 cm^{-1}) is characteristic of an oxo ligand which is "triply bonded" to the metal as a consequence of its strong π-electron donor abilities.[12] Some of these data are collected in Table I along with data for other oxo alkylidene complexes we will be discussing later.

An X-ray study of $W(O)(CHCMe_3)Cl_2(PMe_3)_2$[13] shows that these species are approximately octahedral, with trans phosphine ligands, cis halides, and a neopentylidene ligand whose β carbon atom lies in the $W(O)(C_\alpha)X_2$ plane. The $W{=}C_\alpha$ bond length (2.01 Å) and the W=O bond length (1.70 Å) are about what one would expect.[2,12] These bond lengths, the O–W–C_α angle (107°), and the fact that the *tert*-butyl group points toward the oxo ligand preclude any direct interaction between the oxo and alkylidene ligand.

These octahedral oxo alkylidene complexes have 18 valence electrons if one counts the oxo ligand as a 4e donor. Perhaps for this reason they are relatively stable thermally and only slightly sensitive to water and oxygen. They can be recovered unchanged from acetonitrile or acetone, and they do not react with CO or H_2 at 25 psi and 80 °C in 1 h.

Complexes Prepared by Scavenging Phosphine. We attempted to remove at least one phosphine ligand from $W(O)(CHCMe_3)X_2L_2$ in order to prepare more reactive, coordinatively unsaturated molecules.

One PEt_3 ligand is removed upon adding 0.5 equiv of $PdCl_2(PhCN)_2$ to $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ (eq 2). The

$$W(O)(CHCMe_3)Cl_2(PEt_3)_2 + 0.5PdCl_2(PhCN)_2 \rightarrow W(O)(CHCMe_3)Cl_2(PEt_3) + 0.5PdCl_2(PEt_3)_2 \quad (2)$$

reaction is complete after 1 h at room temperature. $W(O)(CHCMe_3)Cl_2(PEt_3)$ can be crystallized selectively as yellow prisms. One PMe_3 ligand can be removed from $W(O)(CHCMe_3)Cl_2(PMe_3)_2$ similarly, but probably because PMe_3 is smaller than PEt_3, benzonitrile (if toluene is the solvent) or tetrahydrofuran (if ether/THF is the solvent) takes its place. The THF can be removed by heating solid $W(O)(CHCMe_3)Cl_2(PMe_3)(THF)$ in vacuo.

$W(O)(CHCMe_3)Cl_2(PEt_3)$ was shown to be a monomer in benzene by cryoscopy. (Compare this with formation of a dimer when $Ta(CHCMe_3)Cl_3L_2$ loses a phosphine ligand.[11]) This is probably the reason $W(O)(CHCMe_3)Cl_2(PEt_3)$ is less stable than $W(O)(CHCMe_3)Cl_2(PEt_3)_2$; it decomposes (presumably bimolecularly) to give *cis*- and *trans*-2,2,5,5-tetramethyl-3-hexene at 80 °C. Details of the five-coordinate structure have been elucidated by an X-ray

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study.[14] $W(O)(CHCMe_3)Cl_2(PEt_3)$ is a slightly distorted trigonal bipyramid, with PEt_3 and one of the chlorides in apical positions. The O–W–C_α angle is again 107°, but the $W{=}C_\alpha$ bond length and W=O bond length (1.88 Å and 1.66 Å, respectively) are both significantly shorter than in $W(O)(CHCMe_3)Cl_2(PEt_3)_2$. The shorter W=O bond can account for the shift of $\nu_{W=O}$ to slightly higher energy (979 cm^{-1}, Table I).

Addition of 1 equiv of $PdCl_2(PhCN)_2$ to $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ only yields $W(O)(CHCMe_3)Cl_2(PEt_3)$ and $PdCl_2(PhCN)(PEt_3)$. Addition of 1 equiv of $PdCl_2$(1,5-cyclooctadiene) gives $PdCl_2(PEt_3)_2$, but we could not observe any alkylidene complex by NMR. In the presence of tetramethylethylenediamine, however, $W(O)(CHCMe_3)Cl_2(TMEDA)$ is formed (eq 3). The reaction

$$\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2 + PdCl_2(1,5\text{-}COD) \xrightarrow[2\ days]{toluene} W(O)(CHCMe_3)Cl_2(TMEDA) + PdCl_2(PEt_3)_2 + 1,5\text{-}COD} \quad (3)$$

is slow, probably because $PdCl_2(TMEDA)$ forms first. The oxo and alkylidene ligands are almost certainly cis in $W(O)(CHCMe_3)Cl_2(TMEDA)$ also. Since all TMEDA methyl groups are different, one end of the TMEDA ligand is in a position cis to both the oxo and the neopentylidene ligands.

Cationic Complexes. Formation of a cationic complex is another important way of producing a coordinatively unsaturated species. Since aluminum alkyls or halides are often cocatalysts in olefin metathesis systems[15] we chose to prepare cationic species by adding aluminum reagents to $W(O)(CHCMe_3)Cl_2(PEt_3)_2$.

One equivalent of $AlCl_3$ reacts immediately with $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ in dichloromethane to give a yellow saltlike complex (upon addition of pentane) and with a second equivalent to give an orange saltlike complex (upon addition of pentane). The yellow species has an equivalent conductivity of 34 in dichloromethane (at 10^{-3} M) while the orange species has an equivalent conductivity of 64 (at 10^{-3} M). Therefore we believe they are mono- and dicationic complexes, respectively (eq 4). Each reacts with

$$\mathrm{W(O)(CHCMe_3)Cl_2L_2 \xrightarrow[CH_2Cl_2]{AlCl_3} [W(O)(CHCMe_3)ClL_2]^+(AlCl_4^-) \xrightarrow[CH_2Cl_2]{AlCl_3} [W(O)(CHCMe_3)L_2]^{2+}(AlCl_4^-)_2} \quad (4)$$

ether, phosphines, TMEDA, and other Lewis bases to give $W(O)(CHCMe_3)Cl_2L_2$. Their NMR spectra are similar to those of their neutral parents (Table I). A potentially important difference between the IR spectra of the two cations and those of the neutral complexes is that $\nu_{W=O}$ *increases* to 985 cm^{-1} in the cations. Therefore we believe the major species, at least in dichloromethane, is not one in which the aluminum halide interacts with either the oxo[6c] or the neopentylidene ligand. The anion could still interact with the metal to some extent, so we cannot confidently predict that they will be discrete monocationic trigonal-bipyramidal and dicationic tetrahedral complexes, respectively.

It is important to note that both the monocationic and dicationic complexes are significantly more stable than the neutral five-coordinate species, or $[W(O)(CHCMe_3)(OCMe_3)_2]_2$ (see later). For example, $[W(O)(CHCMe_3)(PEt_3)_2]^{2+}(AlCl_4^-)_2$ can be heated in 1,2-dichloroethane to 80 °C for 1 h with negligible decomposition (by ^1H NMR integration).

$W(O)(CHCMe_3)Cl_2(PEt_3)_2$ reacts with 1 equiv of $AlMe_3$ to give a thermally unstable yellow crystalline complex (on addition of pentane) whose initial equivalent conductivity in dichloromethane (35) is consistent with it being analogous to $[W(O)(CHCMe_3)Cl(PEt_3)_2]^+(AlCl_4^-)$. Its low-temperature NMR spectra show it to be a methyl complex (eq 5), probably a trigonal bipyramid with equivalent axial

$$\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2 + AlMe_3 \xrightarrow{CH_2Cl_2} [W(O)(CHCMe_3)(CH_3)(PEt_3)_2]^+(AlMe_2Cl_2^-)} \quad (5)$$

phosphine ligands. This species has a half-life of only ~5 min in $CDCl_3$ at 25 °C. A new alkylidene complex forms (H_α at 8.15 ppm), but it also decomposes at this temperature. The equivalent conductivity of a dichloromethane solution is essentially zero after this second neopentylidene complex has decomposed No metal-containing products have been identified. The only significant organic products are methane and 3,3-dimethyl-1-butene (eq 6).

$$\mathrm{[W(O)(CHCMe_3)(Me)(PEt_3)_2]^+(AlMe_2Cl_2^-) \xrightarrow[25\ ^\circ C,\ CDCl_3]{dec} CH_4 + Me_3CCH{=}CH_2} \quad (6)$$

It is interesting that $[W(O)(CHCMe_3)(Me)(PEt_3)_2]^+(AlMe_2Cl_2^-)$ reacts with TMEDA (2 equiv) to give $W(O)(CHCMe_3)(Me)(Cl)(TMEDA)$, not $W(O)(CHCMe_3)(Me)(Cl)(PEt_3)_2$. $W(O)(CHCMe_3)(Me)(Cl)(TMEDA)$ is stable at 25 °C in benzene for several hours [cf. $[W(O)(CHCMe_3)(Me)(PEt_3)_2]^+(AlMe_2Cl_2^-)$ in $CDCl_3$]. The signal for the methyl group bound to tungsten is found at 1.17 ppm (J_{HW} = 10 Hz) in the ^1H NMR spectrum and 19.9 ppm (J_{CW} = 117 Hz) in the ^{13}C NMR spectrum. Only one isomer is observed, but we cannot tell which of the four possible asymmetric isomers containing cis oxo and alkylidene ligands it is.

