Some Reactions Involving $[W(N\text{-}2,6\text{-}Me_2C_6H_3)(OCMe_2CF_3)_2]_2$, a Symmetric d^2/d^2 Dimer that Contains No Bridging Ligands

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$(Me_2CF_3CO)_2(Ar'N)W{=}W(NAr')(OCMe_2CF_3)_2$ ($Ar' = 2,6\text{-}Me_2C_6H_3$) reacts immediately at room temperature with 1 equiv of CCl_4 to give the sparingly soluble $[W(OCMe_2CF_3)_2Cl]_2(\mu\text{-}NAr')_2$. $[W(NAr')(OCMe_2CF_3)_2]_2$ forms 1:1 adducts with simple donor ligands such as PMe_3, $PPhMe_2$, and pyridine, in which the base is likely to be coordinated to a single W center. Addition of ethylene to $[W(NAr')(OCMe_2CF_3)_2]_2$ yields $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}C_2H_4)$, in which ethylene is bound essentially to one W, although it also could be argued that a 1,2-dimetallacyclobutane ring is present. Heating a toluene solution of $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}C_2H_4)$ produces $(OCMe_2CF_3)_2(Et)W(\mu\text{-}NAr')(\mu\text{-}N\text{-}2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)W(OCMe_2CF_3)_2$, in which the proton required to form the ethyl ligand arises through CH activation in one of the methyl groups of the NAr′ ligand. Treatment of $[W(NAr')(OCMe_2CF_3)_2]_2$ with 2-butyne yields $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}MeCCMe)$. Addition of 4 equiv of CH_3CN to $[W(NAr')(OCMe_2CF_3)_2]_2$ in benzene gives a mixture of two products, **A** and **B**, which have the empirical formula $W(NAr')(OCMe_2CF_3)_2(CH_3CN)$, according to elemental analyses. Compound **B** was found to contain the $[\mu\text{-}NC(Me){=}C(Me)N]^{4-}$ ligand in an unsymmetric dimer in which one nitrogen of the $[\mu\text{-}NC(Me){=}C(Me)N]^{4-}$ ligand is bridging while the other is bound in a terminal fashion to one metal. Compound **A** is proposed to be a C_s-symmetric structural isomer of **B** in which the $[N(Me)C{=}C(Me)N]^{4-}$ ligand is symmetrically bridging the two metal centers. X-ray studies are reported for $[W(OCMe_2CF_3)_2Cl]_2(\mu\text{-}NAr')_2$, $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}MeCCMe)$, and **B**.

Introduction

In 1990 we reported the syntheses of a variety of tungsten imido alkylidene bis(alkoxide) complexes of the type $W(NR)(CHR')(OR'')_2$, in which R = $2,6\text{-}Me_2C_6H_3$ (Ar′), $2,6\text{-}i\text{-}Pr_2C_6H_3$ (Ar).[1] We found that compounds in which the alkylidene is relatively small (CHR′ = CHEt) decompose to give dimeric species with the empirical formula $W(NR)(OR'')_2$ (according to NMR and elemental analyses) that we proposed to be bimetallic species in which the two metals are bridged by imido ligands: i.e., $[W(\mu\text{-}NR)(OR'')_2]_2$. (A bridging imido formulation was proposed by analogy with the X-ray structure obtained for $[Mo(\mu\text{-}NAr)(O\text{-}t\text{-}Bu)_2]_2$, a compound obtained upon decomposition of the unsubstituted molybdacyclobutane complex $Mo((CH_2CH_2CH_2)(NAr)(O\text{-}t\text{-}Bu)_2$.[2]) For example, $\{W(NAr')[OCMe(CF_3)_2]_2\}_2$ was isolated from the reaction between $W(NAr')(CH\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_2$ and 3-hexene to yield intermediate, unstable $W(NAr')(CHEt)[OCMe(CF_3)_2]_2$. An attempted X-ray study of brown crystalline "$W(NAr')[OCMe(CF_3)_2]_2$" was not of sufficient quality to conclude whether bridging imido ligands were present or not. Other propylidene complexes also were found to be unstable with respect to formation of dimers via bimolecular coupling of alkylidenes.

We have now shown that several of these $[W(NR)(OR'')_2]_2$ compounds, including $\{W(NAr')[OCMe(CF_3)_2]_2\}_2$, as well as several compounds of the type $[W(NR)(CH_2\text{-}t\text{-}Bu)(OR'')]_2$ (both heterochiral and homochiral forms) actually contain W=W bonds that are *not* bridged by imido or alkoxide ligands.[3] All species contain an unbridged W(IV)/W(IV) double bond with a W=W bond distance of 2.4−2.5 Å, an approximate 90° angle between the imido ligands and the W=W bond, and a transoid relationship between the two imido ligands across the W=W bond. There is no indication that W=W bonds are broken spontaneously in any of these species: e.g., heterochiral and homochiral $[W(NR)(CH_2\text{-}t\text{-}Bu)(OR'')]_2$ species do not interconvert readily. Molybdenum imido alkylidene complexes also decompose to yield dimeric species. Dimeric Mo compounds that contain imido bridging ligands, as noted above for $[Mo(\mu\text{-}NAr)(O\text{-}t\text{-}Bu)_2]_2$,[2] as well as compounds that contain unbridged Mo=Mo bonds analogous to W=W species have been isolated. In one case, $\{Mo(N\text{-}1\text{-}adamantyl)[OCMe(CF_3)_2]_2\}_2$, both isomers have been crystallographically characterized.[4] Rhenium complexes of the type $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OR'')_2$,[5] which are isoelectronic with $W(NAr)(CH\text{-}t\text{-}Bu)(OR'')_2$ species, have been shown to react with $CH_2{=}CHOEt$ to yield observable but unstable intermediate $Re(C\text{-}t\text{-}Bu)(CHOEt)(OR'')_2$ species. These species decompose to yield $[Re(C\text{-}t\text{-}Bu)(OR'')_2]_2$ complexes that also contain unbridged Re=Re bonds, a staggered, ethane-like geometry, and a transoid relationship between the two neopentylidyne ligands across the Re=Re bond. Upon irradiation with 360 nm light the $[Re(C\text{-}t\text{-}Bu)(OR)_2]_2$ complexes are transformed into $[Re(\mu\text{-}C\text{-}t\text{-}Bu)(OR)_2]_2$ species whose structures contain μ-C-t-Bu groups, according to NMR studies and an X-ray study of

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10.1021/om800182g CCC: $40.75

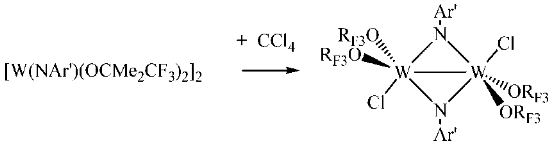
a derivative.[6] Therefore, it has been established that d^2/d^2 imido species can be formed in which the M═M bond (M = Mo, W, Re) is not bridged by any potentially bridging ligand. It should be noted that reduction of W(N-t-Bu)(Silox)$_2$Cl$_2$ yields pseudo-trigonal-planar W(N-t-Bu)(Silox)$_2$; presumably a W═W bond cannot form for steric reasons under these circumstances.[7]

Dimeric species that contain M═M bonds are extremely rare. The only compounds whose reactivities have been studied in some depth are [Os$_2$(CO)$_8$],[8] [W$_2$(OCH$_2$-t-Bu)$_8$],[9] and [(η^5-C$_5$Me$_5$)$_2$Re$_2$(CO)$_4$].[10] The d^2/d^2 W═W and Mo═Mo species are especially interesting, as a consequence of the fact that they will metathesize certain olefins slowly,[11] possibly as a consequence of reacting with some olefins to produce M(NR)(CHR′)(OR″)$_2$ species in low yield. How this might be accomplished is not known. However, one attractive possibility is that the manner in which M═M bonds are formed is reversible to some degree in some circumstances: i.e., M═M bonds react with certain C═C bonds to yield M═C species. This reaction would be analogous to that between M≡M bonds and C≡C bonds to yield M≡C bonds.[12] There are several other possibilities, among them rearrangement of an olefin to an alkylidene in a manner described by Wolczanski in Nb and Ta chemistry[13] and formation of an alkylidene through contraction of a metallacyclopentane to a metallacyclobutane ring.[14]

In this paper we report some exploratory reactions of one unbridged W═W species, [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$. This species can be obtained on a multigram scale from W(NAr′)(CH-t-Bu)(OCMe$_2$CF$_3$)$_2$.[1] We have avoided reactions involving dimers of the type [W(NAr′)(CH$_2$-t-Bu)(OR)]$_2$ in this initial study, in order to avoid complications arising from (inter alia) formation of diastereomers and in order to eliminate possible reactions involving the neopentyl ligand.

