2060 (m), 1995 (vs), 1978 (m), 1962 (vs), 1949 (s)) are similar to the spectrum of **3** and as these authors noted, C, H analyses will not unambiguously distinguish $(CO)_9$ and $(CO)_{10}$ formulations. We suspect Vahrenkamp's compounds are $(CO)_9$ derivatives analogous to **3**, a conclusion which could be verified by the ^{31}P NMR chemical shift position of the μ-PMe_2 ligand in $WRe(\mu\text{-}PMe_2)(CO)_x$, but this data was not reported.

The donor–acceptor W–Re bond in **3** is relatively weak as it is readily cleaved by better donor ligands such as CH_3CN and $PMePh_2$ to form **4** and **5**. Both of these ligands appear to bond irreversibly, thus prohibiting the metal–metal bond from reforming. This easy generation of an open coordination site on Re from W–Re bond cleavage in **3** also provides a low-energy decomposition pathway for the formyl derivatives of **3**. The latter are not stable above −20 °C as they readily undergo deinsertion concomitant with W–Re bond cleavage to form the hydride complex **6**. Also, reaction of **3** with RLi reagents led directly to the methyl and phenyl complexes **9** and **10**. Such easy cleavage of donor–acceptor bonds to open coordination sites will likely limit the formyl and acyl derivative chemistry of such compounds. To circumvent this problem, we first displaced the W–Re bond by adding $PMePh_2$ to **3** to form complex **4**. This latter complex then gave more stable formyl and acyl derivatives.

The relative thermal stabilities of the formyl complex **8** and the isoelectronic acetyl complex **11** are somewhat surprising. Recall that **11** undergoes deinsertion at lower temperatures than does **8**. Previous studies[15,16] have shown that deinsertion of a formyl ligand is kinetically and thermodynamically favored over deinsertion of an acetyl ligand. The decomposition of **8** and **11** presumably occurs via initial phosphine loss to open a coordination site. Apparently, loss of phosphine from the acetyl complex **11** is more favored than loss of $PMePh_2$ from the formyl complex **8**, and hence the former undergoes more rapid deinsertion.

An interesting aspect of the chemistry of these W–Re complexes is the domination of the reactivity by the rhenium center. In the case of nucleophilic attack at metal-bound carbonyls by RLi and $Li[BHEt_3]$ reagents, this is probably due to the higher oxidation state of rhenium in the complex. Recall that in the donor–acceptor formulation, the oxidation states were W(0) and Re(I). This would render the carbonyls bound to rhenium more electrophilic and more susceptible to nucleophilic attack. Even when a basic phosphine ligand is bound to Re as in **4**, nucleophilic addition to the rhenium bound carbonyls is still preferred, suggesting that the increased electron density at the rhenium center due to phosphine binding is not sufficient to counter the oxidation state difference.

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Registry No. **2**, 92763-14-9; **3**, 92763-15-0; **4**, 92763-16-1; **5**, 92763-17-2; **6**, 92763-19-4; **7a**, 92763-20-7; **8**, 92786-71-5; **9**, 92763-21-8; **10**, 92763-22-9; **11**, 92763-23-0; $Li[W(CO)_5PPh_2]$, 92763-24-1; $Re(CO)_5Br$, 14220-21-4; $Li[BEt_3H]$, 22560-16-3; Re, 7440-15-5; W, 7440-33-7.

Supplementary Material Available: Tables of anisotropic temperature factors, calculated hydrogen atom positions, and structure factors (22 pages). Ordering information is given on any current masthead page.

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A General Route to Tri-*tert*-butoxytungsten Alkylidyne Complexes. Scission of Acetylenes by Ditungsten Hexa-*tert*-butoxide†[1]

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Alkylidyne complexes of the type $W(CX)(OCMe_3)_3$ can be prepared by reacting $W_2(OCMe_3)_6$ with XC≡CX or RC≡CX (R = Me or Et; X = Me, Et, Pr, CMe_3, Ph, $CH{=}CH_2$, CH_2NR_2, CH_2OMe, CH_2OSiMe_3, $CH(OEt)_2$, CO_2Me, CH_2CO_2Me, C(O)Me, $SCMe_3$, or H). Several others have been prepared by reacting $W(CMe)(OCMe_3)_3$ with XC≡CX or RC≡CX (X = $SiMe_3$, NEt_2, CH_2CN, C≡CEt, or CN). In one case a diacetylene (EtC≡CC≡CEt) reacts with $W_2(OCMe_3)_6$ to give $[(Me_3CO)_3W{\equiv}C]_2$. Approximately half of the compounds can be isolated only as adducts, $W(CX)(OCMe_3)_3(B)$, where B = pyridine or quinuclidine. By analogy with WC_3 tungstenacyclobutadiene and "tungstenatetrahedrane" (η^3-cyclopropenyl) complexes it is proposed that alkylidyne complexes can form only from a molecule having a planar 1,3-W_2C_2 core and that added nitrogenous base can play a direct role in the scission reaction. Derivatized alkylidyne complexes that contain electron donors react most rapidly with 3-heptyne; those that contain electron acceptors directly attached to the α-carbon do not react with 3-heptyne to any significant extent at 25 °C. We conclude that the W≡C bond behaves as if it were polarized W(+)≡C(−).

Introduction

$W(CCMe_3)(OCMe_3)_3$ is a remarkably effective catalyst for the metathesis of dialkylacetylenes (eq 1).[2] Its synthesis consists of first preparing $W(CCMe_3)(CH_2CMe_3)_3$ from $W(OMe)_3Cl_3$ and 6 equiv of Me_3CCH_2MgCl, treating $W(CCMe_3)(CH_2CMe_3)_3$ with 3 equiv of HCl in the presence of dimethoxyethane to give $W(CCMe_3)$(1,2-dimethoxyethane)Cl_3, and reacting $W(CCMe_3)(dme)Cl_3$ with 3 equiv

$$RC{\equiv}CR + R'C{\equiv}CR' \rightleftarrows 2RC{\equiv}CR' \qquad (1)$$

†This paper is dedicated to the memory of Earl Muetterties.

(1) Multiple Metal Carbon Bonds. 35. For part 34 see: McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4067.
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of $LiOCMe_3$.[3] There are two disadvantages to this route. First, the formation of $W(CCMe_3)(CH_2CMe_3)_3$ involves a controlled α-hydrogen abstraction[4] reaction in some as yet unknown intermediate, possibly $W(OMe)_2(CH_2CMe_3)_2Cl_2$,[3] and since α-hydrogen abstraction appears to be limited to alkyl ligands not having β-hydrogen atoms (neopentyl and trimethylsilylmethyl in particular), other $W(CX)(OCMe_3)_3$ complexes would have to be prepared indirectly by a metathesis reaction between $W(CCMe_3)(OCMe_3)_3$ and XC≡CX or RC≡CX. Second, the yield of $W(CCMe_3)(CH_2CMe_3)_3$ is only ~50–60% and the neopentyl groups are sacrificed. Fortunately we discovered a potentially more general route to tri-*tert*-butoxytungsten alkylidyne complexes which consists of a metathesis-like reaction between $W_2(OCMe_3)_6$ and an acetylene.[5] In theory we can now prepare a large variety of alkylidyne complexes, even those containing functional groups, more simply and directly. In this paper we report our first in-depth study of reactions of this type. Our primary goals are, first, to determine what types of functionalized alkylidyne complexes can be made and, second, to compare the reactivities of different functionalized alkylidyne complexes toward ordinary acetylenes. Both goals anticipate designing catalysts for the metathesis of functionalized acetylenes.

Results

Simple Alkylidyne Complexes. $W_2(OR)_6$ (OR = $OCMe_3$ throughout) reacts rapidly at room temperature in pentane with one or more equivalents of 2-butyne, 3-hexyne, or 4-octyne to yield white, crystalline $W(CMe)(OR)_3$, $W(CEt)(OR)_3$, and $W(CPr)(OR)_3$, respectively, in good yield. These volatile compounds are very soluble in pentane and therefore best isolated by sublimation of the solid reaction product mixture at 25 °C onto a −78 or 0 °C cold finger. The reaction with 2-butyne must be conducted at −30 °C in order to avoid polymerization of the 2-butyne. (The mechanism of polymerization is not known.) The other two reactions are complete in 2–3 h at room temperature. For larger scale preparations, it is important to use no more than 1.05 equiv of acetylene to prevent formation of oily side products. The sensitivity of the complexes to air, water, and miscellaneous reagents, and therefore the difficulty of handling them, varies in the order ethylidyne > propylidyne ≈ butylidyne.

The ethylidyne complex has been shown by X-ray studies[6] to be a dimer containing weakly bridging *tert*-butoxide ligands donating in a position *trans* to the ethylidyne ligand. The result is a pseudo-trigonal-bipyramidal arrangement of ligands about each metal center. We have found that pyridine and quinuclidine form adducts with some alkylidyne complexes. We propose that the base also coordinates trans to the alkylidyne ligand. $W(CMe)(OR)_3(py)$ can be sublimed in a *static* vacuum with most of the pyridine intact, but pyridine is lost when $W(CMe)(OR)_3(py)$ is sublimed in a dynamic vacuum over a period of 16 h at 25 °C. Addition of 1 equiv of pyridine to $W(CMe)(OR)_3(py)$ in an NMR tube results in a single set of pyridine proton resonances midway between the positions for free and coordinated pyridine. The exchange process is likely to be dissociative in view of the steric congestion imposed by the *tert*-butoxide ligands. $W(CMe)(OR)_3(quin)$ also sublimes intact in a static vacuum, and free quinuclidine exchanges rapidly with coordinated quinuclidine at room temperature. It is interesting to note that $W(CCMe_3)(OR)_3(py)$ loses pyridine in vacuo more readily than $W(CMe)(OR)_3(py)$ while $W(CCMe_3)(OR)_3(quin)$ is relatively stable toward loss of quinuclidine in vacuo. These qualitative observations suggest that quinuclidine (the stronger Brønsted base), in spite of its larger size, coordinates more strongly than pyridine, and that the stability of the nitrogenous base adducts of these complexes toward loss of that base depends sensitively upon the size of the substituent on the alkylidyne ligand's α-carbon atom.

