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Reductive Cleavage of Ketonic Carbon–Oxygen Bonds in the Reactions between Ketones and Ditungsten Hexaalkoxides. Structural Characterization of a Ditungsten μ-Propylidene Derivative

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The reaction between $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and each of acetone and 9-fluorenone is shown to proceed in hydrocarbon solvents at 0 °C to give oxo(μ-alkylidene)ditungsten alkoxides, $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(\mu\text{-}CR_2)$, by reductive cleavage of the ketonic C–O bond. The X-ray structural characterization of a derivative $W_2(OCH_2\text{-}t\text{-}Bu)_4(O_2CCF_3)_2(py)(O)(CMe_2)$ reveals a W_2^{10+} center, W–W = 2.70 Å, bridged by one alkoxide and a μ-propylidene ligand. One tungsten atom is in a pseudooctahedral environment, and the other trigonal bipyramidal with the μ-alkylidene and terminal W–oxo groups, W–O = 1.694 (4) Å, occupying equatorial positions. Crystal data for $W_2(OCH_2\text{-}t\text{-}Bu)_4(O_2CCF_3)_2(py)(O)(CMe_2)$ at −147 °C are as follows: $a = 12.411$ (2) Å, $b = 16.996$ (4) Å, $c = 10.178$ (2) Å, $\alpha = 93.07$ (1)°, $\beta = 104.32$ (1)°, $\gamma = 83.66$ (1)°, $z = 2$, $d_{\text{calcd}} = 1.74$ g cm^{-3}, and space group $P\bar{1}$. The (μ-propylidene)ditungsten compound reacts further with acetone or ketones at room temperature with the formation of olefins.

Introduction

Previously we noted that $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and acetone react in hydrocarbon solvents according to the stoichiometric reaction in eq 1, and we reported on the novel molecular structure of the black crystalline compound $W_4(O)_2(O\text{-}i\text{-}Pr)_{12}$.[1]

$$2W_2(O\text{-}i\text{-}Pr)_6(py)_2 + 2Me_2C{=}O \rightarrow W_4(O)_2(O\text{-}i\text{-}Pr)_{12} + Me_2C{=}CMe_2 \quad (1)$$

One of us speculated that the reaction leading to the reductive coupling of acetone probably proceeded via initial pinacolate formation and provided a molecular model for the McMurry reaction[2] that involves a reagent prepared from the reduction of $TiCl_3$ by one of $LiAlH_4$ or Na/K. Sharpless reported[3] in 1972 discovery of the reductive coupling of ketones and aldehydes in reactions involving reduced tungsten halides (e.g., WCl_6 + Li-n-Bu in THF), and more recently Riecke and co-workers[4] have made extensive studies of related reactions involving a number of highly activated metals including lanthanides and actinides. There is good evidence that initial pinacolate formation is involved in these reactions. Indeed when reactions employing the McMurry reagent are carried out at low temperatures and quenched (H^+/H_2O), pinacols and not olefins are liberated. Cotton, Walton, and co-workers[5] also noted that $W_2Cl_4(OEt)_4(HOEt)_2$ and ketones reacted in acidic alcohol solutions to give d^1–d^1 pinacolate complexes, e.g., with acetone $W_2Cl_4(O_2C_2Me_2)_2(HOEt)_2$ was formed.

In this paper we describe our studies of the reactions between $W_2(OR)_6(py)_n$, where $n = 0$ or 2, and ketones aimed at establishing the nature of the initial reaction. We show that contrary to the initial speculation, there is good evidence to believe that these reactions proceed via a different mechanism, namely, one involving cleavage of the ketonic C–O bond. An initial report of this discovery together with a preliminary examination of the scope of this reaction for olefin synthesis has recently been published.[6] We shall return to an evaluation of the synthetic utility of this reaction at a later date when more extensive studies have been completed. In the following paper[7] we describe reactions involving benzophenone and related diaryl ketones that proceed somewhat differently insomuch as olefins are not the major organic products in the reductive deoxygenation.

Results and Discussion

General Remarks. As with much of metal alkoxide chemistry, steric factors greatly influence the course of the reaction. In reactions between $W_2(OR)_6$ compounds and ketones, R'_2CO, bulky combinations of R and R′ fail to show any reactivity. Thus $W_2(O\text{-}t\text{-}Bu)_6$ and acetone (~6 equiv) show no sign of reaction in hydrocarbon solvents at room temperature over a period of several days. The sterically encumbered ketones $(t\text{-}Bu)_2CO$ and $(t\text{-}Bu)(Me)CO$ failed to show any evidence of reactivity toward $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ in hydrocarbon solutions. Most of the present studies have employed the less sterically demanding neopentoxide ligand, for which the compound $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ provides, by loss of pyridine, a source of coordinately unsaturated $W_2(OCH_2\text{-}t\text{-}Bu)_6$.

1:1 Adducts: $W_2(OCH_2\text{-}t\text{-}Bu)_2$. When hydrocarbon solutions of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ were allowed to react with acetone (ca. 3 equiv) at 0 °C, a formal 1:1 adduct of composition $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(OCMe_2)$ was formed. This could be isolated as an orange–brown analytically pure microcrystalline compound. All attempts to obtain crystals suitable for a single-crystal X-ray molecular structure determination were unsuccessful. The crystals were always too small or failed to show good diffraction data. Similar 1:1 adducts were obtained in the reactions between $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and each of the ketones cyclopentanone, 9-fluorenone, *trans*-4-phenyl-3-buten-2-one, and 4-phenyl-3-butyn-2-one.