$W(O)(CHCMe_3)Cl_2(PEt_3)_2$ reacts with 2 equiv of $AlMe_3$ to give another thermally unstable yellow crystalline product which appears to be an $AlMe_3$ adduct of $[W(O)(CHCMe_3)(Me)(PEt_3)_2]^+$ by ^1H NMR, ^{13}C NMR, and conductivity (39 at 10^{-3} M in CH_2Cl_2). at −25 °C in the ^1H NMR spectrum the signal for H_α is broad and a signal for a methyl group bound to tungsten could not be found. At 25 °C signals due to $[W(O)(CHCMe_3)(Me)(PEt_3)_2]^+$ appear and decomposition begins. Methane is observed, but no *tert*-butylethylene. The organometallic product has single proton signals at 12.61 (m), 9.98 (dt), and 6.01 (d) ppm. Unfortunately, this interesting product also decomposes, and we have not yet succeeded in isolating or further characterizing it.

$W(O)(CHCMe_3)Cl_2(PEt_3)$ reacts with $AlCl_3$ to give a red-orange crystalline complex which has an equivalent conductivity in dichloromethane (33) similar to the other 1:1 electrolytes we have discussed. Therefore we suspect this complex is that shown in eq 7, at least in dichloromethane.

$$\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3) + AlCl_3 \xrightarrow{CH_2Cl_2} [W(O)(CHCMe_3)Cl(PEt_3)]^+(AlCl_4^-)} \quad (7)$$

However, this species is somewhat soluble in toluene and more soluble in chloroform than the cationic bis(phosphine) complexes. Also, the value for $\nu_{W=O}$ (946 cm^{-1}) in the solid state is significantly lower than that for either $W(O)(CHCMe_3)Cl_2(PEt_3)$ (979 cm^{-1}) or $[W(O)(CHCMe_3)Cl(PEt_3)_2]^+$ (985 cm^{-1}). These facts lead us to

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suspect that $AlCl_3$ may coordinate weakly to the oxo ligand in nonpolar solvents or in the solid state. Osborn has found recently[6c] that $AlBr_3$ can coordinate fairly strongly to the oxo ligand in several tungsten(VI) oxo complexes, and it is reasonable to expect that $AlCl_3$ can also (though less strongly) in some circumstances.

Ideally it would be desirable to prepare cationic complexes with relatively innocuous anions in place of aluminates. This was not immediately successful with BF_4^- or PF_6^-. Thallium chloride precipitates almost immediately when $TlBF_4$ is added to $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ in acetonitrile in the presence of PEt_3. However, a cationic complex does not form cleanly. A significant product is a monofluoride complex (eq 8). Similar results were obtained by using $AgPF_6$ in THF. Abstraction of fluoride from the anion by an incipient cation is almost certainly the way the tungsten monofluoride complex is formed. Reactions in the absence of added phosphine give lower yields of the monofluoride complex but still no observable $[W(O)(CHCMe_3)(Cl)L_2]^+$.

$$\mathrm{W(O)(CHCMe_3)Cl_2L_2 + TlBF_4 + L \xrightarrow[L\,=\,PEt_3]{CH_3CN} W(O)(CHCMe_3)(Cl)(F)L_2 + TlCl + BF_3{\cdot}L} \tag{8}$$

Complexes Containing Dimethyldithiocarbamate or *tert*-Butoxide Ligands. $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ reacts with 2 equiv of sodium dimethyldithiocarbamate to give the expected bis(dithiocarbamate) oxo alkylidene complex quantitatively (eq 9). It is analogous to a large class of molybdenum and tungsten cis dioxo, diimido, or oxo imido dithiocarbamate complexes.[12,16,17] At room temperature only one signal for the dithiocarbamate methyl groups is observed. At −30 °C two H_α signals, two *tert*-butyl signals, and at least four dithiocarbamate methyl resonances are observed. One of the two isomers observed at low temperature is almost certainly an octahedral species in which the *tert*-butyl group points toward the cis oxo ligand [cf. $W(O)(CHCMe_3)Cl_2(PMe_3)_2$]. The simplest explanation is that the other isomer is an analogous octahedral species in which the *tert*-butyl group points away from the oxo ligand. We did not examine in detail the process which on the NMR time scale at room temperature generates only one type of dithiocarbamate methyl group and one type of neopentylidene ligand.

$$\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2 + 2NaS_2CNMe_2 \xrightarrow[-2PEt_3]{THF} W(O)(CHCMe_3)(S_2CNMe_2)_2} \tag{9}$$

$W(O)(CHCMe_3)Cl_2L_2$ reacts with 2 equiv of lithium *tert*-butoxide to form $W(O)(CHCMe_3)(OCMe_3)_2L$ complexes (L = PMe_3, PEt_3, PMe_2Ph). When only 1 equiv is added, 0.5 equiv of $W(O)(CHCMe_3)Cl_2L_2$ remain; no mono-*tert*-butoxide complex could be detected. $W(O)(CHCMe_3)(OCMe_3)_2L_2$ does not form, probably for steric as well as electronic reasons (cf. $M(CHCMe_3)(OCMe_3)_2Cl(L)$; M = Nb or Ta[18]). Unfortunately, this reaction is not quantitative, and the $W(O)(CHCMe_3)(OCMe_3)_2L$ complexes decompose in a few minutes at 25 °C in solution or in the solid state. Therefore they have been characterized at low temperature by NMR methods.

NMR spectra at −20 °C suggest that two isomers are present in about a 5:1 ratio. (Two isomers are also found for $M(CHCMe_3)(OCMe_3)_2Cl(L)$; M = Nb or Ta.[18]). The major isomer has inequivalent *tert*-butoxide ligands and therefore most likely has the TBP geometry shown in Figure 1. The minor isomer, whose *tert*-butoxide resonances we cannot identify unambiguously, could be either a similar type with the neopentylidene ligand rotated 180° or one with axial *tert*-butoxide ligands (Figure 1). When ^{31}P NMR samples are warmed to 10 °C, the two peaks due to the phosphine ligands in the two isomers broaden and coalesce; any resonance due to added phosphine also broadens and coalesces with the resonances due to coordinated phosphine. Therefore $W(O)(CHCMe_3)(OCMe_3)_2L$ is in equilibrium with "$W(O)(CHCMe_3)(OCMe_3)_2$" and free L. In fact PMe_3 can be removed from $W(O)(CHCMe_3)(OCMe_3)_2(PMe_3)$ in vacuo to give $[W(O)(CHCMe_3)(OCMe_3)_2]_2$ (see below).

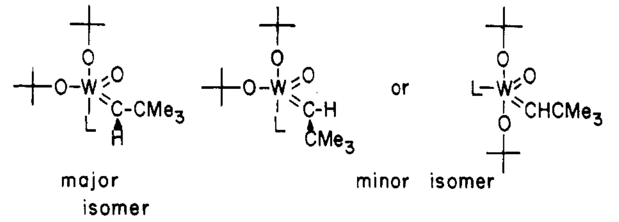

Figure 1. Proposed structures for $W(O)(CHCMe_3)(OCMe_3)_2L$.

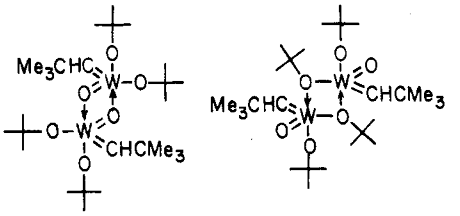

Figure 2. Possible structures for $[W(O)(CHCMe_3)(OCMe_3)_2]_2$.

When the $W(O)(CHCMe_3)(OCMe_3)_2L$ complexes decompose, phosphine oxide is the main product detectable by ^{31}P NMR. No organometallic product has been isolated from or identified in the resulting red-brown oil.

The best way to prepare $[W(O)(CHCMe_3)(OCMe_3)_2]_2$ is by reacting $[NEt_4]^+[Ta(CHCMe_3)Cl_4]^-$ (ref 19) with $W(O)(OCMe_3)_4$ in dichloromethane (eq 10).

$$\mathrm{W(O)(OCMe_3)_4 + [Ta(CHCMe_3)Cl_4]^- \rightarrow 0.5[W(O)(CHCMe_3)(OCMe_3)_2]_2 + [Ta(OCMe_3)_2Cl_4]^-} \tag{10}$$

$[W(O)(CHCMe_3)(OCMe_3)_2]_2$ is very soluble in pentane and therefore easily separated from $[NEt_4]^+[Ta(OCMe_3)_2Cl_4]^-$. It is an orange oil at 25 °C, a solid at −30 °C. It can be sublimed (50 °C, 1 μm) onto a dry-ice cold finger, but only 5–10% of it survives. It decomposes readily when very pure but is more stable in the presence of impurities, especially $W(O)(OCMe_3)_4$. Typically a yellow solution of $[W(O)(CHCMe_3)(OCMe_3)_2]_2$ in benzene changes to blue-brown in about 10 min, and a dark oil comes out of solution. $[W(O)(CHCMe_3)(OCMe_3)_2]_2$ also is the major component of the mixture of products from the reaction between $Ta(CHCMe_3)Cl_3(dmpe)$ or $Ta(CHCMe_3)Cl_3(THF)_2$ and $W(O)(OCMe_3)_4$. The major tantalum-containing product in the first case is a polymer containing *tert*-butoxide and DMPE (cf. the polymeric form of $Ta(CHCMe_3)Cl_3(DMPE)$[11]), while in the second case it is white, pentane-soluble $Ta(OCMe_3)_3Cl_2(THF)$.