$W_2(OR)_6$ does not react readily with $Me_3CC{\equiv}CCMe_3$, $Me_3SiC{\equiv}CSiMe_3$, $Me_3SnC{\equiv}CSnMe_3$, or PhC≡CPh. In the first three cases steric problems are most likely at fault, but in the last case unfavorable electronics are probably at least as important. (We believe that the first step in a metathesis-like reaction may be described as attack on substrate by an electrophilic metal center; see Discussion.) If the reaction between PhC≡CPh and $W_2(OR)_6$ is forced by going to higher temperatures then more complex reactions ensue.[7a] The same is true of reactions involving 3-hexyne at higher temperatures.[7b]

In general, unsymmetrically substituted acetylenes appear to react more readily with $W_2(OR)_6$ than do symmetrically substituted acetylenes. In a reaction between $W_2(OR)_6$ and 2 equiv of $MeC{\equiv}CCMe_3$ in an NMR tube $W(CMe)(OR)_3$ and $W(CCMe_3)(OR)_3$ are formed in close to the expected 1:1 ratio. If $MeC{\equiv}CCMe_3$ is present in large excess (10 equiv) and if a dynamic vacuum is applied to the reaction mixture in pentane, only $W(CCMe_3)(OR)_3$ is isolated (eq 2). We suspect that $W(CCMe_3)(OR)_3$ does

$$W_2(OR)_6 + 10MeC{\equiv}CCMe_3 \rightarrow 2W(CCMe_3)(OR)_3 + MeC{\equiv}CMe \quad (2)$$

not react with $MeC{\equiv}CCMe_3$ to give $W(CMe)(OR)_3$ as rapidly as $W(CMe)(OR)_3$ reacts with $MeC{\equiv}CCMe_3$ to give $W(CCMe_3)(OR)_3$ and that the 2-butyne is removed relatively selectively in vacuo, thereby driving the reaction to the right.

The method shown in eq 2 does not work for preparing $W(CSiMe_3)(OR)_3$. Under conditions identical with those used to prepare $W(CCMe_3)(OR)_3$ only an approximately 2:1 mixture favoring $W(CSiMe_3)(OR)_3$ results (eq 3). White, crystalline, sublimable $W(CSiMe_3)(OR)_3$ can be prepared pure as shown in eq 4.

$$W_2(OR)_6 + 10MeC{\equiv}CSiMe_3 \rightarrow W(CSiMe_3)(OR)_3 + W(CMe)(OR)_3 \quad (3)$$
$$\sim 2{:}1$$

$$W(CMe)(OR)_3 + 5Me_3SiC{\equiv}CSiMe_3 \rightarrow W(CSiMe_3)(OR)_3 \quad (4)$$

Functionalized Alkylidyne Complexes. Complexes in which the W≡C bond is conjugated with another multiple-bond form readily (eq 5 and 6). The benzylidyne

$$W_2(OR)_6 + 2EtC{\equiv}CR' \rightarrow EtC{\equiv}CEt + 2W(CR')(OR)_3 \quad (5)$$
$$R' = C_6H_5,\ CH{=}CH_2$$

$$W_2(OR)_6 + EtC{\equiv}CC{\equiv}CEt \rightarrow EtC{\equiv}CEt + (RO)_3W{\equiv}CC{=}W(OR)_3 \quad (6)$$

and vinylmethylidyne complexes are yellow and sublime readily; the dinuclear complex is red and relatively nonvolatile, but soluble in pentane. Preliminary studies show

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that $(RO)_3W{\equiv}CC{\equiv}W(OR)_3$ is not a rapid metathesis catalyst for 3-heptyne (see later). Therefore, it may be formed preferentially in the reaction shown in eq 6 simply because it is the least reactive of the three possible alkylidyne complexes. We shall see later that it is possible to isolate the suspected intermediate in this reaction $W(CC{\equiv}CEt)(OR)_3$ as a quinuclidine adduct, by using a different approach (eq 18).

A (dimethylamino)methyl derivative can be prepared as shown in eq 7. This compound is obtained as tiny white

$$W_2(OR)_6 + Me_2NCH_2C{\equiv}CCH_2NMe_2 \rightarrow [W(CCH_2NMe_2)(OR)_3]_x \quad (7)$$

needles directly from the reaction mixture (pentane solvent). Because of its insolubility (compared to $W(CCH_2NEt_2)(OR)_3$ below), we believe it to be a polymer formed by coordination of the amine nitrogen trans to the W≡C bond in another molecule. In the presence of pyridine the polymer dissolves in pentane, presumably due to adduct formation; the polymer reforms when the pentane (and pyridine) is removed in vacuo. Similar results are observed in the case of $[W(N)(OR)_3]_x$,[8] a molecule that is known to form W≡N→W chains.[6] In contrast to $[W(CCH_2NMe_2)(OR)_3]_x$ the diethylamino derivative (eq 8) dissolves readily in pentane. We presume it is a monomer.

$$W_2(OR)_6 + Et_2NCH_2C{\equiv}CCH_2NEt_2 \rightarrow 2W(CCH_2NEt_2)(OR)_3 \quad (8)$$

The reactions shown in eq 9 require ~24 h to produce a maximum product yield of ~50%; there appears to be some decomposition. The reactions proceed qualitatively

$$W_2(OR)_6 + R'OCH_2C{\equiv}CCH_2OR' \xrightarrow{\text{pentane}} W(CCH_2OR')(OR)_3 \quad (9)$$
$$\sim 50\%$$
$$R' = Me, SiMe_3$$

more rapidly and more cleanly in ether or DME and still more rapidly and cleanly in THF. In the presence of 12 equiv of pyridine the reactions shown in eq 9 are essentially complete in ~3 h. The best results (nearly quantitative yields by NMR) are obtained in THF in the presence of pyridine. Quinuclidine is equally effective at increasing the rate and preventing decomposition, and the white, crystalline quinuclidine adducts can be isolated readily. In the presence of 12 equiv of 2,6-dimethylpyridine, which does not form an adduct with $W(CMe)(OR)_3$, no improvement relative to the base-free system is noted. Although these and other data are sparse and only qualitative, they suggest to us that contrary to intuition, some bases will accelerate rather than retard reaction of an acetylene with $W_2(OR)_6$, in addition to simply stabilizing the product by coordinating to it. We will return to this point later.

Addition of 2 equiv of *n*-$BuC{\equiv}CCH_2OSiMe_3$ to $W_2(OR)_6$ in pentane produces a 2:1 mixture of the expected products (in favor of $W(CCH_2OSiMe_3)(OR)_3$) within a few minutes at 25 °C. If the reaction mixture is taken to dryness in vacuo, only $W(CCH_2OSiMe_3)(OR)_3$ is observed by NMR. The reaction is cleaner in the presence of quinuclidine, and $W(CCH_2OSiMe_3)(OR)_3$(quin) can be isolated.

The addition of 2 equiv of $EtC{\equiv}CCH(OEt)_2$ to $W_2(OR)_6$ in THF yields initially a light orange solution, characteristic of a clean reaction of the acetylene with the tungsten–tungsten triple bond. However, in a few minutes the solution darkens abruptly and extensive decomposition is apparent. The reaction shown in eq 10 is essentially

$$W_2(OR)_6 + 2EtC{\equiv}CCH(OEt)_2 + 12B \rightarrow 2W[CCH(OEt)_2](OR)_3(B) \quad (10)$$
$$B = py, quin$$

complete in the presence of 12 equiv of pyridine or quinuclidine. The quinuclidine reaction is cleaner and the quinuclidine adduct can be isolated as white, pentane-soluble crystals. $W(CMe)(OR)_3$ reacts with $EtC{\equiv}CCH(OEt)_2$ in the presence of pyridine to give only $W[CCH(OEt)_2](OR)_3$(py), while under the same conditions in the presence of quinuclidine, ~25% of $W(CMe)(OR)_3$(quin) remains. We suspect that the stronger base (quinuclidine) slows down the metathesis reaction between $W(CMe)(OR)_3$ and $EtC{\equiv}CCH(OEt)_2$.

Only in the presence of quinuclidine can the carbomethoxymethylidyne complex (eq 11) be isolated cleanly

$$W_2(OR)_6 + 2EtC{\equiv}CCO_2Me + 12quin \rightarrow W(CCO_2Me)(OR)_3(quin) \quad (11)$$

(light green crystals from pentane). $W(CMe)(OR)_3$(quin) also reacts with $EtC{\equiv}CCO_2Me$ to yield the desired product. Dimethyl acetylenedicarboxylate does not react cleanly with $W_2(OR)_6$ *or* $W(CMe)(OR)_3$ under the most favorable circumstances (in the presence of py or quin). $W(CCO_2Me)(OR)_3$(quin) decomposes slowly in solution in the presence of $EtO_2CC{\equiv}CCO_2Et$, and we see no evidence for formation of $W(CCO_2Et)(OR)_3$(quin).

Moving the carbomethoxy group out of conjugation with the triple bond has a dramatic effect. The reaction shown in eq 12 is successful in pentane or THF in the absence

$$W_2(OR)_6 + 2MeC{\equiv}CCH_2CO_2Me \rightarrow 2W(CCH_2CO_2Me)(OR)_3 \quad (12)$$

of base. The product is best isolated as a quinuclidine adduct by addition of quinuclidine to the crude reaction mixture obtained by removing all solvent (and 2-butyne) in vacuo. Unfortunately, even after crystallization from ether/acetonitrile a small amount of $W(CMe)(OR)_3$(quin) remains in the isolated product. When pyridine or (especially) quinuclidine is added *before* taking the solution to dryness, mixtures containing substantial amounts of the ethylidyne complex are obtained. Again, we believe that the base slows down the metathesis reaction between $W(CMe)(OR)_3$ and $MeC{\equiv}CCH_2CO_2Me$.

An extremely sensitive system, apparently requiring both pyridine and quinuclidine simultaneously, is that shown in eq 13. The compound can be isolated as clear

$$W_2(OR)_6 + 2EtC{\equiv}CCOCH_3 + 5py + 2quin \xrightarrow[-30\ °C]{\text{pentane}} W(CCOMe)(OR)_3(quin) \quad (13)$$

light yellow crystals from the reaction mixture. It decomposes readily in the solid state or in solution at 25 °C. It is stable long enough in the presence of excess quinuclidine to obtain a fairly clean ^1H NMR spectrum, but within a few hours at room temperature the solution is dark purple, and the NMR spectra are complex.

Let us turn our attention to more electron-rich acetylenes. $W_2(OR)_6$ does not react with $Et_2NC{\equiv}CNEt_2$, even in the presence of pyridine or quinuclidine. $W_2(OR)_6$ does react with $MeC{\equiv}CNEt_2$, but decomposition is extensive. The reaction between $W_2(OR)_6$ and $MeC{\equiv}CNEt_2$ is cleaner in the presence of base, but only mixtures of the W(CMe) and $W(CNEt_2)$ products are obtained. The (diethylamino)methylidyne complex can be prepared from $W(CMe)(OR)_3$ and $Et_2NC{\equiv}CNEt_2$, and the yellow, crys-

(8) Pedersen, S. F. Ph.D. Thesis, Massachusetts Institute of Technology, 1983.

talline quinuclidine adduct can be isolated (eq 14). The

$$W(CMe)(OR)_3 + Et_2NC{\equiv}CNEt_2 + 6quin \rightarrow W(CNEt_2)(OR)_3(quin) \quad (14)$$

reaction requires ~5 h to go to completion. The quinuclidine-free (dimethylamino)methylidyne complex has been prepared from $W_2(OR)_6$ and Me_2NCN and has been structurally characterized.[9] It is a dimer similar to $[W(CMe)(OR)_3]_2$; the coordination about the N atom is approximately planar, indicative of strong donation of the nitrogen lone pair into the π-system.