Results and Discussion

Oxidation of the W═W Bond. [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ reacts immediately at room temperature with 1 equiv of CCl$_4$ to give a sparingly soluble, light red product in high yield (93%). Proton and fluorine NMR spectra suggest that only one type of alkoxide ligand is present in a highly symmetric species. An X-ray structure of crystals grown from toluene at −30 °C showed the compound to be [W(OCMe$_2$CF$_3$)$_2$Cl]$_2$(μ-NAr′)$_2$ (eq 1). The product results from a net oxidation of each metal center from W^{IV} to W^{V}. Only 1 equiv of carbon tetrachloride (per dimer) is required, but the fate of the "CCl$_2$" byproduct has not been determined. Further oxidation of [W(OCMe$_2$CF$_3$)$_2$Cl]$_2$(μ-NAr′)$_2$ by CCl$_4$ was not observed at room temperature in solution.



(1)

The solid-state structure of [W(OCMe$_2$CF$_3$)$_2$Cl]$_2$(μ-NAr′)$_2$ (Table 1) is shown in Figure 1, and the pertinent bond lengths and angles are given in Table 2. The structure exhibits approximate trigonal -bipyramidal geometry about each metal, with equatorial alkoxide and bridging imido groups and an axial Cl ligand. The structure is slightly folded about the W−W bond, with a dihedral "butterfly" angle of 155.70(12)°. However, NMR data at 22 °C suggest that the folded structure is not maintained in solution: i.e., the two alkoxides are equivalent on the NMR time scale. The W−W bond length of 2.6296(2) Å is consistent with a (W−W)$^{10+}$ core which contains a formal d^1−d^1 M−M single bond,[9a,c] in agreement with the observed diamagnetism of the compound. Lengthening of the W−N bonds by ~0.2 Å and the decrease in W−N−C bond angles (to ~135°) relative to those of the parent compound (W═N = 1.753(3) Å and W═N−C = 172.1(3)°) are what one might expect from the observed change in coordination mode of the imido ligands. The W−Cl distances are not unusual,[15] and other bond lengths and angles are not much different from those in the parent species, [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$.

Attempts to further oxidize the dimer to give W(NAr′)(OCMe$_2$CF$_3$)$_2$Cl$_2$ consisted of treatment of a hydrocarbon solution of [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ with 2 equiv of C$_2$Cl$_6$ at −30 °C. Only substantial decomposition was observed. Similarly, the reaction between [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ and 2 equiv of I$_2$ did not yield W(NAr′)(OCMe$_2$CF$_3$)$_2$I$_2$ but a complex mixture that contained (inter alia) W(NAr′)(OCMe$_2$CF$_3$)$_3$I and *mer*-W(OCMe$_2$CF$_3$)$_3$I$_3$, the identities and connectivities of which were determined through X-ray crystallographic techniques.[16] Complete structural characterization of these W(VI) compounds was not pursued. It is clear that ligand transfer from one metal to another and W−W bond cleavage to yield monomeric species are potentially facile under some conditions.

Reactions Involving Two-Electron Donors. Studies revealed that [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ forms 1:1 adducts with Lewis bases such as PMe$_3$, PPhMe$_2$, and pyridine, even in the presence of an excess of base (eq 2). The ^{1}H NMR spectra of the monoadducts are all characteristic of molecules that have no symmetry. For example, the ^{1}H NMR spectrum of [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$(PMe$_3$) reveals four inequivalent OCMe$_2$CF$_3$ ligands with eight distinct singlets being observed for the Me groups. All four CF$_3$ groups likewise appear as well-separated resonances in the ^{19}F NMR spectrum. The ^{31}P NMR

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Table 1. Crystal Data and Structure Refinement Details for $[W(OCMe_2CF_3)_2Cl]_2(\mu\text{-}NAr')_2$ (05145), $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeCCMe)$ (05058), and $(OCMe_2CF_3)_2W(\mu\text{-}NAr')[\mu\text{-}N(Me)C{=}C(Me)N{=}]W(NAr')(OCMe_2CF_3)_2$ (05134)[a]

	05145	05058	05134
empirical formula	$C_{32}H_{42}Cl_2F_{12}N_2O_4W_2$	$C_{38.5}H_{54}F_{12}N_2O_4W_2$	$C_{36}H_{48}F_{12}N_4O_4W_2$
formula wt	1185.28	1204.54	1196.48
cryst syst	orthorhombic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
unit cell dimens			
a (Å)	11.3299(3)	12.9753(14)	10.6803(9)
b (Å)	18.5670(7)	11.3961(13)	12.2820(9)
c (Å)	18.7721(7)	30.151(4)	16.3289(12)
α (deg)	90	90	86.482(3)
β (deg)	90	98.649(4)	82.954(3)
γ (deg)	90	90	74.284(3)
V (Å^3)	3948.9(2)	4407.6(9)	2045.4(3)
Z	4	4	2
calcd density (Mg/m^3)	1.994	1.815	1.943
abs coeff (mm^{-1})	6.051	5.306	5.717
$F(000)$	2280	2348	1160
cryst size (mm^3)	0.03 × 0.03 × 0.03	0.15 × 0.10 × 0.10	0.11 × 0.04 × 0.02
θ range for data collecn (deg)	1.54−29.57	1.91−29.57	1.72−28.28
index ranges	$-15 \le h \le 15$, $-25 \le k \le 25$, $-25 \le l \le 26$	$-18 \le h \le 18$, $-15 \le k \le 15$, $-41 \le l \le 41$	$-14 \le h \le 14$, $-16 \le k \le 16$, $-21 \le l \le 21$
no. of rflns collected	88 550	80 658	423 211
no. of indep rflns	11 077 (R(int) = 0.0490)	12 346 (R(int) = 0.0537)	10 173 (R(int) = 0.0408)
completeness to θ = 29.57° (%)	100.0	100.0	99.9
max, min transmissn	0.8393, 0.8393	0.6190, 0.5033	0.8942, 0.5720
no. of data/restraints/params	11 077/0/499	12 346/34/566	10 173/0/537
goodness of fit on F^2	1.048	1.100	1.023
final R indices ($I > 2\sigma(I)$)	R1 = 0.0226, wR2 = 0.0477	R1 = 0.0304, wR2 = 0.0671	R1 = 0.0255, wR2 = 0.0552
R indices (all data)	R1 = 0.0246, wR2 = 0.0485	R1 = 0.0378, wR2 = 0.0701	R1 = 0.0354, wR2 = 0.0588
largest diff peak, hole (e Å^{-3})	1.771, −0.743	2.275, −0.900	1.369, −0.611

[a] In all cases the wavelength was 0.710 73 Å, the temperature 100(2) K, the absorption method semiempirical from equivalents, and the refinement method full-matrix least squares on F^2. For 05145 the absolute structure parameter is −0.014(5).