The NMR data for these 1:1 adducts indicate the lack of any element of symmetry. Specifically, there are six different types of OR ligands of equal integral intensity.

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[1] Blatchford, T. P.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1984** 1295.

[2] McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405.

[3] Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6538.

[4] Kahn, B. E.; Riecke, R. T. *Chem. Rev.* **1988**, *88*, 733.

[5] Cotton, F. A.; DeMarco, D.; Falvello, L. R.; Walton, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 7375.

[6] Chisholm, M. H.; Klang, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2324.

[7] *Organometallics*, following paper in this issue.

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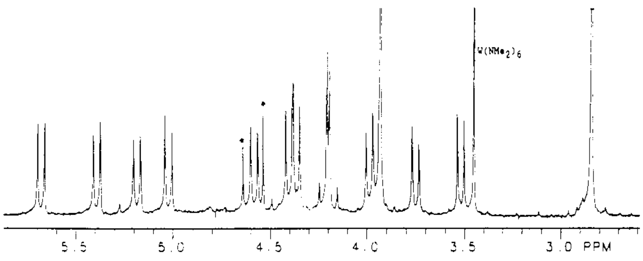


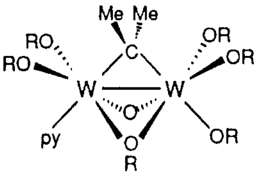
Figure 1. ^{1}H NMR spectrum of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(\mu\text{-}CMe_2)$ recorded in toluene-d_8, 22 °C, at 300 MHz showing six sets of AB or AX spin systems for the methylene protons and the two methyl singlets derived from acetone. Minor impurities are denoted with an asterisk.

In the case of the *trans*-4-phenyl-3-buten-2-one derivative there were two isomers present in solution, each lacking any element of symmetry.

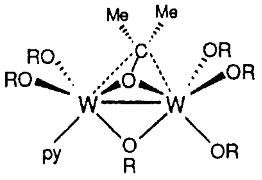
The ^{1}H NMR spectrum of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(OCMe_2)$, shown in Figure 1, reveals six AB spin systems for the neopentoxide methylene protons and two singlets for the methyl groups of acetone. The ^{13}C NMR spectrum of the ^{13}C-labeled derivative formed in the reaction employing $Me_2{}^{13}CO$ shows a singlet at $\delta = 163.7$ flanked by satellites due to coupling to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance of integral intensity 24%, $^1J_{^{183}W-^{13}C} = 83$ Hz. The methyl proton resonances appear as doublets due to ^{13}C–C–H coupling.

The NMR data indicate that the ketonic carbon is bridging two tungsten atoms and the magnitude of $^1J_{^{183}W-^{13}C}$ is typical of a $^{183}W-^{13}C_{sp^3}$ coupling constant.[8]

Collectively the NMR data are consistent with a μ-propylidene-containing compound in which the ketonic C–O bond has been cleaved ($W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(CMe_2)$) but could equally well be reconciled with a μ-perpendicular acetone complex. Plausible structures are shown in A and B.



A



B

We attempted to devise a chemical test to distinguish between a μ-propylidene and a μ-acetone complex by reactions with the acid CF_3COOH and CH_3COOH. Our reasoning was as follows. A ketone complex would react with acid to liberate the ketone or alcohol, whereas the alkylidene would liberate alkane. The fluorenone derivative did react with acetic acid to generate fluorene, which was identified by NMR and melting point analysis. However, the acetone complex reacted with CF_3COOH to give substitution of $OCH_2\text{-}t\text{-}Bu$ ligands. On the basis of the former reactions (formation of fluorene) and the structural characterization of $W_2(OCH_2\text{-}t\text{-}Bu)_4(O_2CCF_3)_2(py)(O)(CMe_2)$ (described below) we conclude that the initial 1:1 adducts are in fact μ-alkylidene derivatives of formula $W_2(OR)_6(py)(O)(\mu\text{-}CR'_2)$.