The interesting feature of the reaction shown in eq 15 is that no $W(CMe)(OR)_3$ is observed, even when the reaction is followed by NMR. $W(CSCMe_3)(OR)_3$ is yellow and crystalline, sublimes readily at 30–40 °C, and is extremely moisture sensitive. In the presence of quinuclidine in pentane, ~20% $W(CMe)(OR)_3(quin)$ can be observed, while after the same length of time in THF, only $W(CSCMe_3)(OR)_3(quin)$ is observed. Apparently even quinuclidine is not particularly effective in blocking the reaction between $W(CMe)(OR)_3$ and $MeC{\equiv}CSCMe_3$, perhaps because of the greater nucleophilicity of this acetylene's triple bond.

$$W_2(OR)_6 + 2MeC{\equiv}CSCMe_3 \rightarrow 2W(CSCMe_3)(OR)_3 \quad (15)$$

$W_2(OR)_6$ does not react cleanly with 2 equiv of $MeC{\equiv}COEt$ in the absence of quinuclidine. In the presence of quinuclidine ~1:1 mixtures of $W(CMe)(OR)_3$ and $W(COEt)(OR)_3$ are found, presumably as quinuclidine adducts, according to ^1H and ^{13}C NMR spectra. In $W(COEt)(OR)_3(quin)$ the $OCMe_3$ resonance is found at 1.19 ppm, rather than the more characteristic 1.4–1.6 ppm.

Since $W_2(OR)_6$ reacts readily with both C≡C and C≡N functionalities[5] and less hindered alkylidynes such as $W(CMe)(OR)_3$ react with nitriles to afford $[W(N)(OR)_3]_x$,[8] we decided to investigate the reactivity of acetylenes containing the cyano functionality. $W_2(OR)_6$ does not react cleanly with 2 equiv of $EtC{\equiv}CCH_2CN$ in the absence or presence of base; light, insoluble, presumably polymeric solids are observed. We suspect that the C≡C and C≡N bonds react at comparable rates. In contrast, $W(CMe)(OR)_3$ reacts with $EtC{\equiv}CCH_2CN$ in the presence of pyridine to yield dark green $W(CCH_2CN)(OR)_3(py)$ (eq 16) in good yield; it crystallizes directly from the reaction mixture. The reaction is not clean in the absence of a base. In the presence of quinuclidine a 4:1 mixture of $W(CCH_2CN)(OR)_3(quin)$ and $W(CEt)(OR)_3(quin)$ (respectively) results.

$$W(CMe)(OR)_3 + EtC{\equiv}CCH_2CN + 6py \xrightarrow[-30\ °C]{pentane} W(CCH_2CN)(OR)_3(py) \quad (16)$$

When the nitrile is moved into conjugation with the acetylenic bond, it becomes possible to observe both C≡C and C≡N bond cleavages. As shown in eq 17 the C≡N bond is cleaved more rapidly by $W_2(OR)_6$. The orange, base-stabilized $W(CC{\equiv}CEt)(OR)_3(quin)$ complex is actually more conveniently prepared as shown in eq 18. Recall from our earlier discussion that the reaction of $W(CEt)(OR)_3$ with $EtC{\equiv}CC{\equiv}CEt$ in the absence of base yields largely $(RO)_3W{\equiv}CC{\equiv}W(OR)_3$. Apparently an excess of quinuclidine is effective in preventing further metathesis of $W(CC{\equiv}CEt)(OR)_3$ with $EtC{\equiv}C\text{–}C{\equiv}CEt$. This argument is supported by the result shown in eq 19, where we do observe slow formation of the dinuclear alkylidyne complex.

$$W_2(OR)_6 + EtC{\equiv}CCN + 12quin \xrightarrow[-30\ °C]{pentane} W(CC{\equiv}CEt)(OR)_3(quin) + [W(N)(OR)_3]_x \quad (17)$$

$$W(CMe)(OR)_3 + EtC{\equiv}CC{\equiv}CEt + 10quin \xrightarrow[2\ days]{pentane} W(CC{\equiv}CEt)(OR)_3(quin) \quad (18)$$

$$W(CC{\equiv}CEt)(OR)_3(quin) + W(CEt)(OR)_3 \xrightarrow[slow]{pentane} (RO)_3W{\equiv}CC{\equiv}W(OR)_3(quin) \quad (19)$$

The reaction shown in eq 20 should be contrasted with that shown in eq 17. Apparently a W≡C bond reacts more readily with a C≡C bond than it does with a C≡N bond.

$$W(CMe)(OR)_3 + EtC{\equiv}CCN + 12quin \xrightarrow{THF} W(CCN)(OR)_3(quin) \quad (20)$$

Preparation of the Methylidyne Complex. Terminal acetylenes react with $W_2(OR)_6$ to give only the substituted alkylidyne complex in ~50% yield, even in the presence of pyridine (eq 21). We suspect that $W(CH)(OR)_3(py)$ is not stable. However, in the presence of quinuclidine a 1:1 mixture of $W(CR')(OR)_3(quin)$ and $W(CH)(OR)_3(quin)$ is formed relatively cleanly in good yield by NMR. The methylidyne proton is observed at 5.15 ppm with J_{HW} = 90 Hz and the methylidyne α-carbon at 247.1 ppm with J_{CW} = 287 Hz and J_{CH} = 147 Hz. These numbers are similar to those obtained for other tri-*tert*-butoxy alkylidyne complexes and for the only other known terminal methylidyne complex $W(CH)(PMe_3)_4Cl$.[10] Evidently only quinuclidine binds strongly enough to prevent decomposition or further reaction of the methylidyne complex. It is possible to obtain small samples (<50 mg) of $W(CH)(OR)_3(quin)$ by fractionally subliming it away from $W(CPh)(OR)_3(quin)$.

$$W_2(OR)_6 + R'C{\equiv}CH + 12py \rightarrow W(CR')(OR)_3(py) \quad R' = Pr, i\text{-}Pr, SiMe_3, t\text{-}Bu, Ph \quad (21)$$

Acetylene itself reacts with $W_2(OR)_6$ to give a high yield of $W(CH)(OR)_3(quin)$ under carefully controlled conditions. Addition of 1 equiv of acetylene gas to a pentane solution of $W_2(OR)_6$, pyridine, and quinuclidine at −78 °C results initially in a dark, forest green solution. As the solution is warmed slowly to room temperature, the color changes to brown. The brown solid remaining after the solvent was removed in vacuo is relatively pure $W(CH)(OR)_3(quin)$ in >80% yield. The crude product may be purified by slowly subliming it at room temperature to yield an extremely sensitive white powder, but only in ~30% yield. We suspect that some quinuclidine is lost in vacuo and that the resulting "$W(CH)(OR)_3$" decomposes. If only pyridine is present, the reaction between $W_2(OR)_6$ and acetylene is considerably more complicated, and no $W(CH)(OR)_3(py)$ can be isolated. These results are consistent with the observations concerning reactions of terminal acetylenes and $W_2(OR)_6$ (see above). We feel confident in concluding that $W(CH)(OCMe_3)_3(quin)$ is considerably more stable than $W(CH)(OR)_3(py)$ and that $W(CH)(OR)_3$ itself is probably quite unstable.

Reactivity of Alkylidyne Complexes toward Acetylenes. One of our reasons for preparing functionalized alkylidyne complexes was to assess their reactivity in metathesis-like reactions. We have done this semiquantitatively in two ways. First, we examined the reaction of

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Table I. A Summary of Preparative Methods and ^{13}C NMR Data[a]

complex	method	$\delta(C_\alpha)$	J_{CW}, Hz
$W(CR')(OR)_3$	$W_2(OR)_6$ + R'C≡CR' (R' = Me, Et, Pr)	254.3, 262.6, 261.7, respectively	
$W(CCMe_3)(OR)_3$	$W_2(OR)_6$ + $Me_3CC{\equiv}CMe$	271.0	
$W(CSiMe_3)(OR)_3$	$W(CMe)(OR)_3$ + $Me_3SiC{\equiv}CSiMe_3$	292.1	
$W(CPh)(OR)_3$	$W_2(OR)_6$ + 2EtC≡CPh	257.0	
$W(CCH{=}CH_2)(OR)_3$	$W_2(OR)_6$ + $2EtC{\equiv}CCH{=}CH_2$	258.0	
$[(RO)_3W{\equiv}C]_2$	$W_2(OR)_6$ + $(EtC{\equiv}C)_2$	278.6	
$[W(CCH_2NMe_2)(OR)_3]_x$	$W_2(OR)_6$ + $(Me_2NCH_2C)_2$	262.7	295
$W(CCH_2NEt_2)(OR)_3$	$W_2(OR)_6$ + $(Et_2NCH_2C)_2$	260.1	302
$W(CCH_2OMe)(OR)_3$(quin)	$W_2(OR)_6$ + $(MeOCH_2C)_2$ + quin	253.6	286
$W(CCH_2OSiMe_3)(OR)_3$(quin)	$W_2(OR)_6$ + $(Me_3SiOCH_2C)_2$ + quin	254.8	288
$W[CCH(OEt)_2](OR)_3$(quin)[b]	$W_2(OR)_6$ + $2EtC{\equiv}CCH(OEt)_2$ + quin	254.7	292
$W(CCO_2Me)(OR)_3$(quin)[b]	$W_2(OR)_6$ + $2EtC{\equiv}CCO_2Me$ + quin	246.8	293
$W(CCH_2CO_2Me)(OR)_3$	$W_2(OR)_6$ + $2MeC{\equiv}CCH_2CO_2Me$	240.4	300
$W(CCOMe)(OR)_3$(quin)	$W_2(OR)_6$ + $2EtC{\equiv}CCOMe$ + py + quin		
$W(CNEt_2)(OR)_3$(quin)[b]	$W(CMe)(OR)_3$ + $Et_2NC{\equiv}CNEt_2$ + quin	223.2	332
$W(CSCMe_3)(OR)_3$	$W_2(OR)_6$ + $2MeC{\equiv}CSCMe_3$	222.7	
$W(CCH_2CN)(OR)_3$(py)	$W(CMe)(OR)_3$ + $EtC{\equiv}CCH_2CN$ + py	235.0	312
$W(CC{\equiv}CEt)(OR)_3$(quin)	$W(CMe)(OR)_3$ + $EtC{\equiv}C{-}C{\equiv}CEt$ + quin	232.2	296
$W(CCN)(OR)_3$(quin)[b]	$W(CMe)(OR)_3$ + $EtC{\equiv}CCN$ + quin	215.2	310
$W(CH)(OR)_3$(quin)	$W_2(OR)_6$ + C_2H_2 + py + quin	247.1	287

[a] Not all adducts are listed. Only the preferred preparative method is listed. Solvent = pentane, unless otherwise noted. Details such as the quantity of added base are omitted. [b] Solvent = THF.