A difficult cryoscopic molecular weight determination of $[W(O)(CHCMe_3)(OCMe_3)_2]_2$ in cyclohexane gave a value between that expected for a monomer (417) and that expected for a dimer (834). Since its ^1H NMR spectrum shows three *tert*-butyl resonances, we believe this molecule

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[16] Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.

[17] Spivack, B.; Dori, Z. *Coord. Chem. Rev.* **1975**, *17*, 99–136.

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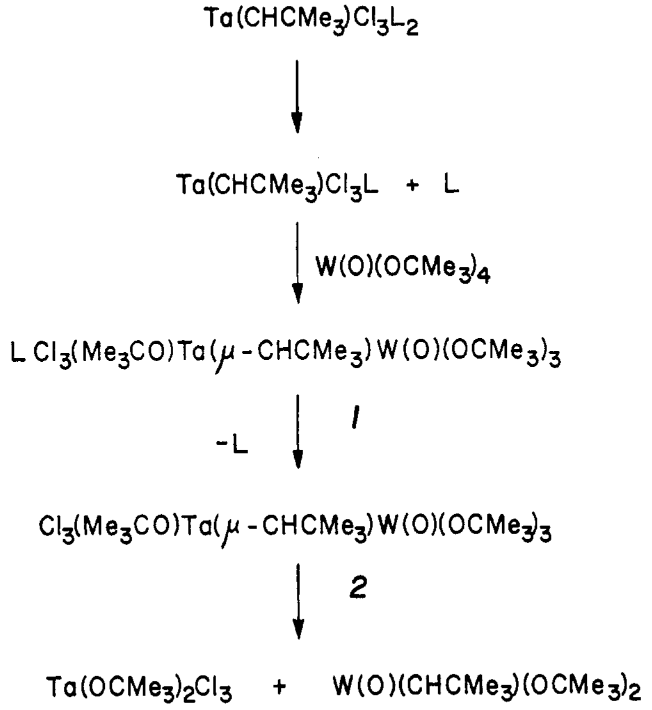
[19] Sturgeoff, L., unpublished results.

Scheme I. A Reasonable Mechanism for Neopentylidene Ligand Transfer



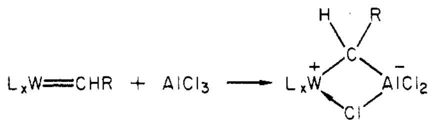
is dimeric. Its $\nu_{W=O}$ peak is located at 940 cm^{-1}. Since this is not much lower than $\nu_{W=O}$ in $W(O)(CHCMe_3)(OCMe_3)_2(PMe_2Ph)$ (949 cm^{-1}) or $W(O)(CHCMe_3)(S_2CNMe_2)_2$ (950 cm^{-1}), we cannot say for certain which of the two plausible structures shown in Figure 2 is more likely.

Discussion

A reasonable mechanism for transfer of a neopentylidene ligand from tantalum to tungsten is shown in Scheme I. Phosphine ligands in $Ta(CHCMe_3)Cl_3L_2$ are known to be labile.[11] A *tert*-butoxide ligand in $W(O)(OCMe_3)_4$ therefore has the opportunity to bridge between tungsten and tantalum. Subsequent transfer to tungsten could yield a species having a μ-neopentylidene ligand (1, Scheme I). Subsequent loss of L followed by transfer of a second *tert*-butoxide would yield $Ta(OCMe_3)_2Cl_3$ and $W(O)(CHCMe_3)(OCMe_3)_2$. When L = THF or Cl^- the reaction stops at this point. When L = a tertiary phosphine two more *tert*-butoxide ligands transfer to tungsten in exchange for two chlorides. The reason why further exchange occurs when L = PR_3 is not clear. Part of the reason may be the fact that L is relatively nonlabile in $W(O)(CHCMe_3)Cl_2L_2$ and that $W(O)(CHCMe_3)Cl_2L_2$ is relatively insoluble. We cannot exclude the possibility that the oxo ligand bridges the two metals at some point, but feel that chloride or *tert*-butoxide ligands may have more readily accessible electron pairs.

The oxo neopentylidene complexes appear to be related to the well-known dioxotungsten(VI) complexes;[12] i.e., the alkylidene ligand can be viewed as a dianion.[2] The oxo ligand is a powerful π-electron donor which uses two metal t_{2g} orbitals to form what amounts to a triple bond.[12] In an octahedral complex only one t_{2g} orbital remains for forming a π bond between tungsten and carbon. Therefore the alkylidene ligand should prefer to occupy the position cis to the oxo ligand and its β-carbon atom should lie in the $W(O)(C_\alpha)$ plane. The alkylidene ligand is not distorted by donation of electron density from the C–H_α bond to the metal, a phenomenon which has been observed in several tantalum complexes.[10a–c] A likely explanation is that donation of C–H_α electron density from a neopentylidene ligand and π-electron density from the oxo ligand occur under similar circumstances, but in a competitive situation a free electron pair from the oxo ligand is simply donated more readily. None of the above considerations can help explain why the *tert*-butyl group points toward the oxo ligand in the two complexes whose structures are known. However, the isomer in which the *tert*-butyl group points away from the oxo ligand had been postulated several times in this work. There is no obvious reason why it should not be present, or even favored, in some systems.

Cationic species are important types of oxo alkylidene complexes since they appear to be more stable toward bimolecular decomposition to give $Me_3CHC{=}CHCMe_3$ than neutral complexes. This may simply be due to Coulombic forces. But since the only cations which we have been able to prepare contain aluminate anions, less obvious phenomena may be responsible for their stability. For example, the aluminate could bind to the metal (thereby blocking two coordination positions) or it could "protect" the alkylidene ligand by binding to it as shown in eq 11 (cf. $Cp_2\overline{TiCH_2AlCl_2Cl}$[20]). The cationic complexes are especially good olefin metathesis catalysts,[21] possibly in part because intermediate alkylidene complexes are also more stable than their neutral analogues toward chain termination by bimolecular decomposition.

 (11)

Future publications will be aimed at answering the question as to whether other π-bonding ligands can be used in place of the oxo ligand, or whether other monoanionic ligands such as alkoxides, which also show some tendency to donate π-electron density to the metal, can take the place of a single powerful π-electron donor.

Experimental Section

$W(O)Cl_4$ was prepared as reported in the literature[22] except the product was sublimed at 95 °C (5 μm). $Ta(CHCMe_3)Cl_3(PMe_3)_2$, $Ta(CHCMe_3)Cl_3(PMe_2Ph)_2$, $Ta(CHCMe_3)Cl_3(THF)_2$, and $Ta(CHCMe_3)Cl_3(DMPE)$ were prepared as reported in the literature.[11] $AlMe_3$, WO_3, S_2Cl_2, $AgPF_6$, and $TlBF_4$ were purchased and used as received. NEt_4Cl and NaS_2CNMe_2 were purchased in hydrated form and were dehydrated by heating in vacuo (NEt_4Cl, 60 °C for 25 h; NaS_2CNMe_2, 90 °C for 30 h). Lithium *tert*-butoxide was prepared in pentane from butyllithium and *tert*-butyl alcohol and was recrystallized in pentane or sublimed before use. ^{19}F NMR spectra were recorded at 84.26 MHz and referenced to external hexafluorobenzene (162.9 ppm). ^1H and ^{13}C NMR data are referenced to Me_4Si and ^{31}P NMR data to external phosphoric acid. All spectra were recorded at 25–30 °C unless otherwise noted.

Preparation of $W(O)(OCMe_3)_4$. A solution of $LiOCMe_3$ (18.74 g, 0.23 mol) dissolved in 100 mL of THF was added dropwise to a solution of $W(O)Cl_4$ (20.0 g, 0.059 mol) dissolved in 10 mL of THF at 0 °C ($W(O)Cl_4$ should be added to THF very slowly as much heat is evolved). During the addition of $LiOCMe_3$ to $W(O)Cl_4$, the color of the reaction mixture changes from orange to blue to yellow, and LiCl precipitates. The reaction mixture was warmed to room temperature and stirred for 0.5 h and the THF was removed in vacuo. The off-white reaction solids were sublimed at 60 °C (5 μm) for 12 h to give 19.0 g (66%) of pale-yellow, crystalline $W(O)(OCMe_3)_4$. Lower yields are obtained

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[22] Funk, H.; Weiss, W.; Mohaupt, G. *Z. Anorg. Chem.* **1960**, *304*, 238–240.

when LiOCMe$_3$ is added at 25 °C. ^{1}H NMR (C$_6$D$_6$) 1.43 ppm (CMe$_3$); IR (Nujol) 940 cm^{-1} (br s, $\nu_{W=O}$).

Preparation of W(O)(CHCMe$_3$)Cl$_2$(PMe$_3$)$_2$. Ta(CHCMe$_3$)Cl$_3$(PMe$_3$)$_2$ (4.0 g, 7.85 mmol) and W(O)(OCMe$_3$)$_4$ (3.86 g, 7.85 mmol) were mixed together in 30 mL of ether/pentane (2:1). The solution turned deep red. Yellow crystals of the product formed on the walls of the flask during the next 12 h. The product was collected by filtration and washed with pentane. A second crop was obtained after refrigerating the mother liquors at −30 °C for 4 h; total yield 3.21 g (83%).