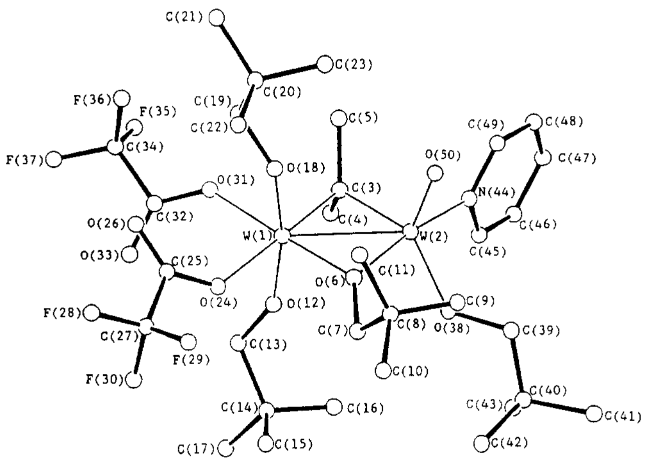


Figure 2. Ball-and-stick diagram of the molecular structure of the $W_2(O_2CCF_3)_2(OCH_2\text{-}t\text{-}Bu)_4(py)(O)(\mu\text{-}CMe_2)$ molecule giving the atom number scheme used in the tables.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for $W_2(OCH_2\text{-}t\text{-}Bu)_4(O_2CCF_3)_2(py)(O)(CMe_2)$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	2986.4 (2)	2366.8 (1)	4421.2 (2)	13
W(2)	5153.3 (2)	2665.3 (1)	5173.5 (2)	14
C(3)	4427 (5)	1749 (4)	3884 (6)	15
C(4)	4716 (6)	895 (4)	4342 (7)	21
C(5)	4475 (6)	1784 (4)	2392 (7)	22
O(6)	3766 (3)	3178 (2)	5715 (4)	16
C(7)	3470 (6)	3692 (4)	6792 (7)	20
C(8)	3611 (6)	4554 (4)	6624 (6)	21
C(9)	4832 (7)	4689 (4)	6848 (8)	28
C(10)	3125 (8)	5045 (5)	7686 (8)	34
C(11)	2970 (6)	4822 (4)	5213 (7)	24
O(12)	3134 (3)	1663 (2)	5781 (4)	16
C(13)	2787 (6)	1018 (4)	6355 (7)	23
C(14)	3226 (6)	1019 (4)	7906 (7)	24
C(15)	2743 (8)	1774 (5)	8513 (8)	37
C(16)	4491 (7)	945 (5)	8288 (8)	34
C(17)	2818 (7)	291 (5)	8398 (8)	35
O(18)	2574 (3)	3004 (2)	2949 (4)	17
C(19)	1929 (6)	3050 (4)	1557 (7)	22
C(20)	1833 (6)	3865 (4)	986 (7)	24
C(21)	1215 (7)	3810 (5)	−501 (8)	29
C(22)	1129 (8)	4444 (5)	1713 (8)	40
C(23)	2968 (8)	4135 (6)	1134 (9)	46
O(24)	1469 (3)	2810 (3)	4987 (4)	20
C(25)	450 (6)	2963 (4)	4345 (7)	23
O(26)	11 (4)	2822 (3)	3161 (5)	30
C(27)	−243 (6)	3371 (5)	5284 (9)	39
F(28)	−1305 (4)	3555 (3)	4634 (6)	58
F(29)	157 (4)	4028 (3)	5850 (7)	68
F(30)	−269 (5)	2893 (4)	6289 (6)	63
O(31)	2154 (4)	1547 (3)	3008 (4)	18
C(32)	1314 (5)	1168 (4)	2942 (6)	18
O(33)	870 (4)	1027 (3)	3830 (5)	28
C(34)	867 (6)	817 (4)	1514 (7)	29
F(35)	1574 (5)	213 (3)	1270 (5)	58
F(36)	758 (5)	1316 (3)	546 (4)	53
F(37)	−90 (5)	530 (4)	1391 (5)	67
O(38)	5852 (3)	2546 (3)	7064 (4)	18
C(39)	6829 (6)	2873 (4)	7876 (7)	25
C(40)	7089 (6)	2647 (4)	9359 (7)	30
C(41)	8097 (8)	3079 (6)	10084 (9)	47
C(42)	6094 (8)	2924 (6)	9934 (8)	40
C(43)	7386 (7)	1754 (5)	9493 (8)	38
N(44)	6711 (4)	1984 (3)	4934 (6)	19
C(45)	7198 (6)	1371 (4)	5785 (7)	23
C(46)	8136 (6)	909 (5)	5613 (9)	32
C(47)	8634 (6)	1074 (5)	4613 (9)	34
C(48)	8163 (6)	1697 (5)	3785 (8)	32
C(49)	7217 (6)	2141 (5)	3960 (7)	25
O(50)	5320 (4)	3346 (3)	4100 (4)	22

Molecular Structure of $W_2(OCH_2\text{-}t\text{-}Bu)_4(O_2CCF_3)_2(py)(O)(\mu\text{-}CMe_2)$. A ball-and-stick drawing of the molecule is shown in Figure 2. Atomic positional parameters and selected structural parameters are given in Tables I–III. An octahedrally coordinated tungsten atom, W(1), is linked to a five-coordinate trigonal-bipy-

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[8] See Table VIII in: Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

Table II. Selected Bond Distances for $W_2(OCH_2\text{-}t\text{-}Bu)_4(O_2CCF_3)_2(py)(O)(CMe_2)$

A	B	dist, Å	A	B	dist, Å
W(1)	W(2)	2.7046 (6)	F(29)	C(27)	1.317 (9)
W(1)	O(6)	2.009 (4)	F(30)	C(27)	1.346 (10)
W(1)	O(12)	1.838 (4)	F(35)	C(34)	1.328 (9)
W(1)	O(18)	1.829 (4)	F(36)	C(34)	1.305 (8)
W(1)	O(24)	2.149 (4)	F(37)	C(34)	1.308 (9)
W(1)	O(31)	2.106 (4)	O(6)	C(7)	1.457 (8)
W(1)	C(3)	2.146 (6)	O(12)	C(13)	1.422 (8)
W(2)	O(6)	2.028 (4)	O(18)	C(19)	1.446 (8)
W(2)	O(38)	1.916 (4)	O(24)	C(25)	1.277 (8)
W(2)	O(50)	1.694 (4)	O(26)	C(25)	1.217 (8)
W(2)	N(44)	2.200 (5)	O(31)	C(32)	1.271 (7)
W(2)	C(3)	2.111 (6)	O(33)	C(32)	1.215 (8)
F(28)	C(27)	1.331 (9)	O(38)	C(39)	1.438 (8)