Table II. Reaction of Some Alkylidyne Complexes with 1 Equiv of 3-Hexyne[a] and 20 Equiv of 3-Heptyne[b]

	compd	$[W(CEt)(OR)_3]/[W(CX)(OR)_3]$ at (time)	approx time to equilibrium[b] for 3-heptyne metathesis
1	$W(CCMe_3)(OR)_3$	2.4 (35 min)	<5 min
2	$W(CSiMe_3)(OR)_3$	3.9 (160 min)	<5 min
3	$W(CCH{=}CH_2)(OR)_3$	1/6.7 (160 min) 1/4.7 (230 min)	<7 min
4	$W(CCH_2NEt_2)(OR)_3$	4.5 (80 min)	<7 min
5	$W(CCH_2OMe)(OR)_3$(quin)	1/3.5 (75 min)	10 min
6	$W(CCH_2OSiMe_3)(OR)_3$(quin)	1/3.8 (85 min)	20 min
7	$W[CCH(OEt)_2](OR)_3$(quin)[d]	1/2.5 (80 min) 1/4.1 (26 h)	<5 min
8	$W(CCH_2CO_2Me)(OR)_3$(quin)	1/4.0 (40 min) 1.2 (98 h)	
9	$W(CNEt_2)(OR)_3$(quin)[d]	1/5.2 (150 min) 1.6 (21 h)	<5 min
10	$W(CCH_2CN)(OR)_3$(py)[d]	1/24 (45 min) 2.4 (191 h)	6 min
11	$W(CC{\equiv}CEt)(OR)_3$(quin)	~0 (50 h)	15 h
12	$W(CCN)(OR)_3$(quin)	~0 (47 h[e])	*f, g*
13	$W(CCO_2Me)(OR)_3$(quin)	~0 (50 h)	35 h
14	$(RO)_3W{\equiv}CC{\equiv}W(OR)_3$	~0 (49 h)	60 min
15	$W(CSCMe_3)(OR)_3$	~0 (49 h)	<5 min

[a] Reactions monitored by ^1H NMR, 250 MHz, 25 °C. Solvent is C_6D_6 unless otherwise noted. We estimate 0.1% reaction as the lower limit. [b] Alkylidyne complex = 0.055 mmol, 3-heptyne = 1.1 mmol, *n*-octane = 0.22 mmol, and solvent = pentane (3–4 mL). Aliquots were quenched with 1 M aqueous KOH. The pentane layer was dried by passage through activity I Woelm N alumina and analyzed by GLC on an SE-30 column. [c] The equilibrium composition was close to 1:2:1 (3-hexyne:3-heptyne:4-octyne). [d] Decomposition of catalyst with time was noted. [e] Solvent = $CDCl_3$. [f] Solvent = ether. [g] Acetylene polymer observed after 72 h. No metathesis products observed in 72 h.

$W(CX)(OR)_3$ with 3-hexyne, determining the ratio of $W(CEt)(OR)_3$ to $W(CX)(OR)_3$ after a given period of time as noted in the first column of Table II. Second, we have tested each as a catalyst for the metathesis of 3-heptyne, determining the appropriate time required to reach equilibrium, as listed in the second column of Table II. The $W(CR)(OCMe_3)_3$ species that forms when $W(CX)(OCMe_3)_3$ reacts with 3-heptyne (R = Et, Pr; X = functionalized substituent) is known to be a rapid metathesis catalyst.[2] Note that another means of generating metathesis products is for $W(CR)(OCMe_3)_3$ to react with the RC≡CX generated when $W(CX)(OCMe_3)_3$ reacts with 3-heptyne. There is no a priori reason why this route to metathesis products cannot compete with the route consisting of reaction of $W(CR)(OCMe_3)_3$ with heptyne. The first entry in Table II, the parent *tert*-butyl-substituted methylidyne complex, is present for purposes of comparison.

Compounds **2–10** all react with 3-hexyne to produce some $W(CEt)(OCMe_3)_3$. The ratio of $W(CEt)(OCMe_3)_3$ to $W(CX)(OCMe_3)_3$ in several cases (**8–10**) changes slowly with time as the system approaches equilibrium. However, in all cases a significant amount of $W(CEt)(OCMe_3)_3$ is present, as evidenced by the fact that the 1:2:1 3-hexyne:3-heptyne:4-octyne equilibrium is reached relatively quickly in the 3-heptyne metathesis reaction. Between 6 and 20 min are required in three cases (**5, 6, 10**), we believe because quinuclidine or pyridine adducts in general do not react as readily with acetylenes as the analogous base-free alkylidyne complexes.

Compounds **11–15** do not react to a detectable extent (<0.1%) with 3-hexyne in ~50 h. One (**12**) does not react

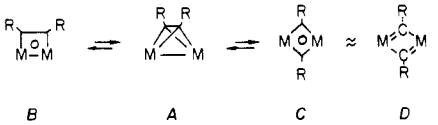
at all, as evidenced by the fact that 3-heptyne metathesis products are not observed after 72 h. A tiny amount of the alkylidyne complexes **11**, **13**, and **14** must react with 3-heptyne, as 20 equiv are metathesized in a period of 1–35 h. The somewhat surprising result is the last one. In spite of the fact that a maximum of only ~0.1% (estimated lower limit) of $W(CR)(OCMe_3)_3$ (R = Et, Pr) is present in the reaction between $W(SCMe_3)(OCMe_3)_3$ and 3-heptyne, 3-heptyne is metathesized to equilibrium in less than 5 min. The two possible explanations are first, that 3-heptyne is metathesized by reaction of $W(CR)(OCMe_3)_3$ complexes, but that ~5 min are required to reach equilibrium. (Metathesis by compound **10** also requires ~6 min to reach equilibrium, in spite of the fact that ~4% of $W(CR)(OCMe_3)_3(py)$ is present, probably because pyridine adducts are involved.) The second possible explanation is that the metathesis route consisting of the reaction between $W(CR)(OCMe_3)_3$ and $RC{\equiv}CSCMe_3$ is the fastest, despite the low concentration of *both* reactants. We favor the first explanation.

The pattern that emerges from these semiquantitative studies is that strong electron-withdrawing groups directly bound to the alkylidyne α-carbon atom slow down the rate at which the $W(CX)(OCMe_3)_3$ complex reacts with a dialkylacetylene, while electron-donating groups in general activate the complex toward reaction with a dialkylacetylene. These results suggest that the $W{\equiv}C$ bond behaves as if it were polarized $W(+){\equiv}C(-)$ and that some $W(CX)(OCMe_3)_3$ complexes are reactive enough to be intermediates in the catalytic metathesis of $RC{\equiv}CX$.

Discussion

There are several examples of scission of a carbon–carbon triple bond in a multimetallic complex. By far the most common system involves an M_3 cluster.[11] Theory suggests that the acetylene is cleaved on one edge of the M_3 triangle where the carbon–carbon bond axis is oriented perpendicular to one M–M bond axis.[11a] Recently scission of an acetylene in an M_4 cluster has been observed.[12] To our knowledge the reaction reported here is the only unambiguous example of scission of an acetylene by a bimetallic complex.

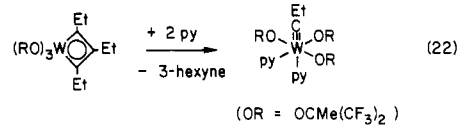
Many bimetallic complexes contain an acetylene bound between the two metals.[13] The most commonly observed mode of acetylene bonding is the tetrahedral M_2C_2 core (A). A planar 1,2-M_2C_2 core (B) is less common, but by



B A C D

no means rare. A third type of M_2C_2 arrangement, a 1,3-M_2C_2 planar arrangement (C), must be considered here even though it is the least recognizeable as an acetylene complex. It is closer to what one would call a head-to-tail dimer of an alkylidyne complex. Only one type of molecule has this 1,3-M_2C_2 planar core—$[M(CSiMe_3)(CH_2SiMe_3)_2]_2$ where M = Nb,[14] Ta,[14] or W.[15] The tungsten complex differs from the niobium and tantalum complexes to the extent that a W–W bond is present. The Nb and Ta molecules do not have symmetrical M_2C_2 cores; each is distorted slightly toward the bond localized form represented by D. While a good deal has been made of the possibility of an A ⇄ B interconversion,[16] the possibility of an A → C conversion or of an A ⇄ C interconversion has received scant attention. To us the A → C conversion seems no less likely than C≡C bond scission along an M—M edge in an M_3 cluster as postulated above.