^{1}H NMR (C$_6$D$_6$) 11.89 (t, 1, $^3J_{HP}$ = 4.0 Hz, C*H*CMe$_3$), 1.44 (t, 18, $^2J_{HP}$ = 4.9 Hz, PMe$_3$), 1.18 ppm (s, 9, CHC*Me*$_3$); ^{13}C NMR (C$_6$D$_6$, gated proton decoupled) 319 (dt, J_{CH} = 121 Hz, $^2J_{CP}$ = 9.9 Hz, *C*HCMe$_3$), 45.5 (s, CH*C*Me$_3$), 33.6 (q, J_{CH} = 123 Hz, CHC*Me*$_3$), 15.9 ppm (qt, J_{CH} = 130 Hz, J_{CP} = 15.4 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) −5.3 ppm (J_{PW} = 334 Hz); IR (Nujol) 971 cm^{-1} (s, $\nu_{W=O}$). Anal. Calcd for WC$_{11}$H$_{28}$Cl$_2$OP$_2$: C, 26.80; H, 5.72. Found: C, 26.90; H, 5.99.

Preparation of W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$)$_2$. A solution of W(O)(OCMe$_3$)$_4$ (15.0 g, 31 mmol) in 100 mL of pentane was cooled to −30 °C. Ta(CHCMe$_3$)Cl$_3$(PEt$_3$)$_2$ (18.1 g, 31 mmol) was added to this solution as a solid. The mixture was stirred until all solid dissolved, and the resulting solution was treated as in the previous preparation; total yield 12.41 g (71%). W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$)$_2$ is easily recrystallized from ether/pentane.

^{1}H NMR (C$_6$D$_6$) 12.04 (t, 1, $^3J_{HP}$ = 3.4 Hz, C*H*CMe$_3$), 1.97 (dm, 12, $^2J_{HP}$ = 34 Hz, PC*H*$_2$CH$_3$), 1.27 (s, 9, CHC*Me*$_3$), 0.98 ppm (tt, 18, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 7.9 Hz, PCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$, gated proton decoupled) 313 (dt, J_{CH} = 126 Hz, $^2J_{CP}$ = 10.3 Hz, J_{CW} = 148 Hz, *C*HCMe$_3$), 45.8 (s, CH*C*Me$_3$), 33.6 (q, J_{CH} = 128 Hz, CHC*Me*$_3$), 17.4 (tt, J_{CH} = 134 Hz, J_{CP} = 13.9 Hz, P*C*H$_2$CH$_3$), 7.6 ppm (q, J_{CH} = 128 Hz, PCH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$) 19.8 ppm (J_{PW} = 320 Hz); IR (Nujol) 969 cm^{-1} (s, sh, $\nu_{W=O}$); mol wt (cryoscopy in benzene) calcd, 577; found, 540. W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$)$_2$ does not conduct in CH$_2$Cl$_2$(10^{-3} M). Anal. Calcd for WC$_{17}$H$_{40}$Cl$_2$OP$_2$: C, 35.38; H, 6.99. Found: C, 35.40; H, 7.01.

[Ta(OCMe$_3$)$_4$Cl]$_2$ can be crystallized in high yield from the mother liquors after filtering off the product. Its ^{1}H NMR spectrum in C$_6$H$_6$ shows a peak at 1.47 ppm and its mass spectrum a peak ascribed to Ta(OCMe$_4$)$_4$$^+$ at 474 ppm.

Preparation of W(O)(CHCMe$_3$)Cl$_2$(PMe$_2$Ph)$_2$. W(O)(CHCMe$_3$)Cl$_2$(PMe$_2$Ph)$_2$ was prepared as described above for W(O)(CHCMe$_3$)Cl$_2$L$_2$ (L = PMe$_3$ and PEt$_3$); yield 73%.

^{1}H NMR (C$_6$D$_6$) 12.23 (t, 1, $^3J_{HP}$ = 3.4 Hz, C*H*CMe$_3$), 7.81, 7.32, and 7.17 (m, 10, P*Ph*), 2.09 (t, 6, $^2J_{HP}$ = 4.9 Hz, PMe), 2.07 (t, 6, $^2J_{HP}$ = 4.9 Hz, PMe), 0.96 ppm (s, 9, CHC*Me*$_3$); ^{13}C NMR (C$_6$D$_6$, gated proton decoupled) 320 (dt, J_{CH} = 117 Hz, $^2J_{CP}$ = 11.0 Hz, *C*HCMe$_3$), 128–131 (m, PP*h*), 45.6 (s, CH*C*Me$_3$), 32.8 (q, J_{CH} = 125 Hz, CHC*Me*$_3$), 15.7 (qt, J_{CH} = 132 Hz, J_{CP} = 22.0 Hz, PMe), 13.9 ppm (qt, J_{CH} = 132 Hz, J_{CP} = 19.8 Hz, PMe′); ^{31}P{^{1}H} NMR (C$_6$D$_6$) 1.4 ppm (J_{PW} = 334 Hz); IR (Nujol) 970 cm^{-1} (s, sh, $\nu_{W=O}$).

Preparation of W(O)(CHCMe$_3$)Br$_2$(PEt$_3$)$_2$. W(O)(CHCMe$_3$)Br$_2$(PEt$_3$)$_2$ was prepared as described for W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$)$_2$.

^{1}H NMR (C$_6$D$_6$) 12.10 (t, 1, $^3J_{HP}$ = 3.3 Hz, C*H*CMe$_3$), 2.14 (br m, 12, PC*H*$_2$CH$_3$), 1.21 (s, 9, CHC*Me*$_3$), 0.99 ppm (tt, 18, $^3J_{HH}$ = 8.1 Hz, $^3J_{HP}$ = 7.3 Hz, PCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$, gated proton decoupled) 312 (dt, J_{CH} = 125 Hz, $^2J_{CP}$ = 9.9 Hz, *C*HCMe$_3$), 46.3 (s, CH*C*Me$_3$), 33.2 (q, J_{CH} = 123 Hz, CHC*Me*$_3$), 18.7 (tt, J_{CH} = 130 Hz, J_{CP} = 14.3 Hz, P*C*H$_2$CH$_3$), 8.0 ppm (q, J_{CH} = 127 Hz, PCH$_2$*C*H$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) 12.7 ppm (J_{PW} = 297 Hz).

Preparation of W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$). W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$)$_2$ (2.65 g, 4.6 mmol) and PdCl$_2$(PhCN)$_2$ (0.88 g, 2.3 mmol) were stirred together in 30 mol toluene for 3 h. The reaction mixture was stirred with activated charcoal for 0.5 h and filtered, and the toluene was removed in vacuo. Pentane was added until crystals began forming. Yellow crystals of W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$) were collected until white needles of PdCl$_2$(PEt$_3$)$_2$ appeared. W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$) was recrystallized from toluene/pentane; total yield 1.67 g (80%).

^{1}H NMR (C$_6$D$_6$) 9.87 (d, 1, $^3J_{HP}$ = 3.3 Hz, C*H*CMe$_3$), 1.65 (m, 6, PC*H*$_2$CH$_3$), 1.24 (s, 9, CHC*Me*$_3$), 0.82 ppm (dt, 9, $^3J_{HH}$ = 7.72 Hz, $^3J_{HP}$ = 16.2, PCH$_2$C*H*$_3$); ^{13}C NMR (C$_6$D$_6$, gated proton decoupled) 295 (dd, J_{CH} = 115 Hz, $^2J_{CP}$ = 13 Hz, J_{CW} = 176 Hz, *C*HCMe$_3$), 45.4 (s, CH*C*Me$_3$), 31.2 (q, J_{CH} = 125 Hz, CHC*Me*$_3$), 17.4 (dt, J_{CH} = 132 Hz, J_{CP} = 29.3 Hz, P*C*H$_2$CH$_3$), 8.0 ppm (q, J_{CH} = 129 Hz, PCH$_2$*C*H$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) 40.9 ppm (J_{PW} = 364 Hz); IR (Nujol) 979 cm^{-1} (s, sh, $\nu_{W=O}$); mol wt (cryoscopy in benzene) calcd, 459; found, 440. Anal. Calcd for WC$_{11}$H$_{25}$Cl$_2$OP: C, 28.78; H, 5.49. Found: C, 29.08; H, 5.59.

Preparation of W(O)(CHCMe$_3$)Cl$_2$(PMe$_3$)(PhCN). W(O)(CHCMe$_3$)Cl$_2$(PMe$_3$)$_2$ (1.0 g, 2.0 mmol) and PdCl$_2$(PhCN)$_2$ (0.39 g, 1.0 mmol) were stirred together in 30 mL of ether for 1 h. At this time, the solution was dark yellow with a few solids present. The solids were filtered off, and the solvent was removed from the filtrate in vacuo. Ether (5 mL) was added to the oil, and the mixture was filtered. Addition of an equal volume of pentane caused yellow crystals to form. Cooling the solution to −30 °C gave a second crop; total yield 0.66 g (64%).

^{1}H NMR (C$_6$D$_6$) 10.02 (d, 1, $^3J_{HP}$ = 4 Hz, C*H*CMe$_3$), 6.7–7.1 (m, 5, *Ph*CN), 1.26 (d, 9, $^2J_{HP}$ = 11 Hz, PMe$_3$), 1.12 ppm (s, 9, CHC*Me*$_3$); ^{13}C NMR (C$_6$D$_6$, gated proton decoupled) 297 (dd, J_{CH} = 121 Hz, $^2J_{CP}$ = 13.7 Hz, *C*HCMe$_3$), 119–132 (m, *Ph*CN), 112 (s, PhCN), 45.3 (s, CH*C*Me$_3$), 31.1 (q, J_{CH} = 127 Hz, CHC*Me*$_3$), 16.2 ppm (dq, J_{CH} = 133 Hz, J_{CP} = 33 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) 9.32 ppm (J_{PW} = 386 Hz).