ramidal tungsten atom, W(2), through the agency of μ-propylidene and μ-neopentoxy ligands. In addition, the two tungsten atoms are joined by a metal–metal single bond, W–W = 2.705 (1) Å. The coordination geometry about W(1) is in no way unusual. The W–O(12) and W–O(18) distances, 1.83–1.84 Å, are typical of terminal W–OR bond distances where alkoxide to metal π-donation is significant.[9] The W–O distances to the TFA ligands are notably longer, 2.106 (4) and 2.149 (4) Å, in the range expected for a W–O single bond.[9] The longer distance is associated with the TFA ligand trans to the μ-alkylidene ligand, consistent with the expected trans-influence order alkylidene > alkoxide.[10]

The trigonal bipyramidal geometry about W(2) has axial pyridine and μ-OR ligands, O(6)–W(2)–N44) = 169.3 (2)°, equatorial oxo and μ-alkylidene, and terminal OR ligands; the sum of the angles in the equatorial plane is 357.5°. The terminal oxo–tungsten bond distance, 1.694 (4) Å, is in the range expected for a W–O triple bond.[11]

A qualitative description of the bonding in the dinuclear compound can be formulated as follows. The octahedral coordination at W(1) will split the d orbitals in the usual manner, e_g above t_{2g}, and the strong π-donating properties of the trans-alkoxide ligands, taken to lie on the z axis, will remove the degeneracy of the t_{2g} orbitals to give two (d_{xz}, d_{yz}) above one (d_{xy}). The formally W^{5+} tungsten atom would therefore have a d^1 configuration with the electron in the plane of the bridging ligands, i.e., a d_{xy} orbital with one of its lobes directed toward W(2).

If for the sake of convenience we define the z axis for W(2) to be the one containing the axial ligands and the x axis to contain the terminal oxo ligand, then the σ-only interactions will split the d orbitals in the usual manner such that d_{z^2} lies highest, ($d_{x^2-y^2}$, d_{xy}) follow, and (d_{xz}, d_{yz}) lie lowest in energy. The strongest π-donation is now from the terminal oxo group, which will π-bond to d_{xz} and d_{xy} orbitals. The $d_{x^2-y^2}$ orbital will be raised in energy too because of the short W–O distance (a σ effect), but this is of no consequence to the overall argument. The remaining d orbital that has not been used in either σ or π bonding is the d_{yz} orbital. It is this d orbital that is suitably oriented and formally carries one electron (if the charge is partitioned W(5+)–W(5+) for the W_2^{10+} dinuclear center). This orbital together with the d_{xy} orbital from W(1) form the W–W σ bond.

This qualitative bonding description is satisfying because not only can we readily account for the formation of the M–M single bond but we see that the combined requirements of oxo–metal π-bonding and M–M bonding render a stereochemically rigid (on the NMR time scale) five-coordinate geometry about W(2). It is presumably also the stability of the five-coordinate W(2) atom with its W–oxo triple bond that causes the observed fused octahedral–trigonal bipyramidal structure relative to the cofacial bioctahedral geometry shown in A.

Table III. Selected Bond Angles for $W_2(OCH_2\text{-}t\text{-}Bu)_4(O_2CCF_3)_2(py)(O)(CMe_2)$

A	B	C	angle, deg
W(2)	W(1)	O(6)	48.23 (12)
W(2)	W(1)	O(12)	93.92 (13)
W(2)	W(1)	O(18)	96.89 (13)
W(2)	W(1)	O(24)	136.22 (12)
W(2)	W(1)	O(31)	131.91 (12)
W(2)	W(1)	C(3)	49.98 (16)
O(6)	W(1)	O(12)	92.37 (17)
O(6)	W(1)	O(18)	95.98 (17)
O(6)	W(1)	O(24)	88.08 (16)
O(6)	W(1)	O(31)	177.88 (16)
O(6)	W(1)	C(3)	98.13 (19)
O(12)	W(1)	O(18)	169.08 (18)
O(12)	W(1)	O(24)	83.93 (17)
O(12)	W(1)	O(31)	89.74 (17)
O(12)	W(1)	C(3)	89.71 (21)
O(18)	W(1)	O(24)	89.32 (18)
O(18)	W(1)	O(31)	81.90 (18)
O(18)	W(1)	C(3)	96.04 (21)
O(24)	W(1)	O(31)	91.86 (16)
O(24)	W(1)	C(3)	171.31 (20)
O(31)	W(1)	C(3)	82.16 (19)
W(1)	W(2)	O(6)	47.63 (11)
W(1)	W(2)	O(38)	115.14 (13)
W(1)	W(2)	O(50)	106.85 (15)
W(1)	W(2)	N(44)	132.79 (13)
W(1)	W(2)	C(3)	51.12 (17)
O(6)	W(2)	O(38)	88.07 (17)
O(6)	W(2)	O(50)	100.57 (19)
O(6)	W(2)	N(44)	169.33 (18)
O(6)	W(2)	C(3)	98.67 (20)
O(38)	W(2)	O(50)	129.09 (20)
O(38)	W(2)	N(44)	82.71 (19)
O(38)	W(2)	C(3)	124.05 (21)
O(50)	W(2)	N(44)	89.45 (21)
O(50)	W(2)	C(3)	104.26 (22)
N(44)	W(2)	C(3)	82.22 (21)
W(1)	O(6)	W(2)	84.14 (16)
W(1)	O(6)	C(7)	134.2 (4)
W(2)	O(6)	C(7)	139.1 (4)
W(1)	O(12)	C(13)	152.1 (4)
W(1)	O(18)	C(19)	143.6 (4)
W(1)	O(24)	C(25)	134.8 (4)
W(1)	O(31)	C(32)	134.0 (4)
W(2)	O(38)	C(39)	129.5 (4)
W(1)	C(3)	W(2)	78.90 (21)
W(1)	C(3)	C(4)	115.4 (4)
W(1)	C(3)	C(5)	116.6 (4)
W(2)	C(3)	C(4)	119.0 (4)
W(2)	C(3)	C(5)	115.4 (4)