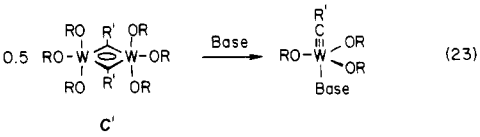
Before we can propose how an acetylene is cleaved by $W_2(OCMe_3)_6$, we should first examine the mechanism of acetylene metathesis by tungsten alkylidyne complexes of the type $W(CR')(OR)_3$. Metallacyclobutadiene complexes that are active for acetylene metathesis have been isolated and structurally characterized.[17] They are roughly trigonal bipyramids with the WC_3 ring in the equatorial plane and axial OR groups bent away from the WC_3 ring (O_{ax}–W–O_{ax} ≈ 165°). Other types of WC_3 arrangements have been observed. In one case the WC_3 ring is bent with localized $\overline{W{=}CC{=}C}$ bonds.[18] In several other cases the WC_3 tetrahedral arrangement is observed.[19] All complexes that do not have a planar WC_3 ring are inactive for acetylene metathesis. We propose that a planar WC_3 ring and a WC_3 tetrahedron can interconvert, but only the planar WC_3 ring system can lose acetylene under mild conditions. Finally, it is important to note that an acetylene can be displaced from a planar WC_3 ring by a nitrogen base such as pyridine (eq 22).[17b]



(22)

(OR = $OCMe(CF_3)_2$)

We propose that there is an analogy between MC_3 complexes and M_2C_2 complexes. In particular, we propose first that a $W_2(CR')_2(OR)_6$ molecule of type A is in *equilibrium* with a molecule of type C. Second, the favored molecule of type C contains two eclipsed trigonal bipyramids (C′, eq 23). Third, C′ *may* cleave spontaneously, depending



C′ (23)

on the size and electronics of R and R′, but also may *require* a base to "displace" $W(CR')(OR)_3$ from the ring

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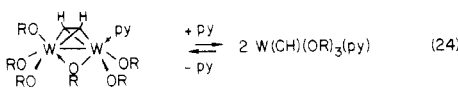
system. Fourth, in some cases only the base adduct W(CR′)(OR)$_3$(base) is stable; loss of base will allow a W_2C_2 dimer to reassemble. If all this is true, then one would suspect that formation of C′ will be difficult if one or more of the OR groups can bridge between the metals, since the cleavage reaction then may not proceed at a reasonable rate relative to the several possible C–C bond forming reactions leading ultimately to acetylene dimerization, cyclotrimerization, or polymerization.[20,21] Not coincidentally, the *tert*-butoxide ligand, relative to smaller alkoxides such as isopropoxide, is for steric reasons both a relatively poor bridging ligand and relatively good ligand for limiting access of acetylene to the metal. One or two bridging alkoxide ligands are commonly observed in all isolated molybdenum or tungsten complexes made from $M_2(OR)_6$ and an acetylene.[20] The fact that many molecules have been isolated from a reaction between $M_2(OR)_6$, acetylene, and base, that contain a variety of combinations of one or more acetylenes (with or without a C–C bond having formed) and one or more molecules of base,[21] we feel actually contributes to, more than it detracts from, our proposal, since it is more often true in general that isolable intermediates are *not* close to the transition state in a chemical reaction. Since trigonal-bipyramidal complexes, that contain a planar MC_3 ring, we now believe to be relatively rare, we suspect that an observable complex of type C′ will also be relatively rare. We are fairly certain that neither will be observable (using ordinary acetylenes) when OR is the apparently rather special *tert*-butoxide ligand.

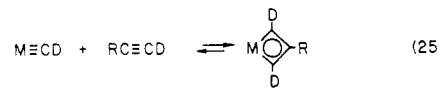
Some interesting results that bear on several questions surrounding the acetylene scission reaction by $W_2(OCMe_3)_6$ have recently appeared from the Chisholm group.[20] They find that addition of acetylene to $W_2(OCMe_3)_6$ in the presence of pyridine yields a green, structurally characterized molecule with the structure shown schematically in eq 24 (OR = $OCMe_3$). However, NMR studies show



(24)

the presence of a methylidyne complex ($\delta(C_\alpha)$ 252.4 (J_{CH} = 150 Hz, J_{CW} = 289 Hz)), while a double labeling study with DC≡CD and H^{13}C≡^{13}CH shows that methylidyne fragments are scrambled statistically, presumably as a result of the rapid interconversion shown in eq 24. The mixture decomposes relatively readily to unidentified products. These studies provide strong evidence that the scission of an acetylene can be reversible. The fact that W(CH)(OCMe$_3$)$_3$(quin), but not W(CH)(OCMe$_3$)$_3$(py), can be isolated suggests that quinuclidine in other W(CR)(OCMe$_3$)$_3$(quin) molecules may also simply be preventing what is otherwise a favorable "recombination" reaction.

Our finding that the W≡C bond behaves as if it were polarized W(+)/C(−) (see above) should allow us to predict how W(CR′)(OCMe$_3$)$_3$ complexes will react with electrophiles, nucleophiles, or other bipolar or polarizable molecules. We propose that the initial interaction between W(CR′)(OCMe$_3$)$_3$ and an acetylene is electrophilic attack by tungsten on the acetylene. This step is followed by nucleophilic attack by the alkylidyne α-carbon atom on an acetylenic carbon atom. This sequence is analogous to the activation of acetylenes by Hg^{2+} toward nucleophilic attack by external nucleophiles.[22] Therefore, any relatively electron-donating ligand on the *metal* should deactivate the alkylidyne complex toward reaction with an acetylene; any electron-accepting substituent on the alkylidyne carbon atom should deactivate the alkylidyne complex toward reaction with an acetylene. Unfortunately, metathesis of functionalized acetylenes will not be straightforward since (inter alia) a strongly polarized M≡C bond should add to a strongly polarized C≡C bond to give only the most favored metallacycle (eq 25) and overall only degenerate metathesis.



(25)

(D = donor; R = alkyl)

It is worth pointing out here that acetylene scission by a W≡W bond is not *unique* to $W_2(OCMe_3)_6$. $W_2(OCHMe_2)_6(py)_2$ reacts smoothly and rapidly with 3-hexyne to give W(CEt)(OCHMe$_2$)$_3$(py).[8] Upon sublimation, W(CEt)(OCHMe$_2$)$_3$(py) loses pyridine to give what ^{1}H NMR studies suggest is a dimer, probably with a structure analogous to that of [W(CMe)(OCMe$_3$)$_3$]$_2$.[6] Interestingly, [W(CEt)(OCHMe$_3$)$_3$]$_2$ will not catalyze the metathesis of acetylenes. We hypothesize that C–C bond formation (acetylene oligomerization[20,21]) competes with the acetylene metathesis reaction. A bulky ligand such as *tert*-butoxide is required in both acetylene metathesis reactions and acetylene scission reactions in order to prevent more than one molecule of acetylene from attacking the metal(s) and leading ultimately to irreversible C–C bond formation.

Experimental Section

All operations were performed under prepurified nitrogen or argon using a Vacuum Atmospheres HE 43-2 drybox system or standard Schlenk techniques.

Commercial pentane (washed with 5% HNO_3/H_2SO_4 and dried over $CaCl_2$), reagent grade THF, toluene, and DME (predried by passage through a column of 13X sieves and storage over sodium chunks), and anhydrous ether were distilled from dark purple sodium benzophenone ketyl under nitrogen. Reagent grade methylene chloride was distilled from CaH_2, while reagent grade acetonitrile was distilled from P_2O_5. Both were deaerated with nitrogen.

$W_2(OCMe_3)_6$ was prepared as described previously. Pyridine was predried over KOH and distilled from BaO, as was TMEDA. Quinuclidine was used as received or sublimed if necessary. Dialkylacetylenes were passed through a column of Woelm N Akt 1 alumina, and all acetylenes were degassed and stored over 3A or 4A sieves. Commercially available acetylenes were otherwise used as received.

Most acetylenes were purchased from standard sources.

1-(Trimethylstannyl)-1-pentyne,[23] 1,4-bis(trimethylsiloxy)-2-butyne,[26] 1-(trimethylsiloxy)-2-heptyne,[26] 2-hexyn-1-ol acetate,[24] bis(diethylamino)acetylene,[25] 1,4-bis(diethylamino)-2-butyne,[28] 1,4-dimethoxy-2-butyne,[30] methyl 3-pentynoate,[27] 1-(*tert*-butylthiolato)-1-propyne,[31] 2-hexynyl cyanide,[32] 1-pentynyl cyanide,[29] and phenyl cyanoacetylene[33] were prepared by literature

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(31) Brandsma, L.; Verkruijsse, H. D. "Studies in Organic Chemistry 8. Synthesis of Acetylenes, Allenes, and Cumulenes"; Elsevier: Amsterdam, 1981; p 109.

procedures.

Elemental analyses (C, H) on samples oxidized with V_2O_5 were performed by Schwartzkopf Microanalytical Laboratories. Samples were at least *triply* recrystallized and/or sublimed, sealed in ampules, and sent by overnight mail. They were stored at 0 °C until they could be analyzed (~1 week). We did not attempt to analyze a compound that was either obviously thermally sensitive or a close analogue of an analyzed compound. Samples that failed twice to analyze are so noted.

^{13}C NMR spectra were obtained in the broad-band ^1H-decoupled mode in order to obtain carbon–^{183}W coupling constants and in the gated ^1H-decoupled mode to obtain CH coupling constants. All coupling constants are reported in Hz. In order to avoid repetition, pyridine and quinuclidine resonances are not listed. Typical pyridine resonances are found at δ 6.7 (meta), 7.0 (para), and 8.9 (ortho) in the ^1H NMR spectrum and at δ 124, 136, and 149 in the ^{13}C NMR spectrum ($J_{CH} \approx 160$–180 Hz). $N(CH_2C H_2)_3CH$ resonances are found at ~3 ppm. In the ^{13}C NMR spectrum $N(CH_2CH_2)_3CH$ is found at ~22 ppm, $N(CH_2CH_2)_3CH$ at ~27 ppm, and $N(CH_2CH_2)_3CH$ at 45-46 ppm with J_{CH} = 130–140 Hz.

Preparations. A useful trick for isolating highly hydrocarbon-soluble compounds is to dissolve them in minimal ether and crystallize them by adding acetonitrile and cooling. In the preparations that follow that is what is meant by "recrystallization from ether/acetontrile".

W(CMe)(OCMe$_3$)$_3$. 2-Butyne (1.02 mmol, 80.1 μL) was added to a solution of $W_2(OCMe_3)_6$ (0.93 mmol, 0.75 g) in 30 mL of pentane at −40 °C. The solution was maintained at −40 °C for 1 h and allowed to warm to room temperature. The orange color faded to light amber, and after 2 h at room temperature the volatile components were removed in vacuo, leaving a light brown solid. Larger scale preparations sometimes yielded a brown oil initially, but the oil always crystallized with time in vacuo or when seeded. Sublimation of the light brown residue at 25 °C, 0.001 μm onto a −78 °C probe, afforded 0.59 g (74%) of pure, white $W(CMe)(OCMe_3)_3$. This material is very oxygen- and moisture-sensitive and darkens slightly when removed from the probe in the drybox. It was generally prepared in pentane or THF and utilized directly for further reactions assuming a quantitative yield: ^1H NMR (C_6D_6) δ 1.43 (s, 27, $OCMe_3$), 3.56 (s, 3, J_{HW} = 7.13 Hz, CMe); ^{13}C NMR (C_6D_6) δ 31.95 (q, J_{CH} = 128 Hz, C*Me*), 32.76 (q, J_{CH} = 124 Hz, OC*Me*$_3$), 80.12 (s, $OCMe_3$), 254.3 (s, *C*Me). Anal. Calcd for $WC_{14}H_{30}O_3$: C, 39.08; H, 7.02. Found: C, 38.51; H, 7.08.