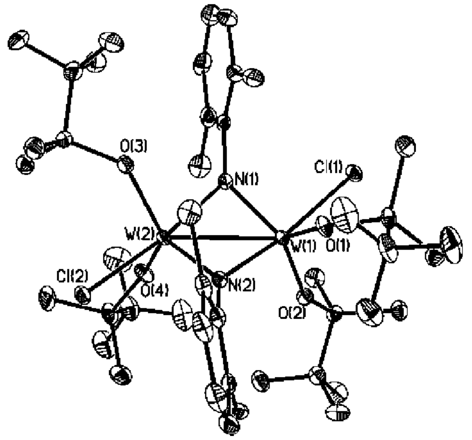
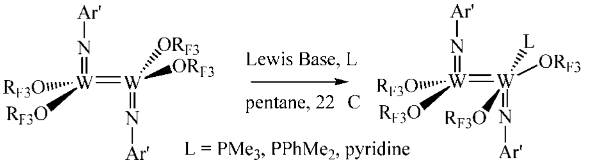


Figure 1. Thermal ellipsoid plot of $[W(OCMe_2CF_3)_2Cl]_2(\mu\text{-}NAr')_2$.

Table 2. Selected Intramolecular Distances (Å) and Bond Angles (deg) in $[W(OCMe_2CF_3)_2Cl]_2(\mu\text{-}NAr')_2$

W(1)−W(2)	2.6296(2)	W(1)−O(1)	1.911(2)
W(1)−Cl(1)	2.4061(8)	W(1)−O(2)	1.823(2)
W(2)−Cl(2)	2.4135(8)	W(2)−O(3)	1.913(3)
W(1)−N(1)	1.931(3)	W(2)−O(4)	1.850(2)
W(1)−N(2)	1.970(3)	N(1)−C(11)	1.436(4)
W(2)−N(1)	1.971(3)	N(2)−C(21)	1.440(4)
W(2)−N(2)	1.931(3)		
W(1)−N(1)−W(2)	84.74(11)	N(2)−W(1)−N(1)	92.48(11)
W(2)−N(2)−W(1)	84.76(11)	N(2)−W(1)−Cl(1)	166.31(8)
N(2)−W(2)−N(1)	92.46(12)	N(1)−W(2)−Cl(2)	166.93(8)

spectrum shows ^{183}W coupling to the phosphorus atom of the PMe_3 ligand ($^1J_{PW}$ = 271 Hz). Note, however, that while bound PMe_3 does not exchange with free PMe_3 at room temperature on the ^{31}P NMR time scale, $PPhMe_2$ and pyridine are relatively



(2)

more labile. Attempts to isolate analytically pure samples of the $PPhMe_2$ and pyridine adducts were hampered by the loss of base in vacuo. No X-ray-quality crystals of any of the three adducts could be obtained. The structure of $[W(NAr')(OCMe_2CF_3)_2]_2(PMe_3)$ shown in eq 2 is one in which the base has added trans to one of the trifluoro-*tert*-butoxides to give a trigonal-bipyramidal arrangement around the metal with the W=W and W=N bonds lying in the equatorial plane. It is only one of several possibilities that include one or more bridging imido or alkoxide ligands.

When ethylene was condensed into hydrocarbon solutions of $[W(NAr')(OCMe_2CF_3)_2]_2$, the green reaction mixture turned yellow upon being warmed to room temperature. NMR spectra of the golden yellow product are consistent with it being a monoethylene adduct. Like other monoadducts described here, NMR spectra suggest that the adduct has no symmetry in solution. The molecule is stereochemically rigid on the NMR time scale at room temperature, with distinct resonances for all four ethylene protons at 4.31 (m, J_{CH} = 158 Hz), 3.11 (m, J_{CH} = 150 Hz), 1.84 (m, J_{CH} = 150 Hz), and 1.62 ppm (m, J_{CH} = 153 Hz). The ethylene carbons were observed at 66.18 (J_{CW} = 60 Hz, $^1J_{CC}$ = 26 Hz) and 33.97 ppm (J_{CW} = 22 Hz, $^1J_{CC}$ = 26 Hz) in the ^{13}C NMR spectrum (toluene-d_8). One set of tungsten satellites is evident on each carbon resonance of the bound ethylene in the ^{13}C NMR spectrum, implying a strong metal−ethylene interaction at room temperature. However, variable-temperature NMR studies revealed that the adduct loses ethylene at elevated temperatures to re-form $[W(NAr')(OCMe_2$-

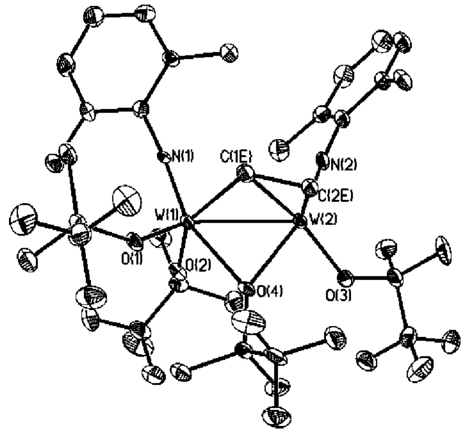


Figure 2. Thermal ellipsoid plot of $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}C_2H_4)$.

Table 3. Selected Intramolecular Distances (Å) and Bond Angles (deg) in $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}C_2H_4)$

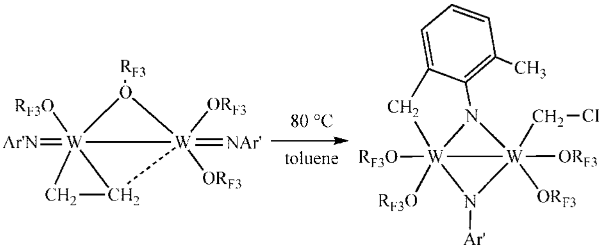
W(1)−W(2)	2.6429(4)	W(2)−N(2)	1.759(5)
C(1E)−C(2E)	1.493(9)	W(1)−O(1)	1.923(4)
W(1)−C(1E)	2.445(7)	W(1)−O(2)	1.871(5)
W(2)−C(1E)	2.322(7)	W(1)−O(4)	2.202(5)
W(2)−C(2E)	2.098(7)	W(2)−O(4)	2.106(4)
W(1)−N(1)	1.759(5)	W(2)−O(3)	1.925(5)
C(2E)−C(1E)−W(2)	62.3(3)	W(2)−O(4)−W(1)	75.65(14)
C(2E)−C(1E)−W(1)	126.2(5)	C(11)−N(1)−W(1)	174.5(5)
C(1E)−C(2E)−W(2)	78.6(4)	C(21)−N(2)−W(2)	174.2(5)
W(2)−C(1E)−W(1)	67.29(18)		

$CF_3)_2]_2$. The adduct also loses ethylene slowly in the solid state, especially in vacuo, a fact that could account for the low carbon content in all attempted elemental analyses.

An X-ray study of crystals grown from pentane at −30 °C shows the structure to be a dimer with an alkoxide and an ethylene ligand bridging the two metal centers, relatively asymmetrically in the case of the ethylene ligand (Figure 2). Bond distances and angles are given in Table 3, but the X-ray data are not given in Table 1. (These data were deposited as Supporting Information in a communication.[11]) All four protons on the ethylene fragment were located, and there is no evidence for any agostic interaction[17] of an ethylene C−H bond with tungsten. The C1E−C2E bond distance of 1.493(9) Å is notably longer than that of free ethylene (cf. 1.337 Å);[18] it is essentially a C−C single bond. This is consistent with the low J_{CC} value (26 Hz), as well as with the loss of planarity of the ethylene ligand, as manifested in the bending back of the hydrogen atoms away from the metal. The parameter commonly used to describe the bending back of the olefin substituents is the dihedral angle formed by the two H−C−H planes,[19] which is 180° for free ethylene; in this case it is 103°. The W−W bond (2.6429(4) Å) is significantly lengthened compared to that of the parent compound (W=W = 2.4905(3) Å) and is more consistent with the view that a single bond is present. The ^{13}C resonances observed at 66.18 ($J_{CW(2)}$ = 60 Hz) and 33.97 ppm ($J_{CW(2)}$ = 22 Hz) are assigned to C(2E) and C(1E), respectively, on the basis of the relatively short W(2)−C(2E) distance of 2.098(7) Å combined with the larger J_{CW} value. The fact that only one coupling to W(2) can be observed for each ethylene carbon atom is consistent with the asymmetric binding of ethylene to the two metal centers, with the interaction between C(1E) and W(1) approaching a nonbonding distance (2.445(7) Å) and a W(2)−C(1E) distance (2.322(7) Å) close to being a W−C single bond (typically ~2.2 Å). Other metal−ligand bond lengths are what might be expected: e.g., bridging W−OR bonds (2.106(4) and 2.202(5) Å) are longer than terminal W−OR bonds (average ~1.9 Å). The W(μ-OR) distances, however, are slightly different, consistent with asymmetric bonding of the bridging alkoxide ligand.