We assume that the structures of the $W_2(OR)_6(py)(O)(CR'_2)$ compounds are related by the substitution of the two TFA liggands by OR ligands. We believe this is reasonable based on the similarity of the NMR data and the satisfactory bonding description noted above. Note the NMR data are quite different from that of known tungsten–ketone complexes.[7,13]

Reactivity. $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(\mu\text{-}CMe_2)$ dissolved in hydrocarbon solvents reacts with acetone at 22 °C to give tetramethylethylene and an alkoxide of tungsten, presumed to be $W_2O_2(OCH_2\text{-}t\text{-}Bu)_6$ on the basis of spectroscopic and analytical data. The addition of a different

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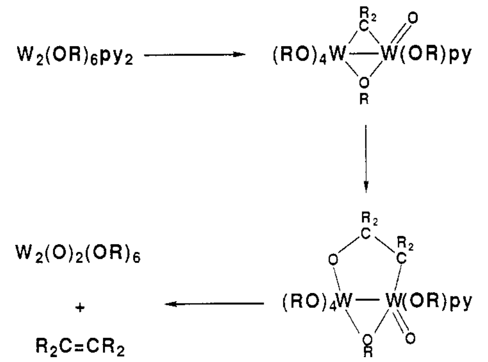
Scheme I



ketone or aldehyde allows selective reductive cross coupling of ketones or ketones and aldehydes in a stepwise reaction sequence. We shall report the details of our studies on this type of reaction elsewhere when selectivity and functional group tolerance are fully investigated. We note here just one specific example that involves the reductive cross coupling of acetone and 4′-methylacetophenone to give $Me_2C{=}C(p\text{-}MeC_6H_4)Me$. See the Experimental Section.

Concluding Remarks. The reductive coupling of acetone to give tetramethylethylene in the reaction involving ditungsten hexaalkoxides proceeds in a two-step process. The first step involves the uptake of acetone at the dimetal center with cleavage of the C–O double bond to give a dinuclear oxo–μ-propylidene complex. A second and slower reaction occurs in which the μ-propylidene ligand is transformed into the olefin in a further reaction with acetone. Presumably this involves C–C bond formation followed by C–O and M–C bond cleavage. A generalized reaction pathway is shown in Scheme I. The details of the second stage of the reaction are, however, unknown at this time. It is merely noted that a second reductive cleavage of acetone to give oxo and propylidene ligands is not possible at a $(W{-}W)^{10+}$ center. Thus, olefin formation by carbene–carbene coupling cannot be operative.

The proposed reaction pathway does not involve the intermediacy of a pinacolate ligand and therefore differs from the mechanism of the McMurry reaction and related reductive couplings at activated metals. The proposed pathway does, however, bring together two well-established reactions in mononuclear chemistry: (1) the reaction between an early transition metal alkylidene ligand and a ketone to yield a metal oxo group and an olefin first noted by Schrock[12] and (2) the cleavage of a C–O double by $WCl_2(PMe_2Ph)_4$ as noted by Mayer in the reaction involving cyclopentanone.[13]

Experimental Section

General reaction procedures and instrumentation have been previously described along with the preparation of $W_2(OR)_6$ and $W_2(OR)_6(py)_2$ compounds.[14]

Preparation of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}CMe_2)(O)$. A toluene (5 mL) solution of $W_2(OCH_2\text{-}t\text{-}Bu)_6py_2$ (1.0 g, 0.96 mmol) was cooled to 0 °C, and acetone (212 μL, 2.89 mmol) was added via syringe. The mixture was maintained at 0 °C for 4 days, during which time a light orange–brown solid precipitated. The solid was collected by filtration, dried in vacuo, and identified as $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}CMe_2)(O)$ (280 mg, 28% yield). A second crop was obtained by removing the volatiles from the filtrate in vacuo, redissolving the residue in ca. 5 mL of hexane, and cooling to −20 °C for 3 days (558 mg, 56%; total yield of 84%).