W(CPh)(OCMe$_3$)$_3$. EtC≡CPh (0.45 mmol, 63.9 μL) was added to a solution of $W_2(OCMe_3)_6$ (0.22 mmol, 0.18 g) in 4 mL of pentane at room temperature. After 2 h the solvent was removed in vacuo, leaving a yellow crystalline solid. This material is pure enough for further use; it is identical with that prepared from $W(CCMe_3)(OCMe_3)_3$ and PhC≡CPh.[2a] Anal. Calcd for $WC_{19}H_{32}O_3$: C, 46.35; H, 6.55. Found: C, 46.29; H, 6.67.

W(CMe)(OCMe$_3$)$_3$(py). To a pentane solution of $W(CMe)(OCMe_3)_3$ was added 1 equiv of pyridine. The crude material is pure enough for further use. Product sublimed in a small volume under a *static* vacuum (25 °C/0.001 μm/0 °C probe/colorless crystals) retains *most* of its pyridine. In a dynamic vacuum the pyridine is lost in ≲16 h at 25 °C: ^1H NMR (C_6D_6) δ 1.55 (s, 27, $OCMe_3$), 3.89 (s, 3, J_{HW} = 8.1 Hz, CMe); ^{13}C NMR (C_6D_6) δ 32.41 (q, J_{CH} = 126 Hz, C*Me*), 33.20 (q, J_{CH} = 125 Hz, OC*Me*$_3$), 78.57 (s, $OCMe_3$), 255.49 (s, J_{CW} = 298 Hz, *C*Me).

W(CMe)(OCMe$_3$)$_3$(quin). To a pentane solution of $W(CMe)(OCMe_3)_3$ was added 1 equiv of quinuclidine. The product was isolated by recrystallization from pentane (colorless slabs) or by slow sublimation (25 °C/0.001 μm/0 °C probe/white powder). The yield is quantitative by NMR and the crude material is pure enough for further use: ^1H NMR (C_6D_6) δ 1.50 (s, 27, $OCMe_3$), 3.81 (s, 3, CMe); ^{13}C NMR (C_6D_6) δ 32.12 (q, J_{CH} = 127 Hz, C*Me*), 33.02 (q, J_{CH} = 125 Hz, OC*Me*$_3$), 78.98 (s, $OCMe_3$), 252.67 (s, *C*Me).

W(CEt)(OCMe$_3$)$_3$. 3-Hexyne (1.30 mmol, 148.0 μL) was added to a solution of $W_2(OCMe_3)_6$ (1.24 mmol, 1.00 g) in 75 mL of pentane, cooled to −40 °C. After 3 h at room temperature the volatiles were removed in vacuo to yield a light tan solid. The product was isolated by sublimation (25 °C/0.001 μm/0 °C probe/1.00 g (91%) of white crystals): ^1H NMR (C_6D_6) δ 1.11 (t, 3, CCH_2CH_3), 1.42 (s, 27, $OCMe_3$), 3.84 (q, 2, J_{HW} = 7.35 Hz, CCH_2CH_3); ^{13}C NMR (C_6D_6) δ 17.65 (q, J_{CH} = 127 Hz, CH_2CH_3), 32.75 (q, J_{CH} = 127 Hz, OC*Me*$_3$), 40.20 (t, J_{CH} = 122 Hz, J_{CW} = 47.2 Hz, CCH_2CH_3), 79.56 (s, $OCMe_3$), 262.6 (s, CCH_2CH_3). Anal. Calcd for $WC_{15}H_{32}O_3$: C, 41.93; H, 7.48. Found: C, 42.03; H, 7.39.

W(CPr)(OCMe$_3$)$_3$. The preparation is analogous to that of $W(CEt)(OCMe_3)_3$, yield 88%: ^1H NMR (C_6D_6) δ 0.87 (t, 3, $CH_2CH_2CH_3$), 1.44 (s, 27, $OCMe_3$), 1.58–1.72 (m, 2, $CH_2CH_2CH_3$), 3.86 (t, 3, $CH_2CH_2CH_3$); ^{13}C NMR (C_6D_6) δ 14.20 (q, J_{CH} = 125 Hz, $CH_2CH_2CH_3$), 26.46 (t, J_{CH} = 129 Hz, $CH_2CH_2CH_3$), 32.72 (q, J_{CH} = 125 Hz, OC*Me*$_3$), 49.49 (t, J_{CH} = 126 Hz, $CH_2CH_2CH_3$), 79.69 (s, $OCMe_3$), 261.7 (s, $CCH_2CH_2CH_3$). Anal. Calcd for $WC_{16}H_{35}O_3$: C, 41.84; H, 7.67. Found: C, 42.03; H, 7.39.

W(CCMe$_3$)(OCMe$_3$)$_3$. 4,4-Dimethyl-2-pentyne (14.9 mmol, 1.99 mL) was added to a solution of $W_2(OCMe_3)_6$ (2.48 mmol, 2.00 g) in 150 mL of pentane. The flask was evacuated and stirred overnight under static vacuum. The solution had lightened from cherry red to amber in ~1 h. The product was isolated by sublimation (50 °C/0.001 μm/water-cooled probe/2.15 g (92%) yellow crystals) or recrystallization from ether/acetonitrile (−30 °C; nearly colorless cubes or flakes). This sample was identical in all respects with reported material.[3]

W(CCMe$_3$)(OCMe$_3$)$_3$(quin). To a solution of recrystallized $W(CCMe_3)(OCMe_3)_3$ in pentane was added 2 equiv of quinuclidine. After 1 h at room temperature the volatiles were removed in vacuo to yield a white solid which may be recrystallized from ether/acetonitrile (−30 °C) to yield white flakes: ^1H NMR (C_6D_6) δ 1.41 (s, 9, $CCMe_3$), 1.50 (s, 27, $OCMe_3$); ^{13}C NMR (C_6D_6) δ 32.96 (q, J_{CH} = 126 Hz, OC*Me*$_3$), 34.80 (q, J_{CH} = 125 Hz, CC*Me*$_3$), 49.33 (s, $CCMe_3$), 77.19 (s, $OCMe_3$), 268.7 (s, J_{CW} = 286 Hz, $CCMe_3$).

W(CSiMe$_3$)(OCMe$_3$)$_3$. Bis(trimethylsilyl)acetylene (2.48 mmol, 562 μL) was added to a solution of $W(CMe)(OCMe_3)_3$ prepared in situ from $W_2(OCMe_3)_6$ (0.496 mmol, 0.400 g) and 2-butyne (0.496 mmol, 38.8 μL) in 8 mL of pentane, and the solution was stirred at room temperature overnight. The product was isolated by sublimation (30–40 °C/0.001 μm/water-cooled probe/0.400 g (83%) of white crystals): ^1H NMR (C_6D_6) δ 0.29 (s, 9, $CSiMe_3$), 1.47 (s, 27, $OCMe_3$); ^{13}C NMR (C_6D_6) δ 2.90 (q, J_{CH} = 119 Hz, CSi*Me*$_3$), 32.01 (q, J_{CH} = 124 Hz, OC*Me*$_3$), 79.26 (s, $OCMe_3$), 292.1 (s, $CSiMe_3$). Anal. Calcd for $WC_{16}H_{36}O_3Si$: C, 39.35; H, 7.43. Found: C, 39.12; H, 7.20.

W(CCH=CH$_2$)(OCMe$_3$)$_3$. 1-Hexen-3-yne (0.521 mmol, 55.7 μL) was added to a solution of $W_2(OCMe_3)_6$ (0.248 mmol, 0.200 g) in 4 mL of pentane. The color lightened to golden yellow in ~5 min. The product was isolated after 2 h by sublimation (25 °C/0.001 μm/0 °C probe/0.200 g (91%) of yellow crystals). Larger crystals grown over 1 day under static vacuum are red: ^1H NMR (C_6D_6) δ 1.43 (s, 27, $OCMe_3$), 4.35 (dd, 1, $J_{H_{vic}H_{trans}}$ = 11.0 Hz, $J_{H_{cis}H_{trans}}$ = 2.6 Hz, CH=CH*H*$_{trans}$), 4.83 (dd, 1, $J_{H_{vic}H_{cis}}$ = 17.2 Hz, $J_{H_{cis}H_{trans}}$ = 2.6 Hz, CH=CH*H*$_{cis}$), 7.57 (dd, 1, $J_{H_{vic}H_{cis}}$ = 17.2 Hz, $J_{H_{vic}H_{trans}}$ = 11.0 Hz, C*H*=CH$_2$); ^{13}C NMR (C_6D_6) δ 32.65 (q, J_{CH} = 126 Hz, OC*Me*$_3$), 81.05 (s, $OCMe_3$), 120.2 (t, J_{CH} = 158 Hz, CCH=CH$_2$), 141.7 (d, J_{CH} = 154 Hz, J_{CW} = 53 Hz, CCH=CH$_2$), 258.0 (s, CCH=CH$_2$). Anal. Calcd for $WC_{15}H_{30}O_3$: C, 40.74; H, 6.84. Found: C, 40.70; H, 6.73.

[(Me$_3$CO)$_3$W(C)]$_2$. 3,5-Octadiyne (0.391 mmol, 50.2 μL) was added to $W_2(OCMe_3)_6$ (0.372 mmol, 0.300 g) in 10 mL of pentane. Within a few minutes the solution lightened to red-brown and a small quantity of solids precipitated. The solution was stirred at room temperature overnight, and the volatiles were removed in vacuo to yield a red-brown solid which was recrystallized from pentane (−30 °C) as dark red tablets in two crops, yield 0.290 g (94%): ^1H NMR (C_6D_6) δ 1.57 (s, 54, $OCMe_3$); ^{13}C NMR (C_5D_5N) δ 33.30 (q, J_{CH} = 125 Hz, OC*Me*$_3$), 79.20 (s, $OCMe_3$), 278.6 (s, W(*C*)). Anal. Calcd for $WC_{13}H_{27}O_3$: C, 37.62; H, 6.55. Found: C, 37.73; H, 6.67.

W(CCH$_2$NMe$_2$)(OCMe$_3$)$_3$. 1,4-Bis(dimethylamino)-2-butyne (0.130 mmol, 21.2 μL) was added to $W_2(OCMe_3)_6$ (0.124 mmol, 0.100 g) in 3 mL of pentane. The solution gradually lightened to amber. Tiny fluffy white needles (0.08 g, 68%) were deposited after the reaction mixture was left standing at room temperature overnight. This compound is appreciably soluble only in strongly coordinating solvents such as THF or pyridine: ^1H NMR (C_6D_6) δ 1.49 (s, 27, $OCMe_3$), 2.30 (s, 6, NMe_2), 4.63 (s, 2, CH_2NMe_2);

(32) Reference 31, p 225.
(33) Reference 31, p 227.