The W_2C_2 core of the ethylene complex can be compared with the WC_3 ring of known metallacyclobutane[20] complexes. For instance, the short W(2)−C(2E) bond (2.098(7) Å) is comparable to the $W-C_\alpha$ bonds in WC_3 rings. Therefore, there is some justification in proposing that $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}C_2H_4)$ contains a 1,2-dimetallacyclobutane ring. The ethylene adduct of $[W(NAr')(OCMe_2CF_3)_2]_2$ is related to the ethylene adducts of $[Os_2(CO)_8]$[8b,c] and $[W_2(OCH_2\text{-t-Bu})_8]$.[9a] However, the ethylene adduct of $[Os_2(CO)_8]$ binds ethylene in a symmetrically bridging fashion to give a C_2-symmetric species.[21] All four ethylene protons are equivalent and were observed in the ^1H NMR spectrum as a single sharp resonance down to −90 °C. $[W_2(OCH_2\text{-t-Bu})_8]$, on the other hand, reacts with 1 equiv of ethylene to give a monoadduct in which ethylene was proposed to bind to a single metal center.[9a] Unfortunately, crystals of the monoethylene adduct of $[W_2(OCH_2\text{-t-Bu})_8]$ suitable for X-ray diffraction studies were not obtained.

Heating a toluene solution of $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}C_2H_4)$ at 80 °C in a sealed glass vessel under ethylene (1 atm) for several days produced a sparingly soluble brick red compound. The ^1H NMR spectrum of this unsymmetric species suggested that an ethyl ligand was present as a consequence of CH activation in an *o*-methyl group in the NAr′ ligand (eq 3). Formulation of the compound was based on the appearance of proton NMR resonances for only three of the four original NAr′ methyl groups, and a doublet at 4.45 ppm (J_{CH} = 18 Hz) for one of the methylene protons in the CH activated NAr′ methyl group, in addition to other ligand peaks.



(3)

The structure was determined in a single-crystal X-ray structure study (Figure 3 and Table 4). (X-ray data for this compound were deposited as part of the Supporting Information in the communication.[11]) The molecular structure clearly shows that ethylene indeed has been converted into an ethyl group with the required proton arising through CH activation of one of the imido methyl groups. Both imido nitrogens are symmetrically bridging the two metal centers and form the shared edge of two pseudo-trigonal-bipyramidal fragments. No bonds or angles (Table 4) in $(OCMe_2CF_3)_2(Et)W(\mu\text{-}NAr')(\mu\text{-}N\text{-}2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)W(OCMe_2CF_3)_2$ are unusual.

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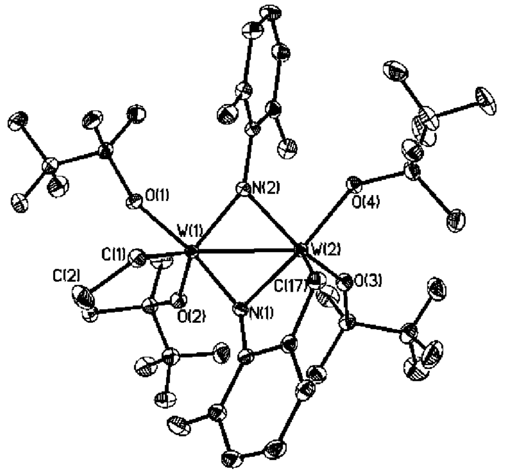


Figure 3. Thermal ellipsoid plot of (OCMe$_2$CF$_3$)$_2$(Et)W(μ-NAr′)(μ-N-2-CH$_2$-6-MeC$_6$H$_3$)W(OCMe$_2$CF$_3$)$_2$.

Table 4. Selected Intramolecular Distances (Å) and Bond Angles (deg) of (OCMe$_2$CF$_3$)$_2$(Et)W(μ-NAr′)(μ-N-2-CH$_2$-6-MeC$_6$H$_3$)-W(OCMe$_2$CF$_3$)$_2$

W(1)−W(2)	2.61757(14)	W(2)−N(1)	1.962(2)
C(1)−C(2)	1.525(4)	W(2)−N(2)	1.966(2)
W(1)−C(1)	2.145(3)	W(1)−O(1)	1.9622(18)
W(2)−C(17)	2.156(3)	W(1)−O(2)	1.8967(17)
W(1)−N(1)	1.964(2)	W(2)−O(3)	1.8461(18)
W(1)−N(2)	1.930(2)	W(2)−O(4)	1.9545(18)
C(2)−C(1)−W(1)	110.95(18)	C(11)−N(1)−W(1)	148.44(17)
C(17)−W(2)−W(1)	110.65(7)	C(11)−N(1)−W(2)	121.18(16)
W(2)−N(1)−W(1)	83.63(8)	C(21)−N(2)−W(1)	146.31(16)
W(1)−N(2)−W(2)	84.42(8)	C(21)−N(2)−W(2)	128.61(16)

It has been established by variable-temperature NMR studies that the ethylene adduct loses ethylene at elevated temperatures (vide supra). Formation of the ethyl complex from [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ in the presence of free ethylene requires bridging of the NAr′ ligands, CH activation in one of the NAr′ methyl groups, and insertion of ethylene into a W−H bond. It is not known exactly how that is accomplished. In any case, the fact that CH activation takes place in a methyl group may compromise some of the chemistry of dimers that contain NAr′ ligands and may involve formation of an isomer of [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ in which the NAr′ ligands are bridging. Although the reaction that gives rise to (OCMe$_2$CF$_3$)$_2$(Et)W(μ-NAr′)(μ-N-2-CH$_2$-6-MeC$_6$H$_3$)W(OCMe$_2$CF$_3$)$_2$ could be reversible, or an α-hydrogen might be removed from the ethyl group to form an ethylidene ligand, there is no indication that such reactions take place to any observable extent under the conditions explored so far.

Reaction Involving 2-Butyne. Treatment of a hydrocarbon suspension of [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ with 2-butyne at room temperature resulted in immediate formation of a red-orange solution from which bright orange crystals were isolated in 82% yield. An X-ray study (Table 1, Figure 4) established that the product is the unsymmetric 1:1 adduct [W(NAr′)(OCMe$_2$CF$_3$)](μ-MeCCMe)(μ-NAr′)[W(OCMe$_2$CF$_3$)$_3$]. Pertinent bond lengths and angles are given in Table 5.

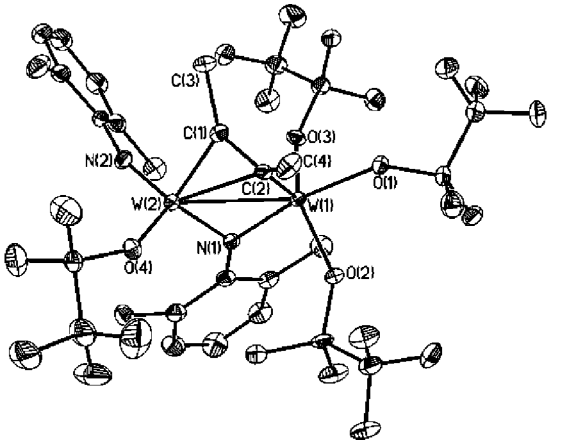
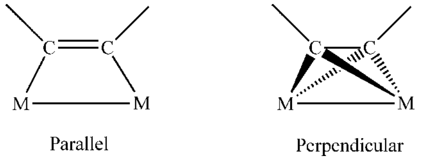


Figure 4. Thermal ellipsoid plot of [W(NAr′)(OCMe$_2$CF$_3$)](μ-MeCCMe)(μ-NAr′)[W(OCMe$_2$CF$_3$)$_3$].