$W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}CMe_2)(O)$: ^1H NMR (C_6D_6) δ *py* 8.65 (br, 2 H), 6.69 (m, 1 H), 6.58 (m, 2 H), OCH_2 5.68 (d, J_{HH} = 9.9 Hz, 1 H), 5.39 (d, J_{HH} = 11.0 Hz, 1 H), 5.18 (d, J_{HH} = 11.0 Hz, 1 H), 5.02 (d, J_{HH} = 11.1 Hz, 1 H), 4.58 (d, J_{HH} = 10.3 Hz, 1 H), 4.40 (d, J_{HH} = 11.7 Hz, 1 H), 4.36 (d, J_{HH} = 10.1 Hz), 4.30 (d, J_{HH} = 10.0 Hz, 1 H), 4.10 (d, J_{HH} = 10.0 Hz, 1 H), 4.00 (d, J_{HH} = 10.8 Hz, 1 H), 3.75 (d, J_{HH} = 10.1 Hz, 1 H), 3.52 (d, J_{HH} = 10.2 Hz, 1 H), $C(CH_3)_2$ 3.93 (s, 3 H), 3.45 (s, 3 H), $C(CH_3)_3$ 1.46 (s, 9 H), 1.33 (s, 9 H), 1.28 (s, 9 H), 0.98 (s, 9 H), 0.94 (s, 9 H), 0.89 (s, 9 H).

$W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}^{13}CMe_2)(O)$: $^{13}C\{^1H\}$ NMR (C_6D_6) 163.7 (J_{WC} = 83 Hz, I = 24.3%); $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}CMe_2)(O)$ $^{13}C\{^1H\}$ NMR (C_6D_6) CMe_2 163.7 (s), py 150.0 (s), 137.4 (s), 124.5 (s), OCH_2 85.3 (s), 83.8 (s), 81.0 (s), 79.4 (s), 78.0 (s), 77.6 (s), $C(CH_3)_2$ 41.4 (s), 38.0 (s), $C(CH_3)_3$ 35.0 (s), 34.9 (s), 34.8 (s), 34.4 (s), 33.5 (s), $C(CH_3)_3$ 28.2 (s), 27.8 (s), 27.5 (s), 27.4 (s), 26.6 (s); IR (KBr) 2950 (s), 2900 (s), 2860 (s), 1485 (m), 1390 (m), 1360 (m), 1050 (s), 1030 (s), 955 (m), 660 (m), 650(m) cm^{-1}. Anal. Calcd for $W_2C_{38}H_{77}NO_7$: C, 44.40; H, 7.57; N, 1.36. Found: C, 44.80; H, 7.47; N, 1.20.

Preparation of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(\mu\text{-}$fluorenylidene). A mixture of $W_2(OCH_2\text{-}t\text{-}Bu)_6py_2$ (0.70 g, 0.67 mmol) and 9-fluorenone (0.135 g, 0.75 mmol) was stirred in toluene (5 mL) at 0 °C for 24 h to form a light orange–brown precipitate, which was filtered off and dried in vacuo to provide 420 mg (53% yield) of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)$(9-fluorenylidene). Analytically pure material could be obtained by recrystallization from toluene at −20 °C.

$W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(\mu\text{-}$fluorenyl): ^1H NMR (C_6D_6) δ fluorenyl and py 8.24 (d, J_{HH} = 8.3 Hz, 2 H), 7.78 (m, 2 H), 7.72 (d, J_{HH} = 7.1 Hz, 1 H), 7.66 (m, 1 H), 7.33 (m, 1 H), 7.06 (m, 1 H), 6.98 (m, 1 H), 6.93 (m, 1 H), 6.38 (m, 1 H), 6.02 (m, 2 H), OCH_2 5.46 (d, J_{HH} = 9.9 Hz, 1 H), 5.14 (d, J_{HH} = 11.1 Hz, 1 H), 4.96 (d, J_{HH} = 10.6 Hz, 1 H), 4.85 (d, J_{HH} = 11.8 Hz, 1 H), 4.49 (d, J_{HH} = 10.4 Hz, 1 H), 4.41 (d, J_{HH} = 10.6 Hz, 1 H), 4.23 (d, J_{HH} = 10.8 Hz, 1 H), 4.15 (d, J_{HH} = 10.5 Hz, 1 H), 4.13 (d, J_{HH} = 11.5 Hz, 1 H), 4.03 (d, J_{HH} = 12.0 Hz, 1 H), 3.69 (d, J_{HH} = 10.6 Hz, 1 H), 3.61 (d, J_{HH} = 11.1 Hz, 1 H), $CH_2C(CH_3)_3$ 1.55 (s, 9 H), 1.30 (s, 9 H), 1.13 (s, 9 H), 0.96 (s, 9 H), 0.94 (s, 9 H), 0.76 (s, 9 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ fluorenyl and py 166.2 (s), 162.0 (s), 155.8 (s), 148.2 (s), 141.2 (s), 137.8 (s), 136.9 (s), 132.1 (s), 129.3 (s), 129.2 (s), 129.1 (s), 124.5 (s), 124.3 (s), 123.4 (s), 123.3 (s), 122.4 (s), 118.0 (s), 116.9 (s), OCH_2 88.9 (s), 86.5 (s), 83.1 (s), 81.7 (s), 80.1 (s), 79.4 (s), $C(CH_3)_3$ 35.2 (s), 34.9 (s), 34.5 (s), 34.4 (s), 34.3 (s), 34.2 (s), $C(CH_3)_3$ 28.6 (s), 28.0 (s), 27.9 (s), 27.4 (s), 27.0 (s), 26.9 (s); IR (KBr) 2950 (s), 2860 (s), 1480 (s), 1465 (s), 1445 (s), 1430 (m), 1390 (s); 1360 (s), 1215 (m), 1090 (s), 1050 (s), 1020 (s), 985 (s), 960 (s), 945 (m), 920 (m), 770 (m), 755 (s), 735 (s), 690 (s), 660 (s), 620 (m) cm^{-1}. Anal. Calcd for $W_2C_{48}H_{79}O_7N$: C, 50.13; H, 6.94; N, 1.22. Found: C, 51.13; H, 6.77; N, 1.10.