^{1}H NMR (C_5D_5N) δ 1.53 (s, 27, $OCMe_3$), 2.34 (s, 6, NMe_2), 4.91 (s, 2, CH_2NMe_2); ^{13}C NMR (C_5D_5N) δ 33.17 (q, J_{CH} = 125 Hz, $OCMe_3$), 46.76 (q, J_{CH} = 131 Hz, NMe_2), 73.53 (t, J_{CH} = 131 Hz, J_{CW} = 50.9 Hz, CH_2NMe_2), 78.09 (s, $OCMe_3$), 262.7 (s, $J_{CW} \approx$ 295 Hz, CCH_2NMe_2). Anal. Calcd for $WC_{16}H_{35}O_3N$: C, 40.60; H, 7.45. Found: C, 40.38; H, 7.49.

W(CCH$_2$NEt$_2$)(OCMe$_3$)$_3$. 1,4-Bis(diethylamino)-2-butyne (0.391 mmol, 89.0 μL) was added to $W_2(OCMe_3)_6$ (0.372 mmol, 0.300 g) in 8 mL of pentane. After 24 h the solvent was removed in vacuo to yield a light brown solid which was recrystallized from ether/acetonitrile (−30 °C) to yield 0.175 g (47%) of white to light amber flakes. The compound is extremely soluble in pentane: ^{1}H NMR (C_6D_6) δ 1.06 (t, 6, NCH_2CH_3), 1.49 (s, 27, $OCMe_3$), 2.67 (q, 4, NCH_2CH_3), 4.76 (s, 2, J_{HW} = 6.25 Hz, CH_2NEt_2); ^{13}C NMR (C_6D_6) δ 12.46 (q, J_{CH} = 125 Hz, $N(CH_2CH_3)_2$), 32.69 (q, J_{CH} = 126 Hz, $OCMe_3$), 47.38 (t, J_{CH} = 131 Hz, $N(CH_2CH_3)_2$), 66.44 (t, J_{CH} = 133 Hz, J_{CW} = 47.7 Hz, CH_2NEt_2), 80.20 (s, $OCMe_3$), 260.1 (s, J_{CW} = 302 Hz, CCH_2NEt_2).

W(CCH$_2$OMe)(OCMe$_3$)$_3$(quin). 1,4-Dimethoxy-2-butyne (1.30 mmol, 157 μL) was added to $W_2(OCMe_3)_6$ (1.24 mmol, 1.00 g) and quinuclidine (12.4 mmol, 1.38 g) in 40 mL of pentane. After 16 h the volatiles were removed in vacuo to yield a nearly white powder which was recrystallized from ether/acetonitrile (−30 °C) affording 1.23 g (87%) of white flakes in two crops. Solutions of the pure compound are faintly green: ^{1}H NMR (C_6D_6) δ 1.50 (s, 27, $OCMe_3$), 3.11 (s, 3, OMe), 5.50 (s, 2, J_{HW} = 6.83 Hz, CH_2OMe); ^{13}C NMR (C_6D_6) δ 32.93 (q, J_{CH} = 126 Hz, $OCMe_3$), 57.81 (q, J_{CH} = 141 Hz, OMe), 78.05 (s, $OCMe_3$), 82.15 (t, J_{CH} = 136 Hz, J_{CW} = 53.0 Hz, CH_2OMe), 253.6 (s, J_{CW} = 286 Hz, CCH_2OMe). Anal. Calcd for $WC_{22}H_{45}O_4N$: C, 46.24; H, 7.94. Found: C, 45.96; H, 7.95.

W(CCH$_2$OSiMe$_3$)(OCMe$_3$)$_3$(quin). 1,4-Bis(trimethylsiloxy)-2-butyne (0.391 mmol, 99.3 μL) was added to $W_2(OCMe_3)_6$ (0.372 mmol, 0.300 g) and quinuclidine (3.72 mmol, 0.414 g) in 10 mL of pentane. After 16 h the solvent was removed in vacuo to yield a somewhat oily light brown solid which was recrystallized from ether/acetonitrile (−30 °C) to give 0.175 g (37%) of light tan powdery crystals. This compound is extremely soluble in pentane: ^{1}H NMR (C_6D_6) δ 0.11 (s, 9, $OSiMe_3$), 1.50 (s, 27, $OCMe_3$), 5.79 (s, 2, CH_2OSiMe_3); ^{13}C NMR (C_6D_6) δ −0.31 (q, J_{CH} = 117 Hz, $OSiMe_3$), 33.02 (q, J_{CH} = 125 Hz, $OCMe_3$), 71.24 (t, J_{CH} = 139 Hz, J_{CW} = 55.5 Hz, CH_2OSiMe_3), 77.98 (s, $OCMe_3$), 254.8 (s, J_{CW} = 288 Hz, CCH_2OSiMe_3).

W[CCH(OEt)$_2$](OCMe$_3$)$_3$(quin). 2-Pentynyl aldehyde diethyl acetal (2.54 mmol, 449.6 μL) was added to $W_2(OCMe_3)_6$ (1.24 mmol, 1.0 g) and quinuclidine (12.4 mmol, 1.38 g) in 40 mL of THF. After 24 h the product was isolated by recrystallization from ether/acetonitrile (−30 °C) in two crops as white flakes (1.30 g, 83%): ^{1}H NMR (C_6D_6) δ 1.23 (t, 6, $CH(OCH_2CH_3)_2$), 1.59 (s, 27, $OCMe_3$), 3.53–3.59 (AB pattern, 2, $CH(OCH_2CH_3)_2$), 3.80–3.86 (AB pattern, 2, $CH(OCH_2CH_3)_2$), 6.09 (s, 1, $CH(OEt)_2$); ^{13}C NMR (C_6D_6) δ 15.62 (q, J_{CH} = 126 Hz, OCH_2CH_3), 32.74 (q, J_{CH} = 126 Hz, $OCMe_3$), 62.03 (t, J_{CH} = 141 Hz, OCH_2CH_3), 78.32 (s, $OCMe_3$), 106.5 (d, J_{CH} = 156 Hz, J_{CW} = 55.7 Hz, $CH(OEt)_2$), 254.7 (s, J_{CW} = 292 Hz, $CCH(OEt)_2$). Anal. Calcd for $WC_{25}H_{51}O_5N$: C, 47.70; H, 8.17. Found: C, 47.81; H, 8.03.

W[CC(O)OMe](OCMe$_3$)$_3$(quin). Methyl 2-pentynoate (1.02 mmol, 119.3 μL) was added to $W_2(OCMe_3)_6$ (0.496 mmol, 0.40 g) and quinuclidine (4.96 mmol, 0.552 g) in 8 mL of THF. After 16 h the product was isolated by recrystallization from pentane (−30 °C) as light green crystals (0.473 g, 81%): ^{1}H NMR (C_6D_6) δ 1.57 (s, 27, $OCMe_3$), 3.54 (s, 3, C(O)OMe); ^{13}C NMR (C_6D_6) δ 32.39 (q, J_{CH} = 125 Hz, $OCMe_3$), 50.86 (q, J_{CH} = 145 Hz, C(O)OMe), 79.88 (s, $OCMe_3$), 163.7 (s, C(O)OMe), 246.8 (s, J_{CW} = 293 Hz, CC(O)OMe); IR (Nujol) 1650 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $WC_{22}H_{43}O_5N$: C, 45.14; H, 7.40. Found: C, 45.16; H, 7.60.

W(CCH$_2$CO$_2$Me)(OCMe$_3$)$_3$(quin). Methyl 3-pentynoate (0.763 mmol, 84.4 μL) was added to $W_2(OCMe_3)_6$ (0.372 mmol, 0.300 g) in 6 mL of pentane. After 45 min the solvent was removed in vacuo to yield a brown-violet oil. The oil was redissolved in pentane and quinuclidine (0.744 mmol, 0.083 g) was added. After 1 h at room temperature the solvent was removed in vacuo and the brown solid was recrystallized from ether/acetonitrile (−30 °C) to give 0.273 g of brown to white needles. A trace of W(CMe)(OCMe$_3$)$_3$(quin) (~8%) was still present in the recrystallized sample: ^{1}H NMR (C_6D_6) δ 1.49 (s, 27, $OCMe_3$), 3.42 (s, 3, CO_2Me), 5.06 (s, 2, $J_{HW} \approx$ 7.8 Hz, CCH_2CO_2Me); ^{13}C NMR (C_6D_6) δ 32.89 (q, J_{CH} = 126 Hz, $OCMe_3$), 50.73 (q, J_{CH} = 146 Hz, CO_2Me), 52.27 (t, J_{CH} = 129 Hz, J_{CW} = 50.4 Hz, CCH_2CO_2Me), 78.36 (s, $OCMe_3$), 172.5 (s, CO_2Me), 240.4 (s, J_{CW} = 300 Hz, CCH_2CO_2Me); IR (Nujol) 1740 cm^{-1} ($\nu_{C=O}$).

W(CCOMe)(OCMe$_3$)$_3$(quin). 3-Hexyn-2-one (0.99 mmol, 108 μL) was added to a solution of $W_2(OCMe_3)_6$ (0.50 mmol, 0.400 g), pyridine (2.48 mmol, 200 μL), and quinuclidine (0.99 mmol, 0.110 g) in 4 mL of pentane at −30 °C. The solution promptly turned red-brown. Clear yellow crystals (0.310 g, 55%) were collected by filtration after the solution was stored at −30 °C overnight. The compound can be stored for short periods at −30 °C, but over a few weeks the crystals turn green and then black. When the yellow crystals are dissolved in benzene, the solutions are red-brown; they turn purple within a few hours. The solutions are somewhat more stable in the presence of excess quinuclidine, but extraneous peaks are evident in ~10 min. The compound was judged too unstable for elemental analysis: ^{1}H NMR ($C_6D_5CD_3$) δ 1.48 (s, 27, $OCMe_3$), 2.20 (s, 3, COMe); IR (Nujol) 1580 cm^{-1} ($\nu_{C=O}$).

W(CNEt$_2$)(OCMe$_3$)$_3$(quin). 1,2-Bis(diethylamino)acetylene (0.521 mmol, 102.3 μL) was added to a THF solution containing quinuclidine (2.98 mmol, 0.331 g) and W(CMe)(OCMe$_3$)$_3$, prepared from $W_2(OCMe_3)_6$ (0.248 mmol, 0.200 g) and 2-butyne (0.260 mmol, 20.8 μL). After 4–5 h the yellow product was isolated by recrystallization from ether/acetonitrile (−30 °C), yield 0.200 g (67%): ^{1}H NMR (C_6D_6) δ 1.05 (t, 6, $N(CH_2CH_3)_2$), 1.51 (s, 27, $OCMe_3$), 3.51 (q, 4, $N(CH_2CH_3)_2$); ^{13}C NMR (C_6D_6) δ 15.12 (q, J_{CH} = 126 Hz, $N(CH_2CH_3)_2$), 33.47 (q, J_{CH} = 126 Hz, $OCMe_3$), 45.90 (t, J_{CH} = 133 Hz, $N(CH_2CH_3)_2$), 76.95 (s, $OCMe_3$), 223.2 (s, J_{CW} = 332 Hz, $CNEt_2$). Anal. Calcd for $WC_{24}H_{50}O_3N_2$: C, 48.16; H, 8.42. Found: C, 48.25; H, 8.52.