Preparation of W(O)(CHCMe$_3$)Cl$_2$(PMe$_3$)(THF). The above procedure was repeated, except the solvent was a mixture of 30 mL of ether and 5 mL of THF. W(O)(CHCMe$_3$)Cl$_2$(PMe$_3$)(THF) was recrystallized from toluene/pentane. THF can be removed in vacuo to give W(O)(CHCMe$_3$)Cl$_2$(PMe$_3$) which can be recrystallized from toluene/pentane.

^{1}H NMR of W(O)(CHCMe$_3$)Cl$_2$(PMe$_3$)(THF) (C$_6$D$_6$) 10.67 (d, 1, $^3J_{HP}$ = 4 Hz, C*H*CMe$_3$), 3.80 (m, 4, OC*H*$_2$CH$_2$), 1.45 (m, 4, OCH$_2$C*H*$_2$), 1.31 (d, 9, $^2J_{HP}$ = 11 Hz, PMe$_3$), 1.15 ppm (s, 9, CHC*Me*$_3$); ^{13}C NMR (C$_6$D$_6$, gated proton decoupled) 300 (dd, J_{CH} = 121 Hz, $^2J_{CP}$ = 13.7 Hz, *C*HCMe$_3$), 69.1 (t, J_{CH} = 147 Hz, O*C*H$_2$CH$_2$), 45.0 (s, CH*C*Me$_3$), 3.15 (g, J_{CH} = 125 Hz, CHC*Me*$_3$), 25.7 (t, J_{CH} = 131 Hz, OCH$_2$*C*H$_2$), 16.3 ppm (dq, J_{CH} = 129 Hz, J_{CP} = 33 Hz, PMe$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) 6.55 ppm (J_{PW} = 408 Hz). ^{1}H NMR of W(O)(CHCMe$_3$)Cl$_2$(PMe$_3$) (C$_6$D$_6$) 9.68 (d, 1, $^3J_{HP}$ = 4 Hz, C*H*CMe$_3$), 1.27 (d, 9, $^2J_{HP}$ = 10 Hz, PMe$_3$), 1.25 ppm (s, 9, CHC*Me*$_3$).

Preparation of W(O)(CHCMe$_3$)Cl$_2$(TMEDA). W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$)$_2$ (0.80 g, 1.4 mmol), PdCl$_2$(1.5 COD)(0.40 g, 1.4 mmol), and TMEDA (0.80 g, 7.0 mmol) were dissolved in 30 mL of toluene. After 2 days the reaction mixture was still yellow and homogeneous. The toluene was removed in vacuo. The crystalline residue was dissolved in ether, and two crops of white crystals were obtained by cooling this solution to −30 °C; yield 0.42 g (75%) of PdCl$_2$(PEt$_3$)$_2$. Pentane was added to the filtrate, and 0.62 g (95%) of W(O)(CHCMe$_3$)Cl$_2$(TMEDA) was collected after crystallization at −30 °C. This product is best recrystallized from ether/pentane. Since W(O)(CHCMe$_3$)Cl$_2$(TMEDA) is difficult to crystallize, it could not be obtained in pure form from the reaction between W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$)$_2$ and PdCl$_2$(PhCN)$_2$ in the presence of TMEDA.

^{1}H NMR (C$_6$D$_6$) 11.02 (s, 1, C*H*CMe$_3$), 2.71, 2.54, 2.48, and 2.41 (s, 3:3:3:3, NCH$_3$), 2.63 and 1.74 (m, 2:2 $^3J_{HH}$ = 14 Hz, NCH$_2$), 1.33 ppm (s, 9, CHC*Me*$_3$); ^{13}C NMR (C$_6$D$_6$) 300 (d, J_{CH} = 127 Hz, J_{CW} = 174 Hz, *C*HCMe$_3$), 61.4 (t, J_{CH} = 137 Hz, NCH$_2$), 58.1 (t, J_{CH} = 140 Hz, NCH$_2$), 58.1 (q, J_{CH} = 143 Hz, NCH$_3$), 56.8 (q, J_{CH} = 133 Hz, NCH$_3$), 51.7 (q, J_{CH} = 137 Hz, NCH$_3$), 48.1 (q, J_{CH} = 141 Hz, NCH$_3$), 43.6 (s, CH*C*Me$_3$), 33.3 ppm (q, J_{CH} = 125 Hz, (CHC*Me*$_3$). Anal. Calcd for WC$_{11}$H$_{26}$N$_2$Cl$_2$O: C, 28.90; H, 5.73. Found: C, 28.94; H, 5.83.

Preparation of [W(O)(CHCMe$_3$)Cl(PEt$_3$)$_2$]$^+$(AlCl$_4$$^-$). Freshly sublimed AlCl$_3$ (0.23 g, 1.7 mmol) was added to a stirred solution of W(O)(CHCMe$_3$)Cl$_2$(PEt$_3$)$_2$ (1.0 g, 1.7 mmol) in 25 mL of CH$_2$Cl$_2$. The solution remained yellow and homogeneous. The volume of the reaction mixture was halved in vacuo. An equal volume of pentane was added, and yellow flakes of [W(O)(CHCMe$_3$)Cl(PEt$_3$)$_2$]$^+$(AlCl$_4$$^-$) fell from solution; total yield 1.15 g (95%). This product is very sensitive toward ether and THF and must be prepared and stored in an atmosphere absolutely free of such solvents.

^{1}H NMR (CDCl$_3$) 10.60 (t, 1, $^3J_{HP}$ = 1.5 Hz, C*H*CMe$_3$), 2.13 (m, 12, PC*H*$_2$CH$_3$), 1.35 (s, 9, CHC*Me*$_3$), 1.22 ppm (dt, 18, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 17.7 Hz, PCH$_2$C*H*$_3$); ^{13}C NMR (CD$_2$Cl$_2$, gated proton decoupled) 313 (dt, J_{CH} = 127 Hz, $^2J_{CP}$ = 7.8 Hz, J_{CW} = 156 Hz, *C*HCMe$_3$), 48.1 (s, CH*C*Me$_3$), 31.8 (q, J_{CH} = 127 Hz,

$\mathrm{CHC}\mathit{Me}_3$), 16.8 (tt, J_{CH} = 129 Hz, J_{CP} = 14.7 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 8.2 ppm (q, J_{CH} = 127 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$) 42.3 ppm (J_{PW} = 298 Hz); IR (Nujol) 985 $\mathrm{cm^{-1}}$ (s, sh, $\nu_{\mathrm{W{=}O}}$); equivalent conductivity (10^{-3} M in $\mathrm{CH_2Cl_2}$) 34. Anal. Calcd for $\mathrm{WC_{17}H_{40}OCl_5P_2Al}$: C, 28.74, H, 5.67. Found: C, 28.80; H, 5.92.

Preparation of $[\mathrm{W(O)(CHCMe_3)(PEt_3)_2}]^{2+}(\mathrm{AlCl_4}^-)_2$. Freshly sublimed $\mathrm{AlCl_3}$ (0.46 g, 3.5 mmol) was added to a stirred solution of $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2}$ (1.0 g, 1.7 mmol) in 25 mL of $\mathrm{CH_2Cl_2}$. The solution turned orange. Traces of solids were filtered off, and the volume of the filtrate was halved in vacuo. An equal volume of pentane was added, and orange flakes of $[\mathrm{W(O)(CHCMe_3)(PEt_3)_2}]^{2+}(\mathrm{AlCl_4}^-)_2$ fell from solution; total yield 1.45 g (99%). The product is very sensitive towards bases such as THF and ether and must be prepared and stored in an atmosphere free of such solvents.

^{1}H NMR ($\mathrm{CDCl_3}$) 10.47 (br s, 1, J_{HW} = 9 Hz, $\mathrm{C}\mathit{H}\mathrm{CMe_3}$), 2.21 (m, 12, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$), 1.40 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 1.26 ppm (dt, 18, $^3J_{\mathrm{HH}}$ = 7.3 Hz, $^3J_{\mathrm{HP}}$ = 17.7 Hz, $\mathrm{PCH_2C}\mathit{H}_3$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$, gated proton decoupled) 317 (dt, J_{CH} = 125 Hz, $^2J_{\mathrm{CP}}$ = 5.9 Hz, $\mathit{C}\mathrm{HCMe_3}$), 52.8 (s, $\mathrm{CH}\mathit{C}\mathrm{Me_3}$), 32.2 (q, J_{CH} = 131 Hz, $\mathrm{CHC}\mathit{Me}_3$), 17.5 (tt, J_{CH} = 129 Hz, J_{CP} = 14.7 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 9.0 ppm (q, J_{CH} = 129 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$) 49.5 ppm (J_{PW} = 259 Hz); IR (Nujol) 985 $\mathrm{cm^{-1}}$ (s, sh, $\nu_{\mathrm{W{=}O}}$); equivalent conductivity (10^{-3} M in $\mathrm{CH_2Cl_2}$) 64. Anal. Calcd for $\mathrm{WC_{17}H_{40}OCl_8P_2Al_2}$: C, 24.20; H, 4.78. Found: C, 24.25; H, 5.03.