Acidolysis of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}$fluorenylidene)(O). A toluene (2 mL) solution of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}$fluorenylidene)(O) (0.08 g, 0.07 mmol) was treated with 1 mL of glacial acetic acid and stirred at amibent temperature for 3 days. Water (ca. 2 mL) was then added, and the solution was neutralized by addition of aqueous NaOH. The mixture was extracted with 3 × 5 mL of Et_2O, the combined organic layers were dried with $MgSO_4$ and filtered, and the volatile components were removed in vacuo. Chromatography of the residue on SiO_2 with hexane eluent gave a white solid (8.6 mg, 75% yield), which was identified as fluorene by comparison of its ^1H NMR spectrum and melting point with published data.

$W_2(OCH_2\text{-}t\text{-}Bu)_5(CF_3CO_2)(py)(CMe_2)(O)$ and $W_2(OCH_2\text{-}t\text{-}Bu)_4(CF_3CO_2)_2(py)(CMe_2)(O)$. To a hexane (4 mL) solution of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(CMe_2)(O)$ (0.40 g, 0.389 mmol) was added CF_3CO_2H (33 μL, 0.43 mmol). A light brown precipitate began to form almost immediately. The mixture was stirred at room temperature for 1 h and then cooled to −20 °C. After ca. 16 h 190 mg of yellow–brown powder was isolated by filtration. This powder proved to be an approximately 3:1 mixture of the mono- and bis-TFA complexes. The volatile components were removed from the filtrate by vacuum transfer, and the residue was redissolved in Et_2O (3 mL) and cooled to −20 °C. After 5 days a few X-ray quality crystals of $W_2(OCH_2\text{-}t\text{-}Bu)_4(CF_3CO_2)_2(CMe_2)(O)$ were isolated.

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Table IV. Crystal Data for $W_2(OCH_2\text{-}t\text{-}Bu)_4(O_2CCF_3)_2(py)(O)(CMe_2)$

empirical formula	$C_{32}H_{55}F_6NO_9W_2$
color of crystal	brownish red
cryst dimens, mm	0.16 × 0.18 × 0.22
space group	$P\bar{1}$
cell dimensions	
temp, °C	−147
a, Å	12.411 (2)
b, Å	16.962 (4)
c, Å	10.178 (2)
α, deg	93.07 (1)
β, deg	104.32 (1)
γ, deg	83.66 (1)
Z, molecules/cell	2
vol, $Å^3$	2062.40
calcd density, g/cm^3	1.738
wavelength, Å	0.71069
mol wt	1079.48
linear abs coeff, cm^{-1}	57.640
detector-to-sample dist, cm	22.5
sample-to-source dist, cm	23.5
av ω-scan width at half-height	0.25
scan speed, deg/min	6.0
scan width (deg + dispersion)	1.8
individual background, s	6
aperture size, mm	3.0 × 4.0
2θ range, deg	6–45
total no. of rflctns collected	10000
no. of unique intensities	5390
no. with $F > 0.0$	5127
no. with $F > 3.0\sigma(F)$	4712
$R(F)$	0.0272
$R_w(F)$	0.0283
goodness of fit for the last cycle	0.855
max δ/σ for last cycle	0.05

$W_2(OCH_2\text{-}t\text{-}Bu)_4(CF_3CO_2)_2(py)(O)(CMe_2)$: ^1H NMR (C_6D_6) δ py 8.39 (m, 2 H), 7.02 (m, 1 H), 6.61 (m, 2 H), OCH_2 5.59 (d, J_{HH} = 10.6 Hz, 1 H), 4.87 (d, J_{HH} = 11.8 Hz, 1 H), 4.69 (d, J_{HH} = 10.5 Hz, 1 H), 4.59 (d, J_{HH} = 11.7 Hz, 1 H), 4.48 (d, J_{HH} = 12.3 Hz, 1 H), 4.18 (d, J_{HH} = 11.5 Hz, 1 H), 3.97 (d, J_{HH} = 10.5 Hz, 1 H), 3.35 (d, J_{HH} = 10.9 Hz, 1 H), CMe_2 3.62 (s, 3 H), 2.67 (s, 3 H), $CH_2C(CH_3)_3$ 1.29 (s, 9 H), 0.91 (s, 9 H), 0.82 (s, 9 H), 0.73 (s, 9 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ CMe_2 178.8 (s, J_{WC} = 97.1 Hz, *I* = 23.5%). IR (KBr) 2950 (s), 2900 (m), 2855 (m), 1730 (s), 1715 (s), 1485 (m), 1465 (m), 1450 (m), 1415 (s), 1405 (s), 1365 (m), 1205 (s), 1200 (s), 1190 (s), 1185 (s), 1145 (s), 1040 (s), 1025 (s), 985 (s), 965 (s), 765 (m), 725 (s), 705 (m), 685 (m) cm^{-1}.