Table 5. Selected Intramolecular Distances (Å) and Bond Angles (deg) in [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$(μ-η^2:η^2-MeCCMe)

W(1)−W(2)	2.7559(3)	W(2)−C(2)	2.518(4)
C(1)−C(2)	1.389(5)	W(1)−N(1)	1.977(3)
W(1)−C(1)	2.466(3)	W(2)−N(1)	1.962(3)
W(1)−C(2)	1.972(3)	W(2)−N(2)	1.755(3)
W(2)−C(1)	1.976(4)		
C(2)−C(1)−C(3)	127.2(3)	C(2)−C(1)−W(2)	95.3(2)
C(1)−C(2)−C(4)	127.1(3)	C(3)−C(1)−W(2)	134.2(3)
C(3)−C(1)−W(1)	141.0(2)	W(2)−N(1)−W(1)	88.79(11)
C(2)−C(1)−W(1)	53.01(17)	C(11)−N(1)−W(1)	137.4(2)
C(1)−C(2)−W(1)	92.8(2)	C(11)−N(1)−W(2)	133.8(2)
C(4)−C(2)−W(1)	135.3(3)	C(21)−N(2)−W(2)	164.5(3)
C(4)−C(2)−W(2)	144.1(2)	O(1)−W(1)−N(1)	163.64(11)
C(1)−C(2)−W(2)	51.40(19)		

Chart 1



Dinuclear complexes bridged by acetylenes generally adopt variations of a "parallel" or a "perpendicular" structure (Chart 1).[22] The two can be distinguished by the angle between the C−C and W−W bonds, which for parallel and perpendicular binding are 0 and 90°, respectively. Several intermediate structures have been documented.[23,24] Of particular interest to us are the nonparallel, nonperpendicular bridging alkyne adducts of the d^2/d^2 dimer [W$_2$(OCH$_2$-t-Bu)$_8$], with C−C/W−W twist angles of ~65°.[24] For the [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$(μ-MeC-CMe) species reported here, the observed C−C/W−W twist angle of 78° is closer to a perpendicular mode of addition, suggestive of a μ-η^2:η^2 coordination mode. If the MeCCMe moiety is viewed as occupying a single coordination site, the geometry about W(1) may be viewed as pseudo trigonal bipyramidal, with the bound 2-butyne and alkoxides (O(2) and O(3)) occupying the equatorial plane. The local geometry about W(2), on the other hand, is approximately tetrahedral. The two tungsten centers share an edge formed by 2-butyne and the N(1) atom of the bridging imido ligand. The W−W distance (2.7559(3) Å) is notably longer than in [W$_2$(OCH$_2$-t-Bu)$_8$](μ-RC≡CR) complexes (2.59−2.65 Å)[13] but is otherwise comparable to other W−W single bonds.[15] The central C−C distance of the coordinated alkyne (1.389(5) Å) is comparable to those

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reported for other bridging acetylenes and is consistent with a C=C double bond.[9a–c,22,24b] Moreover, the bound 2-butyne approaches the geometry of *cis*-2-butene with both the C≡C−C angles ~53° less than 180°. The nonlinear C≡C−C angles, along with the relatively short W−C distances, clearly imply extensive π back-bonding into the 2-butyne. The 2-butyne is also twisted, with a C−C≡C−C torsion angle of 27.7° and substantially different W(1)−C and W(2)−C distances: e.g., W(1)−C(2) = 1.972(3) Å and W(2)−C(2) 2.518(4) Å. Other bonds to the metal center reveal the expected trend. The μ-N−W distances (1.977(3) and 1.962(3) Å), for instance, are typical of bridging imido ligands.[25]

NMR spectra of $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}MeCCMe)$ are not trivial. The C_α atoms are observed at δ 223.19 ppm (J_{CW} = 114 and 12 Hz) and 197.18 ppm (J_{CW} = 134 and 12 Hz) in ^{13}C NMR spectra in toluene-d_8. The two 2-butyne carbons are coupled strongly to one ^{183}W nucleus but only weakly to the other, consistent with the observed unsymmetric binding of 2-butyne to the two metal centers noted above. Spectra of $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}MeCCMe)$ at low temperatures are consistent with the observed solid-state structure. The methyl resonances of the tri-*tert*-butoxide ligands are observed as eight sharp singlets in the region between 0.6 and 2.0 ppm.

As the temperature of the sample is raised, rapid rotation of one of the Ar′ rings on the ^1H NMR time scale and a fluxional process involving two of the alkoxide groups are observed. Above 40 °C only five types of alkoxide methyl groups in the ratio of 1:4:1:1:1 are observed. Since five-coordinate systems are notorious for their fluxionality, it is likely that the observed fluxional behavior involves two of the alkoxides in the distorted pseudo-trigonal-bipyramidal tungsten center (W(1)). However, since the nature of the participation of the other ligands (e.g., MeC≡CMe) in the dynamic process was not elucidated, the exact nature of the fluxional process cannot be stated with certainty.

Reaction with Acetonitrile. Addition of 4 equiv of CH_3CN to a solution of $[W(NAr')(OCMe_2CF_3)_2]_2$ in benzene over a period of 1 h generates a red-brown reaction mixture. Removal of the volatiles in vacuo and recrystallization of the residue from pentane afforded red-brown microcrystals which were found through NMR studies to be a mixture of two products, **A** and **B**. The major product, **A** (~90%), displays sharp singlets at 2.42 ppm for the equivalent methyl groups in the Ar′ group, at 1.48 and 1.45 ppm for the diastereotopic methyl groups in the $OCMe_2CF_3$ groups, and at 1.85 ppm for "CH_3CN" in the ^1H NMR spectrum (C_6D_6, 500 MHz). This spectrum remained virtually unchanged at temperatures as low as −80 °C. Only one type of CF_3 group is present in **A**, giving rise to a singlet at −82.89 ppm in the ^{19}F NMR. An empirical formula of "$W(NAr'')(OCMe_2CF_3)_2(CH_3CN)$" and a C_s-symmetric dimeric structure are proposed for the major product **A**.

On the other hand, the minor product, **B**, has four inequivalent CF_3 groups in the ^{19}F NMR spectrum, indicative of an asymmetric structure in solution. Resonances typical of an asymmetric compound are also observed in the ^1H NMR spectrum. Unfortunately, overlap of these resonances with those of **A** hampers the full spectroscopic characterization of product **B**.

A single crystal picked from the mixture was found in an X-ray study to be that of the minor (asymmetric) product, **B**. The molecular structure is shown in Figure 5, and selected bond lengths and angles are summarized in Table 6. The structure consists of two distorted-trigonal-bipyramidal tungsten fragments joined along the edges by bridging NAr′ and "NC(Me)C(Me)N" ligands. The "NC(Me)C(Me)N" unit is derived from the reductive coupling of two acetonitrile molecules.