Preparation of $[\mathrm{W(O)(CHCMe_3)(Me)(PEt_3)_2}]^+(\mathrm{AlMe_2Cl_2}^-)$. $\mathrm{AlMe_3}$ (166 μL, 1.73 mmol) was added to a solution of $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2}$ (1.0 g, 1.73 mmol) in 25 mL of $\mathrm{CH_2Cl_2}$ at −30 °C. The yellow reaction mixture was filtered, and the volume of the filtrate was reduced in vacuo to about 10 mL. One volume of pentane was added and flaky, pale-yellow crystals formed; total yield 1.03 g (92%). $[\mathrm{W(O)(CHCMe_3)(Me)(PEt_3)_2}]^+(\mathrm{AlMe_2Cl_2}^-)$ must be stored at −30 °C in the absence of Lewis base solvents. It decomposes readily at 25 °C.

^{1}H NMR of $[\mathrm{W(O)(CHCMe_3)(Me)(PEt_3)_2}]^+(\mathrm{AlMe_2Cl_2}^-)$ ($\mathrm{CDCl_3}$, 273 K) 9.50 (br s, 1, $\mathrm{C}\mathit{H}\mathrm{CMe_3}$), 1.97 (m, 12, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$), 1.27 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 1.14 (tt, 18, $^2J_{\mathrm{HH}}$ = 7.3 Hz, $^3J_{\mathrm{HP}}$ = 7.9 Hz, $\mathrm{PCH_2C}\mathit{H}_3$), 0.90 (t, 3, $^3J_{\mathrm{CP}}$ = 16.2 Hz, $\mathrm{WC}\mathit{H}_3$), −0.70 ppm (s, 6, $\mathrm{Al}\mathit{Me}_2$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 273 K, gated proton decoupled) 314 (dt, J_{CH} = 108 Hz, $^2J_{\mathrm{CP}}$ = 8.3 Hz, $\mathit{C}\mathrm{HCMe_3}$), 47.2 (s, $\mathrm{CH}\mathit{C}\mathrm{Me_3}$), 38.3 (qt, J_{CH} = 120 Hz, $^2J_{\mathrm{CP}}$ = 8.3 Hz, $\mathrm{W}\mathit{C}\mathrm{H_3}$), 32.0 (q, J_{CH} = 129 Hz, $\mathrm{CHC}\mathit{Me}_3$), 16.3 (tt, J_{CH} = 127 Hz, J_{CP} = 14.5 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 8.0 ppm (q, J_{CH} = 127 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$) 38.7 ppm (J_{PW} = 281 Hz); equivalent conductivity (10^{-3} M in $\mathrm{CH_2Cl_2}$) 35.

Preparation of $\mathrm{W(O)(CHCMe_3)MeCl(TMEDA)}$. TMEDA (0.28 g, 2.5 mmol) was added to a stirred solution of $[\mathrm{W(O)(CHCMe_3)(Me)(PEt_3)_2}]^+(\mathrm{AlMe_2Cl_2}^-)$ (0.80 g, 1.2 mmol) in 10 mL of $\mathrm{CH_2Cl_2}$ at −30 °C. The $\mathrm{CH_2Cl_2}$ was removed in vacuo, and the remaining yellow oil was extracted with ether/pentane; white crystals of $\mathrm{AlMe_2Cl{\cdot}TMEDA}$ were left behind. The product crystallized reluctantly from pentane/ether; total yield 0.42 g (78%).

^{1}H NMR ($\mathrm{C_6D_6}$) 10.42 (s, 1, $\mathrm{C}\mathit{H}\mathrm{CMe_3}$), 2.56, 2.49, 2.38, and 2.24 (s, 3:3:3:3, $\mathrm{NCH_3}$), 1.65 (t, 2, $^2J_{\mathrm{HH}}$ = 12.8 Hz, $\mathrm{NCH_2}$), 1.35 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 1.17 ppm (s, 3 J_{HW} = 9.8 Hz, $\mathrm{WCH_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$, gated proton decoupled) 286 (d, J_{CH} = 119 Hz, J_{CW} = 186 Hz, $\mathit{C}\mathrm{HCMe_3}$), 59.6 (t, J_{CH} = 136 Hz, $\mathrm{NCH_2}$), 58.9 (t, J_{CH} = 133 Hz, $\mathrm{NCH_2}$), 55.0, 53.9, 50.2, and 47.4 (q, J_{CH} = 139 Hz, $\mathrm{NCH_3}$), 42.6 (s, $\mathrm{CH}\mathit{C}\mathrm{Me_3}$), 32.9 (q, J_{CH} = 125 Hz, $\mathrm{CHC}\mathit{Me}_3$), 19.9 ppm (q, J_{CH} = 122 Hz, J_{CW} = 117 Hz, $\mathrm{WCH_3}$); IR (Nujol) 960 $\mathrm{cm^{-1}}$ (s, sh, $\nu_{\mathrm{W{=}O}}$). Anal. Calcd for $\mathrm{WC_{12}H_{29}N_2OCl}$: C, 33.04; H, 6.69. Found: C, 33.57; H, 6.82.

Preparation of $[\mathrm{W(O)(CHCMe_3)(AlMe_4)(PEt_3)_2}]^+(\mathrm{AlMe_2Cl_2}^-)$. $\mathrm{AlMe_3}$ (133 μL, 1.39 mmol) was added to a solution of $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2}$ (0.40 g, 0.69 mmol) in 20 mL of $\mathrm{CH_2Cl_2}$ at −30 °C. The pale-orange solution was filtered to remove traces of solids, and the volume of the filtrate was reduced in vacuo to 5 mL. One volume of pentane was added, and yellow crystals fell from solution; total yield 0.38 g (76%). The product must be stored at −30 °C in an atmosphere free of Lewis base solvents.

^{1}H NMR ($\mathrm{CDCl_3}$, 247 K) 9.44 (br s, 1, $\mathrm{C}\mathit{H}\mathrm{CMe_3}$), 2.04 (m, 12, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$), 1.30 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 1.17 (tt, 18, $^3J_{\mathrm{HH}}$ = 7.3 Hz, $^3J_{\mathrm{HP}}$ = 7.9 Hz, $\mathrm{PCH_2C}\mathit{H}_3$), −0.70 ppm (s, 6, $\mathrm{Al}\mathit{Me}_2$); ^{13}C NMR ($\mathrm{CDCl_3}$, 273 K, gated proton decoupled) 315 (dt, J_{CH} = 116 Hz, $^2J_{\mathrm{CP}}$ = 7.7 Hz, $\mathit{C}\mathrm{HCMe_3}$), 48.3 (s, $\mathrm{CH}\mathit{C}\mathrm{Me_3}$), 32.0 (q, J_{CH} = 127 Hz, $\mathrm{CHC}\mathit{Me}_3$), 16.2 (tt, J_{CH} = 127 Hz, J_{CP} = 14.3 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 8.3 (q, J_{CH} = 127 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$), −5.9 ppm (br s, $\mathrm{AlMe_2}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 273 K) 38.6 ppm (J_{PW} = 283 Hz); equivalent conductivity 10^{-3} M in $\mathrm{CH_2Cl_2}$) 39.

Preparation of $[\mathrm{W(O)(CHCMe_3)Cl(PEt_3)}]^+(\mathrm{AlCl_4}^-)$. Freshly sublimed $\mathrm{AlCl_3}$ (0.10 g, 0.76 mmol) was added to a stirred solution of $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)}$ (0.35 g, 0.76 mmol) in 2 mL of $\mathrm{CH_2Cl_2}$. The color changed immediately from yellow to orange. The reaction mixture was filtered, and the $\mathrm{CH_2Cl_2}$ removed in vacuo. This orange oil was extracted into toluene, and pentane was added until a slight haze formed. The product crystallized as orange-red cubes at −30 °C. The product must be prepared and stored in the absence of Lewis bases.

^{1}H NMR ($\mathrm{CDCl_3}$) 9.10 (br s, 1, $\mathrm{C}\mathit{H}\mathrm{CMe_3}$), 1.72 (m, 6, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$), 1.06 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 0.72 ppm (dt, 9, $^3J_{\mathrm{HH}}$ = 7.32 Hz, $^3J_{\mathrm{HP}}$ = 17.1 Hz, $\mathrm{PCH_2C}\mathit{H}_3$); ^{13}C NMR ($\mathrm{CDCl_3}$, gated proton decoupled) 302 (dd, J_{CH} = 109 Hz, $^2J_{\mathrm{CP}}$ = 11.7 Hz, J_{CW} = 162 Hz, $\mathit{C}\mathrm{HCMe_3}$), 49.9 (s, $\mathrm{CH}\mathit{C}\mathrm{Me_3}$), 31.5 (q, J_{CH} = 129 Hz, $\mathrm{CHC}\mathit{Me}_3$), 17.7 (tt, J_{CH} = 129 Hz, J_{CP} = 31.3 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_3}$), 8.5 ppm (dq, J_{CH} = 127 Hz, $^2J_{\mathrm{CP}}$ = 3.9 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$) 45.8 ppm (J_{PW} = 308 Hz); IR (Nujol) 946 $\mathrm{cm^{-1}}$ (s, sh, $\nu_{\mathrm{W{=}O}}$); equivalent conductivity (10^{-3} M in $\mathrm{CH_2Cl_2}$) 33. Anal. Calcd for $\mathrm{WC_{11}H_{25}OCl_5PAl}$: C, 22.30; H, 4.25. Found: C, 22.48; H, 4.30.