$W_2(OCH_2\text{-}t\text{-}Bu)_5(CF_3CO_2)(py)(CMe_2)(O)$: ^1H NMR (C_6D_6) δ py 8.56 (m, 2 H), 6.85 (m, 1 H), 6.50 (m, 2 H), OCH_2 5.37 (s, 2 H), 5.35 (d, J_{HH} = 7.3 Hz, 1 H), 4.75 (d, J_{HH} = 10.3 Hz, 1 H), 4.43 (d, J_{HH} = 11.8 Hz, 1 H), 4.28 (d, J_{HH} = 11.2 Hz, 1 H), 4.05 (d, J_{HH} = 11.5 Hz, 1 H), 4.00 (d, J_{HH} = 11.2 Hz, 1 H), 3.92 (d, J_{HH} = 11.2 Hz, 1 H), 3.34 (d, J_{HH} = 10.3 Hz, 1 H), $C(CH_3)_2$ 3.44 (s, 3 H), 2.67 (s, 3 H), $C(CH_3)_3$ 1.38 (s, 9 H), 1.36 (s, 9 H), 0.97 (s, 9 H), 0.90 (s, 9 H), 0.78 (s, 9 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ CMe_2 171.9 (s, J_{WC} = 104.9 Hz, *I* = 21.5%).

Preparation of $(p\text{-}MeC_6H_4)(Me)C{=}C(Me)_2$. A hexane (3 mL) solution of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(CMe_2)(O)$ (0.20 g, 0.19 mmol) was treated with 4′-methylacetophenone (0.028 g, 0.21 mmol) and stirred at room temperature for 12 h. Water (ca. 3 mL) was added, and the mixture stirred vigorously for about 4 h. The mixture was then extracted with 2 × 5 mL of Et_2O, and the combined organic layers were dried with $MgSO_4$, filtered, and dried in vacuo. The residue was chromatographed on SiO_2 with 5% Et_2O/hexane eluant to give 20 mg (66% yield) of $(p\text{-}MeC_6H_4)(Me)C{=}C(Me)_2$. The organic product was identified by ^1H NMR spectroscopy and mass spectrometry.

Crystal and Molecular Structure of $W_2(OCH_2\text{-}t\text{-}Bu)_4(O_2CCF_3)_2(py)(O)(\mu\text{-}CMe_2)$. General operating procedures at the Indiana University molecular structure center have been described.[15] A summary of crystal data is given in Table IV.

A small well-formed crystal was selected by using inert-atmosphere handling techniques. The crystal was transferred to the goniostat, where it was cooled to −147 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited no symmetry other than $\bar{1}$. The choice of the triclinic space $P\bar{1}$ was confirmed by the successful solution and refinement of the structure. Data collection was undertaken as detailed in Table IV. A total of 10000 reflections (including standards) were collected in the given range. Following the usual data reduction and averaging of equivalent reflections, a unique set of 5390 reflections was obtained; 4712 reflections were considered observed by the criterion $F > 3.0\sigma(F)$. The *R* for the averaging was 0.026 for 4466 redundant data. A plot of the standard reflections revealed no significant trends. No correction for absorption was performed.

The structure was solved by using a combination of direct methods and Patterson and Fourier techniques. The heavy atoms when located were used to phase a difference map where all of the non-hydrogen atoms were located. Almost all of the hydrogen atoms except for a few on the OR groups were located in a difference map. The full-matrix least-squares refinement was completed by using anisotropic thermal parameters on all non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. The final *R* was 0.027, $Rw(F)$ was 0.029.

The final difference map was essentially featureless, except for a few peaks of 1.5 e/$Å^3$ in the immediate vicinity of the W atoms.

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Registry No. $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}CMe_2)(O)$, 119272-32-1; $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(\mu\text{-}^{13}CMe_2)(O)$, 124992-04-7; $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(\mu$-fluorenylidene), 125023-02-1; $W_2(OCH_2\text{-}t\text{-}Bu)_5(CF_3CO_2)(py)(CMe_2)(O)$, 124992-05-8; $W_2(OCH_2\text{-}t\text{-}Bu)_4(CF_3CO_2)_2(py)(CMe_2)(O)$, 119272-31-0; $(p\text{-}MeC_6H_4)(Me)C{=}C(Me)_2$, 25570-44-9; $(p\text{-}MeC_6H_4)(Me)CO$, 122-00-9; $(t\text{-}Bu)_2CO$, 815-24-7; $(t\text{-}Bu)(Me)(CO)$, 75-97-8; $(Me)_2CO$, 67-64-1; $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$, 88608-50-8; 9-fluorenone, 486-25-9; cyclopentanone, 120-92-3; *trans*-4-phenyl-3-buten-2-one, 1896-62-4; 4-phenyl-3-butyn-2-one, 1817-57-8; tetramethylethylene, 563-79-1.

Supplementary Material Available: Complete listings of bond distances and angles and anisotropic thermal parameters (5 pages); a listing of F_o and F_c values (13 pages). Ordering information is given on any current masthead page.

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