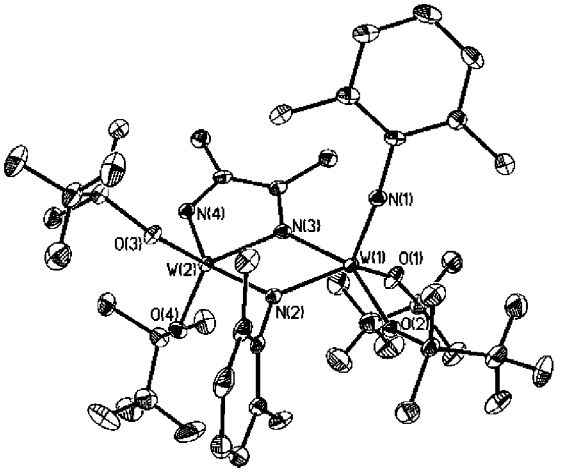
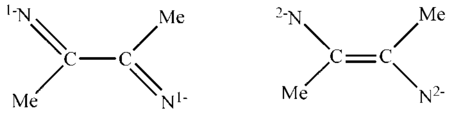


Figure 5. Thermal ellipsoid plot of the coupled acetonitrile complex **B**.

Table 6. Selected Intramolecular Distances (Å) and Bond Angles (deg) in $(OCMe_2CF_3)_2W(\mu\text{-}NAr')[\mu\text{-}N(Me)C{=}C(Me)N]W(NAr')(OCMe_2CF_3)_2$

W−W	3.2703(3)	W(2)−N(4)	1.817(3)
C(1)−C(2)	1.377(5)	N(3)−C(1)	1.387(4)
W(1)−N(1)	1.739(3)	N(4)−C(2)	1.367(4)
W(1)−N(2)	2.000(3)	C(1)−C(3)	1.496(5)
W(2)−N(2)	2.003(3)	C(2)−C(4)	1.501(5)
W(1)−N(3)	2.026(3)	N(1)−C(11)	1.395(4)
W(2)−N(3)	2.031(3)	N(2)−C(21)	1.430(4)
W(1)−N(2)−W(2)	109.55(12)	C(1)−N(3)−W(1)	134.6(2)
W(1)−N(3)−W(2)	107.41(12)	C(1)−N(3)−W(2)	116.4(2)
C(11)−N(1)−W(1)	170.9(2)	C(21)−N(2)−W(1)	133.5(2)
C(2)−N(4)−W(2)	126.8(2)	C(21)−N(2)−W(2)	116.0(2)

Chart 2



$[\text{diiminato}]^{2-}$ $[\text{enediimido}]^{4-}$

Dimerization of acetonitrile ligands to yield "NC(Me)C(Me)N" ligands has been observed in a number of circumstances.[26] Isolation and structural characterization of these compounds have established two possible formulations for the "NC(Me)C(Me)N" ligand. These are [butane-2,3-diiminato]$^{2-}$ and [butene-2,3-diimido]$^{4-}$, which result from two- and four-electron reductive acetonitrile coupling, respectively (see Chart 2). These two forms are readily distinguished by their structural parameters. The [butane-2,3-diiminato]$^{2-}$ linkage, where the C−C bond is typically longer than the C−N bonds, has been

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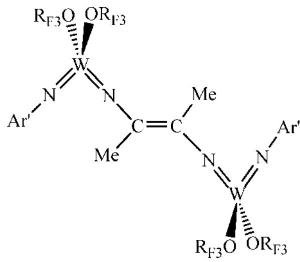

Figure 6. One possible structure of complex **A**.

observed in [μ-NC(Me)C(Me)N][W(CO)$_2${HB(Me$_2$pz)$_3$}]$_2$,[26f] where [HB(Me$_2$pz)$_3$]$^-$ = hydrotris(3,5-dimethylpyrazol-1-yl)borate anion, and in [μ-NC(Me)C(Me)N]{Mo[N(t-Bu)Ar]$_3$}$_2$.[26g] The formation of [butene-2,3-diimido]$^{4-}$ from four-electron reductive coupling of acetonitrile has been observed more often.[26a–e] The [μ-NC(Me)=C(Me)N]$^{4-}$ moiety is distinguished by the double-bond character of the central C−C bond, as well as by the M=N bonds formed between the nitrogen atoms and the metal (M=N).

In the planar "N(Me)CC(Me)N" ligand in **B** the newly formed C(1)−C(2) bond has a length of 1.377(5) Å, consistent with a double bond (cf. C−C = 1.54 Å, C=C = 1.34 Å).[18] The C−N distances of 1.387(4) and 1.367(4) Å are longer than typical C=N double bonds (cf. 1.27 Å)[18] and are indicative of single-bond character. Clearly, the distances and angles observed in the "NC(Me)C(Me)N" ligand present in the compound reported here are only consistent with a formal butene-2,3-diimido^{4-} electronic description. The W−N(4) bond (1.817(3) Å), although slightly longer than the W=N(1) bond (1.739(3) Å), is nonetheless within the range observed for other terminal imido ligands.[25] The similarity of the W−N bond lengths in μ-NAr′ to those of the nitrile-derived N(3) atom likewise supports the tetraanionic formulation of the coupled acetonitrile ligand. The W···W distance of 3.2703(3) Å is consistent with the absence of any significant M−M bonding interaction. The absence of a W−W bond is in agreement with the four-electron reductive coupling of acetonitrile to give the enediimido ligand, with each metal behaving as a two-electron reducing agent. It is worth noting that the observed binding mode of [N(Me)C=C(Me)N]$^{4-}$ in **B** is atypical of [butene-2,3-diimido]$^{4-}$ ligands derived from dimerization of acetonitrile. This type of binding was first observed in the [Re$_2$X$_3$(μ-HN$_2$C$_2$Me$_2$)(μ-dppm)$_2$(NCMe)]PF$_6$ (X = Cl, Br, dppm = Ph$_2$PCH$_2$PPh$_2$) complexes reported by Walton and co-workers.[27] However, in these dirhenium compounds the reductive coupling of acetonitrile ligands is accompanied by protonation of one of the nitrogen atoms of the coupled ligand to yield the "μ-HN$_2$C$_2$Me$_2$" moiety. In enediimido complexes the bridging [butene-2,3-diimido]$^{4-}$ ligand binds to two metal centers.

The spectroscopic properties of the as yet unidentified product **A** is consistent with a C_s-symmetric "[W(NAr′)(OCMe$_2$CF$_3$)$_2$(CH$_3$CN)]$_2$": i.e., **A** is likely to be a structural isomer of **B** wherein the [N(Me)C=C(Me)N]$^{4-}$ ligand is symmetrically bridging the two metal centers. One possible structure is shown in Figure 6, although other possibilities, e.g. one in which two NAr" ligands are bridging, cannot be discounted.

Summary and Conclusions

The results presented here demonstrate the susceptibility of dimeric species that contain unbridged W(IV)/W(IV) double bonds to associative chemistry, probably initially at one metal center. Reactions of [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ with oxidizing agents and nucleophiles resulted in addition of ligands to one or both metal centers. Ligand addition typically is accompanied by conversion of the W=W double bond into a W−W single bond and bridging of imido and/or alkoxide ligands. In some cases (e.g., reaction with I$_2$), further addition of ligands resulted in the cleavage of the W−W bond and oxidation of W(V) to give monomeric W(VI) species. Structural characterization of the various products obtained revealed the general tendency of the dimer to undergo transfer of imido and/or alkoxide groups from one metal to the other upon ligand binding. It therefore is likely that the controlled cleavage of the M=M bond to give 2 equiv of W(NAr′)(OR)$_2$(L)$_x$ may be the exception rather than the rule. Reactions of the type described here are related to a large number of reactions of M−M triple bonds that have been described primarily by Chisholm.[28]