Preparation of $\mathrm{W(O)(CHCMe_3)(Cl)(F)(PEt_3)_2}$. $\mathrm{TlBF_4}$ (0.25 g, 0.87 mmol) dissolved in 10 mL of acetonitrile was added dropwise to a stirred solution of $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2}$ (0.50 g, 0.87 mmol) and $\mathrm{PEt_3}$ (0.20 g, 1.73 mmol) in 10 mL of $\mathrm{CH_3CN}$. A white precipitate (TlCl) was filtered off, and the solvent was removed in vacuo. Ether was added and the solution filtered again to remove additional solids. Ether was removed in vacuo to yield a yellow, oily solid which is ca. 60% $\mathrm{W(O)(CHCMe_3)(Cl)(F)(PEt_3)_2}$ and ca. 40% $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2}$.

^{1}H NMR of $\mathrm{W(O)(CHCMe_3)(Cl)(F)(PEt_3)_2}$ ($\mathrm{C_6D_6}$) 11.56 (dt, 1, $^3J_{\mathrm{HP}}$ = 2.8 Hz $^3J_{\mathrm{HF}}$ = 14.7 Hz, $\mathrm{C}\mathit{H}\mathrm{CMe_3}$), 1.76 (m, 12, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$), 1.33 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 0.93 ppm (tt, $^3J_{\mathrm{HH}}$ = 7.3 Hz, $^3J_{\mathrm{HP}}$ = 7.9 Hz, $\mathrm{PCH_2C}\mathit{H}_3$); ^{13}C NMR ($\mathrm{C_6D_6}$) 310 ppm ($\mathit{C}\mathrm{HCMe_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$) 23.1 ppm (d, $^2J_{\mathrm{PF}}$ = 48.9 Hz, J_{PW} = 325 Hz); ^{19}F NMR ($\mathrm{C_6D_6}$) 226 ppm (dt, J_{FP} = 48.9 Hz, J_{FH} = 14.7 Hz).

Preparation of $\mathrm{W(O)(CHCMe_3)(S_2CNMe_2)_2}$. $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2}$ (1.0 g, 1.73 mmol) and $\mathrm{NaS_2CNMe_2}$ (0.50 g, 3.46 mmol) were stirred in 30 mL of THF for 2 days. The NaCl was filtered off, and the solvent was removed in vacuo. The yellow crystalline product was recrystallized from toluene/pentane; total yield 0.95 g (98%).

^{1}H NMR ($\mathrm{C_6D_6}$) 12.00 (s, 1, $\mathrm{C}\mathit{H}\mathrm{CMe_3}$), 2.45 (s, 12, NMe), 1.59 ppm (s, 9, $\mathrm{CHC}\mathit{Me}_3$); ^{13}C NMR ($\mathrm{C_6D_6}$, gated proton decoupled) 303 (d, J_{CH} = 127 Hz, $\mathit{C}\mathrm{HCMe_3}$), 43.6 (s, $\mathrm{CH}\mathit{C}\mathrm{Me_3}$), 39.9 (q, J_{CH} = 141 Hz, $\mathrm{NCH_3}$), 34.1 ppm (q, J_{CH} = 121 Hz, $\mathrm{CHC}\mathit{Me}_3$); IR (Nujol) 950 $\mathrm{cm^{-1}}$ (s, sh, $\nu_{\mathrm{W{=}O}}$). Anal. Calcd for $\mathrm{WC_{11}H_{22}N_2OS_4}$: C, 25.88; H, 4.35. Found: C, 26.35; H, 4.39.

Preparation of $\mathrm{W(O)(CHCMe_3)(OCMe_3)_2(PMe_3)}$. $\mathrm{LiOCMe_3}$ (0.57 g, 7.10 mmol) was added to $\mathrm{W(O)(CHCMe_3)Cl_2(PMe_3)_2}$ (1.75 g, 3.55 mmol) in 30 mL of cold ether (−30 °C). No reaction was observed until the reaction mixture had warmed to room temperature. The solvent was removed in vacuo. The resulting yellow oil was extracted with pentane and the LiCl was filtered off. The filtrate was cooled to −30 °C to give 1.25 g (65%) of yellow crystals after 12 h. The product decomposes readily at 25 °C, both in solution and as a solid.

^{1}H NMR of $\mathrm{W(O)(CHCMe_3)(OCMe_3)_2(PMe_3)}$ (toluene-d_8) major isomer 9.64 (br s, 1, $\mathrm{C}\mathit{H}\mathrm{CMe_3}$), 2.14 (s, 18, $\mathrm{OC}\mathit{Me}_3$), 1.18 ppm (s, 9 $\mathrm{CHC}\mathit{Me}_3$). The resonance for $\mathrm{PMe_3}$ is obscured. The resonance for H_α of the minor isomer is found at ppm 10.81. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 223 K) major isomer 267 (d, $^2J_{\mathrm{CP}}$ = 13.7 Hz, $\mathit{C}\mathrm{HCMe_3}$), 75.0 (s, $\mathrm{O}\mathit{C}\mathrm{Me_3}$), 42.2 (s, $\mathrm{CH}\mathit{C}\mathrm{Me_3}$), 33.6 (s, $\mathrm{CHC}\mathit{Me}_3$), 32.5 (s, $\mathrm{OC}\mathit{Me}_3$), 14.4 ppm (d, J_{CP} = 23.8 Hz, $\mathrm{PMe_3}$); minor isomer 272 ppm (d, $^2J_{\mathrm{CP}}$ = 7.3 Hz, $\mathit{C}\mathrm{HCMe_3}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 213 K) major isomer 21.9 ppm (J_{PW} = 320 Hz); minor isomer 23.4 ppm (J_{PW} = 317 Hz); major isomer/minor isomer $\simeq$ 4.

Preparation of $\mathrm{W(O)(CHCMe_3)(OCMe_3)_2(PEt_3)}$. $\mathrm{LiOCMe_3}$ (0.55 g, 6.93 mmol) dissolved in 20 mL ether was added to $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2}$ (2.0 g, 3.46 mmol) in 25 mL of ether at room temperature. The reaction was worked up as in the previous preparation. Crystals were observed, but they redissolved before they could be isolated. The product is an oil at room temperature and turns red after only a few minutes.

^{1}H NMR (toluene-d_8, 243 K) 9.71 ppm (d, 1, $^3J_{\mathrm{HP}} = 2.4$ Hz, $\mathrm{C}H\mathrm{CMe_3}$), 1.59 (s, 9, $\mathrm{OC}Me_3$), 1.56 (s, 9, $\mathrm{OC}Me_3$), 1.35 (s, 9, $\mathrm{CHC}Me_3$), 0.82 (dt, 9, $^3J_{\mathrm{HH}} = 7.32$ Hz, $^3J_{\mathrm{HP}} = 14.7$ Hz, $\mathrm{PCH_2}CH_3$). The minor isomer has an H_α resonance at ppm 10.58 (d, $^3J_{\mathrm{HP}} =$ 4.3 Hz). ^{13}C NMR (toluene-d_8, 253 K, gated proton decoupled) major isomer 268 (dd, $J_{\mathrm{CH}} = 119$ Hz, $^2J_{\mathrm{CP}} = 6.6$ Hz, $C\mathrm{HCMe_3}$), 77.1 (s, $\mathrm{O}C\mathrm{Me_3}$), 75.0 (s, $\mathrm{O}C\mathrm{Me_3}$), 42.2 (s, $\mathrm{CH}C\mathrm{Me_3}$), 34.2 (q, J_{CH} = 125 Hz, $\mathrm{CHC}Me_3$), 32.7 and 31.9 (q, $J_{\mathrm{CH}} = 127$ Hz, $\mathrm{OC}Me_3$). 16.5 (dt, $J_{\mathrm{CH}} = 125$ Hz, $J_{\mathrm{CP}} = 19.8$ Hz, $\mathrm{P}C\mathrm{H_2CH_3}$), 8.5 ppm (q, $J_{\mathrm{CH}} = 125$ Hz, $\mathrm{PCH_2}C\mathrm{H_3}$); ^{31}P{^{1}H} NMR (toluene-d_8, 253 K) major isomer 31.3 ppm ($J_{\mathrm{PW}} = 305$ Hz); minor isomer 29.3 ppm (J_{PW} = 298 Hz); major isomer/minor isomer $\simeq$ 6.

Preparation of W(O)(CHCMe$_3$)(OCMe$_3$)$_2$(PMe$_2$Ph). This complex was prepared in a manner analogous to the preceding two from $\mathrm{LiOCMe_3}$ (0.52 g, 6.5 mmol) in 20 mL of ether and $\mathrm{W(O)(CHCMe_3)Cl_2(PMe_2Ph)_2}$ (2.0 g, 3.24 mmol) in 30 mL of ether at room temperature. The product is a thermally sensitive yellow oil.