W(CSCMe$_3$)(OCMe$_3$)$_3$. 1-(*tert*-Butylthiolato)-1-propyne (1.27 mmol, 182.9 μL) was added to $W_2(OCMe_3)_6$ (0.620 mmol, 0.500 g) in 10 mL of pentane. After 2 h the solvent was removed in vacuo and the yellow crystalline residue was sublimed (30–40 °C/0.001 μm/0 °C probe/0.44 g (63%)). A significant amount of residue remained, and further sublimations of pure material always resulted in some decomposition. The compound is extremely moisture-sensitive: ^{1}H NMR (C_6D_6) δ 1.45 (s, 9, $SCMe_3$), 1.49 (s, 27, $OCMe_3$); ^{13}C NMR (C_6D_6) δ 29.53 (q, J_{CH} = 126 Hz, $SCMe_3$), 30.58 (q, J_{CH} = 126 Hz, $OCMe_3$), 48.24 (s, $SCMe_3$), 79.66 (s, $OCMe_3$), 222.7 (s, $CSCMe_3$).

W(CCH$_2$CN)(OCMe$_3$)$_3$(py). 2-Hexynyl cyanide (1.27 mmol, 129.7 μL) was added to a −30 °C pentane solution of W(CMe)(OCMe$_3$)$_3$, prepared from $W_2(OCMe_3)_6$ (0.620 mmol, 0.500 g) and 2-butyne (0.651 mmol, 51.9 μL), and pyridine (7.44 mmol, 599.4 μL). The solution promptly turned red-brown. Green crystals (0.58 g, 88%) were isolated by filtration after the mixture had been stored at −30 °C overnight. The product can be recrystallized from ether/pentane as colorless needles: ^{1}H NMR (C_6D_6) δ 1.46 (s, 27, $OCMe_3$), 4.46 (s, 2, J_{HW} = 7.9 Hz, CCH_2CN); ^{13}C NMR (C_6D_6) δ 32.95 (q, J_{CH} = 125 Hz, $OCMe_3$), 33.41 (t, J_{CH} = 134 Hz, CCH_2CN), 79.04 (s, $OCMe_3$), 120.0 (s, CCH_2CN), 235 (s, J_{CW} = 312 Hz, CCH_2CN); IR (Nujol) 2240 cm^{-1} (ν_{CN}). Anal. Calcd for $WC_{20}H_{34}N_2O_3$: C, 44.96; H, 6.41. Found: C, 44.68; H, 6.33.

W(CC≡CEt)(OCMe$_3$)$_3$(quin). 3,5-Octadiyne (1.27 mmol, 163.4 μL) was added to a solution of W(CMe)(OCMe$_3$)$_3$, prepared from $W_2(OCMe_3)_6$ (0.620 mmol, 0.500 g) and 2-butyne (0.651 mmol, 51.9 μL), and quinuclidine (6.20 mmol, 0.689 g), in 12 mL of pentane. The solution turned yellow over several hours but was left at room temperature for 2 days. The solvent was removed in vacuo, and the yellow-orange residue was recrystallized from pentane (−30 °C), yield 0.46 g (64%): ^{1}H NMR (C_6D_6) δ 1.00 (t, 3, CH_2CH_3), 1.59 (s, 27, $OCMe_3$), 2.90 (q, 2, CH_2CH_3, partially obscured by quin resonances); ^{13}C NMR (C_6D_6) δ 11.59 (t, J_{CH} = 131 Hz, CH_2CH_3), 16.81 (q, J_{CH} = 129 Hz, CH_2CH_3), 32.72 (q, J_{CH} = 125 Hz, $OCMe_3$), 73.58 (s, C≡CEt), 79.27 (s, $OCMe_3$), 91.72 (s, J_{CW} = 73 Hz, C≡CEt), 232.2 (s, J_{CW} = 296 Hz, CC≡CEt); IR (Nujol) 2130 cm^{-1} ($\nu_{C\equiv C}$). Anal. Calcd for $WC_{23}H_{45}O_3N$: C, 49.75; H, 7.83. Found: C, 49.64; H, 7.91.

W(CCN)(OCMe$_3$)$_3$(quin). 1-Pentynyl cyanide (0.763 mmol, 71.3 μL) was added to a solution of W(CMe)(OCMe$_3$)$_3$, prepared from $W_2(OCMe_3)_6$ (0.372 mmol, 0.300 g) and 2-butyne (0.391 mmol, 31.2 μL), and quinuclidine (3.72 mmol, 0.414 g) in 6 mL

of THF. The solution rapidly turned light yellow brown. After 24 h the solvent was removed in vacuo, and the residue was extracted with ether. The mixture was filtered and the ether removed in vacuo to yield a yellow powder. Recrystallization from ether/pentane (-30 °C) afforded 0.352 g (86%) of yellow plates in two crops. The compound is insoluble in pentane and benzene: ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 27, $OCMe_3$); ^{13}C NMR (CD_2Cl_2) δ 31.99 (q, J_{CH} = 128 Hz, $OCMe_3$), 81.30 (s, $OCMe_3$), 124.3 (s, J_{CW} = 71 Hz, CCN), 215.2 (s, J_{CW} = 310 Hz, CCN); IR (Nujol) 2100 cm^{-1} (ν_{CN}). Anal. Calcd for $WC_{21}H_{40}O_3N_2$: C, 45.66; H, 7.30. Found: C, 47.49, 48.00; H, 7.77, 7.84. The analysis samples were superb crystals, absolutely pure by high-field ^{1}H NMR. We have no explanation.

W(CH)(OCMe$_3$)$_3$(quin). Acetylene (1.24 mmol, 27.8 mL of gas), purified by passage through a saturated sodium bisulfite trap (to remove acetone) followed by a concentrated sulfuric acid trap (to remove water), was added by syringe to a Schlenk flask containing $W_2(OCMe_3)_6$ (1.24 mmol, 1.00 g), pyridine (6.20 mmol, 500 μL), and quinuclidine (2.48 mmol, 0.276 g) in 70 mL of pentane that had been cooled to -78 °C in a dry ice/ethanol bath. The initially dark red-purple solution slowly changed color to forest green. As the solution warmed slowly to room temperature, the color changed to medium brown. After 24 h the solvent was removed in vacuo to yield a brown powder that is pure W(CH)(OCMe$_3$)$_3$(quin) by ^{1}H NMR. Pure samples can be isolated by sublimation (25 °C/0.001 μm/0 °C probe/0.34 g (26%)) but the compound appears to be thermally sensitive. Sublimation at room temperature is preferred, although it is extremely slow: ^{1}H NMR (C_6D_6) δ 1.52 (s, 27, $OCMe_3$), 5.15 (s, 1, J_{HW} = 90 Hz, W(CH)); ^{13}C NMR (C_6D_6) δ 30.35 (q, J_{CH} = 125 Hz, $OCMe_3$), 74.53 (s, $OCMe_3$), 247.1 (d, J_{CH} = 147 Hz, J_{CW} = 287 Hz, W(CH)). Anal. Calcd for $WC_{20}H_{41}O_3N$: C, 45.55; H, 7.84. Found: C, 45.67; H, 8.21.

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Relative Reactivity and Mechanistic Studies of the Hydride-Transfer Reagents HM(CO)$_4$L$^-$ (M = Cr, W; L = CO, PR$_3$)†

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A series of anionic transition-metal hydrides have been compared according to their ability to reduce halocarbons (primarily alkyl bromides) to hydrocarbons. The 6B hydrides HM(CO)$_4$L$^-$ (M = Cr, W; L = CO, PR$_3$) are highly efficient hydride-transfer reagents, displacing X from a wide variety of C-X bonds, including tertiary centers, and tolerant of functionalities such as nitro groups, ketones, and aldehydes. A facile H/D exchange process with CH_3OD or D_2O readily converts the MH$^-$ reagents into deuterium delivery reagents. There is little difference between the reactivity of HM(CO)$_5^-$ with primary vs. secondary vs. tertiary alkyl bromides; however, the *cis*-HM(CO)$_4$PR$_3^-$ anions are far more reactive with the less hindered primary than branched alkyl halides. A comparison of the second-order rate constants for bromide displacement from *n*-BuBr established an order of reactivity for simple monomeric carbonyl hydrides *cis*-HW(CO)$_4$P$^-$ > *cis*-HCr(CO)$_4$P$^-$ > HW(CO)$_5^-$ > CpV(CO)$_3$H$^-$ > HCr(CO)$_5^-$ > HRu(CO)$_4^-$ > *trans*-HFe(CO)$_3$P$^-$ >> HFe(CO)$_4^-$ (no reaction). The relative reactivity was shown to correlate with the extent of electron density localized at the M-H bond as indicated by hydride site specific contact ion pairing with Na^+ in THF solution. Various mechanistic probes suggested the reagents most prone to contact ion pairing at the M-H$^-$ site to react with RX via S_N2 processes whereas the complexes with the anionic charge delocalized were more prone to electron-transfer mechanisms.

Introduction

The hydride transfer ability of anionic metal hydrides is of significance in formulating reasonable models for the reduction of metal-bound carbon.[1] Additional interest is in developing the chemistry of soluble anionic transition-metal hydrides since their intermediacy in the water-gas shift reaction suggests that such hydrides are catalytically regenerable from inexpensive raw materials, CO, and base. Thus Pettit convincingly showed the utility of HFe(CO)$_4^-$ as reagent and catalyst for the reduction of aromatic nitro compounds to amines[2] as well as the reduction of acid chlorides to aldehydes.[3]

Another potentially useful reduction is that of alkyl halides by active transition-metal hydrides (or deuterides). This reaction has been used as a mechanistic probe of metal hydride reactivity,[4] and it might also be used as a basis for establishing the factors that determine the relative ability of a transition-metal complex to release the H$^-$ ligand. It became obvious to us during our studies of monomeric HM(CO)$_5^-$ anions (M = Cr, Mo, W)[5-7] that no comprehensive (or, for that matter, limited) relative re-

† This contribution is dedicated to our good friend Earl Muetterties, whose valued scientific insight will continue to guide.

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