Some of the reactions noted here are relevant to the observation that unsupported M=M double bonds will slowly catalyze olefin metathesis reactions. Addition of ethylene to [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ yielded a monoethylene adduct, which upon heating is transformed into an ethyl complex as a consequence of the CH activation of one of the *o*-methyl groups of the NAr′ ligand. This is analogous to the rearrangement of (t-Bu$_3$SiO)$_3$Ta(olefin) to tantalum "tuck-in" complexes containing an alkyl ligand through CH activation in one of the Silox ligands, which is the proposed intermediate in the olefin-to-alkylidene transformation reported by Wolczanski.[13] It seems plausible that the metathetically active alkylidene formed when [W(NAr′)(OCMe$_2$CF$_3$)$_2$]$_2$ is treated with alkenes[11] is formed through a similar sequence of reactions. However, the ethyl complex described here was found to polymerize norbornene much more slowly than the ethylene complex. Therefore, other mechanism(s) of alkylidene formation may be more accessible under the conditions employed, or the alkylidene is not formed in a bimetallic species, etc. The low yield of presumed monomeric W(NR)(CHR′)(OR″)$_2$ species from dimeric W=W species upon reaction with an olefin therefore seems unlikely to be a high-yield reaction in general. However, for the purpose of observing some metathesis behavior in the form of polymerization of norbornene, a low yield of alkylidene is sufficient. It remains to be seen whether some of the chemistry discovered here is relevant to the formation of alkylidenes in "classical" Mo or W systems.[29]

Experimental Section

General Considerations. All air-sensitive work was carried out in a Vacuum Atmospheres drybox under a dinitrogen atmosphere or by standard Schlenk techniques. Commercially available chemicals were obtained from Strem Chemicals, Inc., or Aldrich. Solid reagents were used as received unless otherwise stated. Liquids were distilled from CaH$_2$ under dinitrogen. Pentane, toluene, and benzene were sparged with dinitrogen and passed through columns of activated alumina. All deuterated solvents were freeze−pump−thaw degassed. All solvents and liquid reagents were stored over 4 Å molecular sieves. ^{1}H NMR spectra were obtained on an instrument operating at 500 MHz unless otherwise stated. ^{13}C NMR spectra were obtained on an instrument operating at 125 MHz, while ^{19}F NMR spectra were obtained on a 282 MHz instrument. All spectra

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were recorded at room temperature. ^1H and ^{13}C NMR data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protonated solvent resonance. ^{19}F NMR shifts are reported relative to C_6H_5F, while ^{31}P NMR shifts are reported relative to PPh_3 used as external reference. Elemental analyses were performed by Kolbe Microanalytical Laboratories (Mühlheim an der Ruhr, Germany). $[W(N\text{-}2,6\text{-}Me_2C_6H_3)(OCMe_2CF_3)_2]_2$ was prepared as described in the literature.[1]

$[W(OCMe_2CF_3)_2Cl]_2(\mu\text{-N-}2,6\text{-}Me_2C_6H_3)_2$. A solution of 150 mg of $[W(NAr')(OCMe_2CF_3)_2]_2$ (0.135 mmol) in 3 mL of benzene was stirred, and 16 μL of carbon tetrachloride (0.16 mmol) was added. The color immediately changed from dark yellow-brown to dark red-brown. After 2 h all volatiles were removed in vacuo. Recrystallization of the residue from toluene afforded analytically pure product: yield 148 mg (93%); ^1H NMR (C_6D_6) δ 7.01 (d, 2), 6.81 (t, 1), 1.88 (s, 6), 1.45 (s, 6), 1.23 (s, 6); ^{19}F NMR (C_6D_6) δ −81.46 (s). Anal. Calcd for $C_{16}H_{21}F_6NO_2ClW$: C, 32.43; H, 3.57; N, 2.36. Found: C, 32.08; H, 3.44; N, 2.17.

Single crystals suitable for X-ray diffraction studies were grown from toluene solution at −30 °C.

Reaction between $[W(N\text{-}2,6\text{-}Me_2C_6H_3)(OCMe_2CF_3)_2]_2$ and I_2. To a −30 °C suspension of $[W(NAr')(OCMe_2CF_3)_2]_2$ (100 mg, 0.0897 mmol) in 3 mL of pentane was added a cold solution of iodine (45.7 mg, 0.180 mmol) in 3 mL of pentane. The reaction mixture was stirred for 6 h at room temperature, during which time the color slowly changed from dark yellow-brown to red to green. The reaction mixture was then filtered through Celite and all solvents removed from the filtrate in vacuo to yield a solid that was determined by NMR to be a mixture of at least two products. Addition of 3 mL of pentane to the residue gave a mixture of green solution and insoluble brick red solids. The brick red solids were collected on a frit, washed with 3 mL of pentane, and redissolved in 1 mL of toluene. Crystals of $W(NAr')(OCMe_2CF_3)_3I$ suitable for X-ray diffraction studies were obtained by storing the solution at −30 °C. Single crystals of $W(OCMe_2CF_3)_3I_3$, on the other hand, were obtained from the green filtrate upon storage at −30 °C. Full characterization of $W(NAr')(OCMe_2CF_3)_3I$ and $W(OCMe_2CF_3)_3I_3$ and identification of any other products formed in the reaction were not pursued.

$[W(N\text{-}2,6\text{-}Me_2C_6H_3)(OCMe_2CF_3)_2]_2(PMe_3)$. PMe_3 (95 μL, 0.90 mmol, 10 equiv) was added via syringe to a rapidly stirred dark brown suspension of $[W(NAr')(OCMe_2CF_3)_2]_2$ (100 mg, 0.0897 mmol) in 5 mL of pentane. The reaction mixture immediately turned dark green. After 1.5 h, all volatiles were removed in vacuo to give 104 mg of product as a dark green powder in quantitative yield: ^1H NMR (C_6D_6) δ 7.11 (d, 1), 7.06 (s, 3), 6.96 (d, 1), 6.85 (t, 1), 3.31 (s, 3), 2.52 (s, 6), 2.13 (s, 3), 1.65 (s, 3), 1.59 (s, 3), 1.47 (s, 3), 1.32 (s, 3), 1.29 (s, 3), 1.27 (s, 3), 1.22 (s, 3), 1.15 (s, 3), 1.04 (d, 9, $^2J_{HP}$ = 9 Hz); ^{19}F NMR (C_6D_6) δ −80.38 (s, 1), −80.65 (s, 1), −80.88 (s, 1), −81.87 (s, 1); ^{31}P NMR (C_6D_6) δ −1 (s, J_{HW} = 271 Hz). Anal. Calcd for $C_{35}H_{51}F_{12}N_2O_4PW_2$: C, 35.31; H, 4.32; N, 2.35. Found: C, 35.39; H, 4.42; N, 2.28.

$[W(N\text{-}2,6\text{-}Me_2C_6H_3)(OCMe_2CF_3)_2]_2(\mu\text{-}C_2H_4)$. To a 100 mL Schlenk bomb containing a stir bar was added 400 mg of $[W(NAr')(OCMe_2CF_3)_2]_2$ (0.359 mmol) and 20 mL of pentane. The reaction mixture was freeze−pump−thaw degassed three times before being exposed to an atmosphere of ethylene (∼10 equiv). The color changed from green to yellow-orange as the reaction mixture was warmed to room temperature. The reaction was stirred at room temperature for 4 h. The volatiles were then removed in vacuo to give 383 mg of yellow powder (93% yield): ^1H NMR (toluene-d_8) δ 6.71 (m, 5), 6.56 (t, 1), 4.31 (m, 1, J_{CH} = 158 Hz), 3.11 (m, 1, J_{CH} = 150 Hz), 2.31 (s, 6), 2.27 (s, 6), 1.87 (s, 3), 1.84 (m, 1, J_{CH} = 150 Hz), 1.82 (s, 3), 1.64 (s, 3), 1.62 (m, 1, J_{CH} = 153 Hz), 1.43 (s, 3), 1.35 (s, 3), 1.25 (s, 3), 1.18 (s, 3); ^{13}C NMR (toluene-d_8) δ 154.09, 153.67, 136.62, 135.40, 127.86, 127.20, 126.94, 123.31, 84.51 (q, J_{CF} = 29 Hz), 82.14 (q, J_{CF} = 29 Hz), 81.97 (q, J_{CF} = 29 Hz), 80.51 (q, J_{CF} = 29 Hz), 66.18 (J_{CW} = 60 Hz, J_{CC} = 26 Hz), 33.97 (J_{CW} = 22 Hz, J_{CC} = 26 Hz), 27.18, 25.43, 25.10, 24.95, 24.48, 24.47, 23.45, 23.28, 19.18; ^{19}F NMR (C_6D_6) δ −80.07 (s, 1), −80.90 (s, 1), −80.94 (s, 1), −81.44 (s, 1). Multiple attempts at elemental analyses gave low values for C and H. The reason is proposed to be partial loss of of ethylene before analysis.