^{1}H NMR (toluene-d_8, 248 K) major isomer 9.77 (br s, 1, J_{HW} = 9.8 Hz, $\mathrm{C}H\mathrm{CMe_3}$), 6.99–7.44 (m, 5, $\mathrm{P}Ph$), 1.47 (s, 9, $\mathrm{OC}Me_3$), 1.45 (s, 9, $\mathrm{OCMe'_3}$) 1.29 (d, 6, $^2J_{\mathrm{HP}} = 13$ Hz, $\mathrm{PMe_2}$), 1.24 ppm (s, 9, $\mathrm{CHC}Me_3$). The minor isomer has its H_α resonance at ppm 10.64. ^{13}C NMR (toluene-d_8, 223 K, gated proton decoupled) major isomer 269 (dd, $J_{\mathrm{CH}} = 119$ Hz, $^2J_{\mathrm{CP}} = 7.8$ Hz, $J_{\mathrm{CW}} = 186$ Hz, $C\mathrm{HCMe_3}$), 124–135 (m, $\mathrm{P}Ph$), 77.2 (s, $\mathrm{O}C\mathrm{Me_3}$), 74.9 (s, $\mathrm{O}C\mathrm{Me_3}$), 42.4 (s, $\mathrm{CH}C\mathrm{Me_3}$), 33.5 (q, $J_{\mathrm{CH}} = 125$ Hz, $\mathrm{CHC}Me_3$), 32.1 (q, J_{CH} = 123 Hz, $\mathrm{OC}Me_3$), 14.9 (dq, $J_{\mathrm{CH}} = 131$ Hz, $J_{\mathrm{CP}} = 39.1$ Hz, $\mathrm{P}Me$), 13.8 ppm (dq, $J_{\mathrm{CH}} = 131$ Hz, $J_{\mathrm{CP}} = 41.0$ Hz, PMe'). The minor isomer has its C_α resonance at ppm 267 ($^2J_{\mathrm{CP}} = 9.8$ Hz). ^{31}P{^{1}H} NMR (toluene-d_8, 223 K) major isomer 7.2 ppm ($J_{\mathrm{PW}} = 300$ Hz); minor isomer 8.1 ppm ($J_{\mathrm{PW}} = 298$ Hz); major isomer/minor isomer $\simeq$ 6; IR (Nujol) 949 cm^{-1} (s, br, $\nu_{\mathrm{W=O}}$).

Preparation of [W(O)(CHCMe$_3$)(OCMe$_3$)$_2$]$_2$. Anhydrous $\mathrm{NEt_4Cl}$ (1.35 g, 8.12 mmol) was added to a solution of $\mathrm{TaNp_2Cl_3}$ (1.75 g, 4.06 mmol) in 40 mL of $\mathrm{CH_2Cl_2}$. The orange-yellow solution immediately turned red. $\mathrm{W(O)(OCMe_3)_4}$ (2.0 g, 4.06 mmol) was added and the color lightened to orange in 0.5 h. The solvent was removed in vacuo, leaving an orange-tan solid. This solid was washed five times with 20 mL of pentane. The pentane extracts were combined and filtered. The pentane was removed in vacuo, leaving 1.12 g (67%) of $\mathrm{[W(O)(CHCMe_3)(OCMe_3)_2]_2}$ as an orange oil. The pentane-insoluble tan solid had a ^{1}H NMR spectrum in $\mathrm{CH_2Cl_2}$ consistent with $\mathrm{[Ta(OCMe_3)_2Cl_4]^-[NEt_4]^+}$ [3.37 (q, 4, $^3J_{\mathrm{HH}}$ = 7 Hz, $\mathrm{NC}H_2\mathrm{CH_3}$), 1.47 (t, 6, $^3J_{\mathrm{HH}}$ = 7 Hz, $\mathrm{NCH_2C}H_3$), 1.47 ppm (s, 9, $\mathrm{OC}Me_3$)].

^{1}H NMR ($\mathrm{C_6D_6}$) 10.68 (s, 1, $J_{\mathrm{HW}} = 12.1$ Hz, $\mathrm{C}H\mathrm{CMe_3}$), 1.45 (s, 9, $\mathrm{OCMe_3}$), 1.41 (s, 9, $\mathrm{OCMe_3}$), 1.16 ppm (s, 9, $\mathrm{CHC}Me_3$); ^{13}C NMR (toluene-d_8, 268 K, gated proton decoupled) 290 (d, J_{CH} = 135 Hz, $J_{\mathrm{CW}} = 156$ Hz, $C\mathrm{HCMe_3}$), 91.9 (s, $\mathrm{O}C\mathrm{Me_3}$), 90.4 (s, $\mathrm{O}C\mathrm{Me_3}$), 42.5 (s, $\mathrm{CH}C\mathrm{Me_3}$), 32.6 (q, $J_{\mathrm{CH}} = 123$ Hz, $\mathrm{CHC}Me_3$), 29.7 and 29.5 ppm (q, $\mathrm{J_{CH}} = 123$ Hz, $\mathrm{OC}Me_3$); IR (Nujol) 940 cm^{-1} (s, br, $\nu_{\mathrm{W=O}}$) mol wt (cryoscopy in cyclohexane) calcd, 834; found, 640.

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Registry No. $\mathrm{W(O)(OCMe_3)_4}$, 58832-09-0; $\mathrm{W(O)(CHCMe_3)Cl_2(PMe_3)_2}$, 76603-92-4; $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)_2}$, 74666-77-6; $\mathrm{W(O)(CHCMe_3)Cl_2(PMe_2Ph)_2}$, 79329-25-2; $\mathrm{W(O)(CHCMe_3)Br_2(PEt_3)_2}$, 79329-26-3; $\mathrm{W(O)(CHCMe_3)Cl_2(PEt_3)}$, 74658-29-0; $\mathrm{W(O)(CHCMe_3)Cl_2(PMe_3)(PhCN)}$, 79357-00-9; $\mathrm{W(O)(CHCMe_3)Cl_2(PMe_3)(THF)}$, 79329-27-4; $\mathrm{W(O)(CHCMe_3)Cl_2(tmeda)}$, 79329-28-5; $\mathrm{[W(O)(CHCMe_3)Cl(PEt_3)_2]^+(AlCl_4^-)}$, 79357-56-5; $\mathrm{[W(O)(CHCMe_3)(PEt_3)_2]^{2+}(AlCl_4^-)_2}$, 79357-52-1; $\mathrm{[W(O)(CHCMe_3)(Me)(PEt_3)_2]^+(AlMe_2Cl_2^-)}$, 79357-54-3; $\mathrm{W(O)(CHCMe_3)MeCl(tmeda)}$, 79329-29-6; $\mathrm{[W(O)(CHCMe_3)(AlMe_4)(PEt_3)_2]^+(AlMe_2Cl_2^-)}$, 79329-32-1; $\mathrm{[W(O)(CHCMe_3)Cl(PEt_3)]^+(AlCl_4^-)}$, 79357-58-7; $\mathrm{W(O)(CHCMe_3)(Cl)(F)(PEt_3)_2}$, 79329-33-2; $\mathrm{W(O)(CHCMe_3)(S_2CNMe_2)_2}$, 79329-34-3; $\mathrm{W(O)(CHCMe_3)(OCMe_3)_2(PMe_3)}$, 79329-35-4; $\mathrm{W(O)(CHCMe_3)(OCMe_3)_2(PEt_3)}$, 79329-36-5; $\mathrm{W(O)(CHCMe_3)(OCMe_3)_2(PMe_2Ph)}$, 79329-37-6; $\mathrm{[W(O)(CHCMe_3)(OCMe_3)_2]_2}$, 79329-38-7; $\mathrm{W(O)Cl_4}$, 13520-78-0; $\mathrm{Ta(CHCMe_3)Cl_3(PMe_3)_2}$, 70083-62-4; $\mathrm{Ta(CHCMe_3)Cl_3(PEt_3)_2}$, 77126-35-3; $\mathrm{[Ta(OCMe_3)_4Cl]_2}$, 79357-59-8.

Electrochemical Oxidation–Reduction of Organometallic Complexes. Effect of the Oxidation State on the Pathways for Reductive Elimination of Dialkyliron Complexes

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A series of octahedral dialkylbis(α,α'-bipyridine)iron(II) complexes A are synthesized and shown to exist in the cis configuration, both in the crystal and in solution. Transient electrochemical techniques are used to identify two other oxidation states, viz., the dialkyliron(III) cation B and the dialkyliron(IV) dication C. The A $\rightleftharpoons$ B couple is electrochemically reversible, and crystalline dialkyliron(III) salts of B can be isolated and their anisotropic ESR spectra resolved into the three principal elements of the **g** tensor (showing rhombic symmetry). The B $\rightleftharpoons$ C couple is electrochemically irreversible, but cyclic voltammetric studies indicate that C is formed by a rate-limiting oxidation. Both B and C retain the cis configuration of the alkyl ligands in solution. Each of the dialkyliron species undergoes a characteristic pathway for reductive elimination. Thus the disproportionation of the alkyl ligands to alkane and alkene in A derives via β-elimination from a coordinatively unsaturated intermediate. Homolytic fragmentation of B leads to products arising from the cage reactions of alkyl radicals. On the other hand, the concerted loss of both alkyl ligands in C leads to coupled dialkyls in excellent yields. The comparative behavior of the isomeric dialkyliron species A, B, and C is discussed in terms of the driving force for reductive elimination. The general principles are illustrated briefly in the comparative carbonylation of A and B with CO.

Introduction

Owing to the importance of organometallic intermediates in a variety of catalytic reactions,[1-4] it is necessary to identify those factors which determine how the carbon–metal bond can be selectively cleaved. Organometals are

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