Single crystals suitable for X-ray diffraction studies were grown from pentane solution at −30 °C.

Reaction between $[W(N\text{-}2,6\text{-}Me_2C_6H_3)(OCMe_2CF_3)_2]_2$ and Acetonitrile. Acetonitrile (46.8 μL, 0.897 mmol) was added via syringe to a solution of $[W(NAr')(OCMe_2CF_3)_2]_2$ (250 mg, 0.224 mmol) in 5 mL of benzene. The reaction was stirred for 1 h at room temperature. The solvent was then removed in vacuo to afford a brown residue. Recrystallization in pentane gave red-brown microcrystals in 47% yield (127 mg). The ^{19}F NMR showed there to be a mixture of two products, the major one comprising 90% of the mixture. Major product (**A**), "$W(N\text{-}2,6\text{-}Me_2C_6H_3)(OCMe_2CF_3)_2(CH_3CN)$": ^1H NMR (C_6D_6) δ 6.99 (d, 2), 6.77 (t, 1), 2.42 (s, 6), 1.85 (s, 3), 1.48 (s, 6), 1.45 (s, 6); ^{19}F NMR (C_6D_6) δ −82.39 (s). Minor product (**B**), $(OCMe_2CF_3)_2W(\mu\text{-N-}2,6\text{-}Me_2C_6H_3)[\mu\text{-N(Me)C{=}C(Me)N}]W(OCMe_2CF_3)_2$: ^{19}F NMR (C_6D_6) δ −80.73 (s, 1), −80.99 (s, 1), −81.19 (s, 1), −81.42 (s, 1). Anal. Calcd for $C_{18}H_{24}F_6N_2O_2W$: C, 36.14; H, 4.04; N, 4.68. Found: C, 35.88; H, 3.92; N, 4.60.

Single crystals suitable for X-ray diffraction studies were grown from pentane solution at −30 °C. A crystal of the minor product (**B**) was selected (at random) for crystallographic studies.

$\{W(N\text{-}2,6\text{-}Me_2C_6H_3)[OCMe_2(CF_3)]_2\}_2(\mu\text{-}\eta^2,\eta^2\text{-MeCCMe})$. To a rapidly stirred suspension of $[W(NAr')(OCMe_2CF_3)_2]_2$ (500 mg, 0.449 mmol) in 5 mL of pentane was added 70 μL (0.90 mmol) of 2-butyne. The initially dark brown mixture turned red-orange within 2 min. The reaction mixture was then stirred at room temperature. After 2 h the mixture was filtered through Celite and the filtrate was concentrated to dryness in vacuo to give a red-orange residue. Recrystallization of the residue from pentane gave 428 mg of analytically pure sample in 82% yield: ^1H NMR (toluene-d_8) δ 6.99 (d, 1), 6.97 (d, 1), 6.82 (m, 3), 6.67 (t, 1), 3.20 (s, 6), 2.99 (s, 3), 2.96 (s, 3), 2.26 (br s, 6), 1.77 (br s, 6), 1.31 (s, 3), 1.17 (s, 3), 0.99 (s, 3), 0.86 (br s, 6), 0.63 (s, 3); ^{13}C NMR (toluene-d_8) δ 223.19 (J_{CW} = 114 and 12 Hz), 197.18 (J_{CW} = 134 and 12 Hz), 158.38, 154.07, 134.59, 132.99, 131.77, 130.46, 128.25, 126.40, 126.15, 83.46 (q, J_{CF} = 29 Hz), 82.36 (q, J_{CF} = 29 Hz), 25.45, 25.31, 25.25, 25.00, 24.46, 24.05, 23.43, 23.20, 22.97, 19.50; ^{19}F NMR (C_6D_6) δ −80.68 (br s, 2), −81.72 (s, 1), −82.71 (s, 1). Anal. Calcd for $C_{18}H_{24}F_6NO_2W$: C, 37.01; H, 4.14; N, 2.40. Found: C, 36.82; H, 4.08; N, 2.38.

$(OCMe_2CF_3)_2(Et)W(\mu\text{-N-}2,6\text{-}Me_2C_6H_3)(\mu\text{-N-}2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)W(OCMe_2CF_3)_2$. The ethylene adduct $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}C_2H_4)$ was prepared in situ by exposing a freeze−pump−thaw degassed solution of $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ (500 mg, 0.449 mmol) in 20 mL of benzene to an atmosphere of ethylene (7 equiv). The yellow-orange reaction mixture was heated at 90 °C for 6 days. All volatiles were removed in vacuo to give a red-orange residue, which was then triturated in 5 mL of cold pentane. The solids were collected on a frit, washed with more pentane, and dried to give 170 mg of brick red powder. An additional 134 mg of product was recovered from the filtrate to give a combined yield of 304 g (60%): ^1H NMR (toluene-d_8) δ 7.06 (d, 1), 7.01 (t, 1), 6.95 (m, 3), 6.87 (d, 1), 4.45 (d, 1, J_{HH} = 18 Hz), 2.82 (s, 3), 1.88 (s, 3), 1.72 (s, 3), 1.64 (m, 1), 1.51 (s, 3), 1.50 (t, 3), 1.46 (d, 1, J_{HH} = 18 Hz), 1.38 (m, 1), 1.34 (s, 3), 1.25 (s, 3), 1.23 (s, 3), 1.13 (s, 3), 1.11 (s, 3), 1.02 (s, 3), 0.99 (s, 3); ^{13}C NMR (toluene-d_8) δ 169.89, 163.86, 149.27, 132.16, 130.65, 129.91, 129.24, 128.77, 128.63, 128.11, 127.94, 127.30, 86.43 (q, J_{CF} = 31 Hz), 83.84 (q, J_{CF} = 29 Hz), 83.11 (q, J_{CF} = 28 Hz), 80.35 (q, J_{CF} = 28 Hz), 67.57 (J_{CW} = 97 Hz), 57.44 (J_{CW} = 100 Hz), 25.09, 24.55, 24.53, 23.76, 23.29, 22.98, 22.49, 22.27, 20.63, 19.12, 18.33, 18.32, 13.22; ^{19}F NMR (C_6D_6) δ −79.22 (s, 1), −80.90 (s, 1), −82.03 (s, 1), −82.50 (s, 1). Anal. Calcd for $C_{17}H_{23}F_6NO_2W$: C, 35.75; H, 4.06; N, 2.45. Found: C, 35.56; H, 3.97; N, 2.36.

Single crystals suitable for X-ray diffraction studies were grown from toluene solution at −30 °C.

X-ray Crystallography. Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å), performing φ and ω scans. The structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[30] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). A disordered pentane molecule in the structure of $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}\eta^2:\eta^2\text{-MeCCMe})$ (05058) was refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Details of the data quality and a summary of the residual values of the three structures are given in Table 1.

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Supporting Information Available: Tables and figures giving experimental details and labeled thermal ellipsoid drawings, crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $[W(OCMe_2CF_3)_2Cl]_2(\mu\text{-NAr}')_2$ (05145), $[W(NAr')(OCMe_2CF_3)_2]_2(\mu\text{-}\eta^2:\eta^2\text{-MeCCMe})$ (05058), and $(OCMe_2CF_3)_2W(\mu\text{-NAr}')[\mu\text{-N(Me)C=C(Me)N=}]W(NAr')(OCMe_2CF_3)_2$ (05134). This material is available free of charge via the Internet at http://pubs.acs.org. Data for the structures are also available to the public at http://www.reciprocalnet.org/.

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