Reaction between benzophenone and ditungsten hexaalkoxides. Molecular structure and reactivity of W(OCH2-tert-Bu)4(py)(.eta.2-OCPh2)

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Reaction between Benzophenone and Ditungsten Hexaalkoxides. Molecular Structure and Reactivity of $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$

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Reactions of $W_2(OR)_6(py)_2$ (R = OCH_2-*t*-Bu, O-*i*-Pr) with benzophenone are shown to produce a mixture of products, including $W(OR)_4(py)(Ph_2CO)$, $W(OR)_4(OCPh_2CPh_2O)$, one containing a terminal alkylidene ($W{=}CPh_2$), Ph_2CCPh_2, and $Ph_2CHCHPh_2$. The X-ray crystal structure of $W(OCH_2\text{-}t\text{-}Bu)_4(py)(Ph_2CO)$ has been determined and found to contain a highly reduced, asymmetrically bonded benzophenone ligand; W-O = 1.970 (6) Å, W-C = 2.234 (10) Å, and C-O = 1.397 (11) Å. Crystal data for $W(OCH_2\text{-}t\text{-}Bu)_4(py)(Ph_2CO)$ at -144 °C: a = 15.675 (1) Å, b = 13.736 (1) Å, c = 17.936 (2) Å, β = 92.39 (1)°, Z = 4, d_{calc} = 1.365 g cm^{-3}, and space group $P2_1/c$. Reactions of $W_2(OR)_6$ (R = OCH_2-*t*-Bu, O-c-C_6H_{11}) with benzophenone produce tetraphenylethane as the only organic product. Labeling studies show the H atoms of tetraphenylethane are primarily from the alkoxide ligands. A mechanism for these reactions based on an intermediate μ-diphenylalkylidene compound is proposed.

Introduction

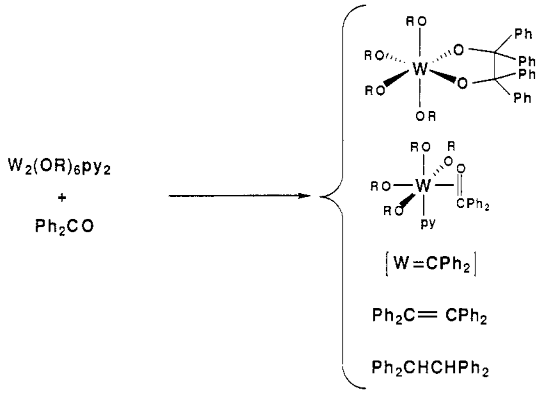
In a preceding paper[1] and in a previous communication,[2] we reported results of reactions of dialkyl or alkyl/aryl ketones and aldehydes with $W_2(OR)_6$ compounds, with specific attention being given to $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ for reasons of steric access to the dimetal center. The overall reaction sequence leads to the reductive coupling and deoxygenation of the ketone/aldehyde to give olefins. Superficially, the reaction would seem to provide a molecular model for the McMurry reaction[3] that finds extensive use in organic synthesis. However, as we showed in the previous report, the mechanisms of the two reactions differ. The McMurry reaction, like those involving other highly reduced or active metals,[4] involves an initial reductive coupling to give pinacolate intermediates that are subsequently deoxygenated. The first step in the reaction with $W_2(OR)_6$ compounds is the reductive cleavage of the ketone C-O double bond to give ditungsten oxo μ-alkylidene complexes. We report here on studies on the reaction between $W_2(OR)_6$ compounds and benzophenone, which, along with reactions of certain other diaryl ketones, proceed differently, yielding complex mixtures of products in which olefins are minor components.

Results and Discussion

General Comments. As with other ketones, no reaction was observed between $W_2(O\text{-}t\text{-}Bu)_6$ and benzophenone, presumably for steric reasons. With the less sterically demanding alkoxide ligands OR = OCH_2-*t*-Bu, O-*i*-Pr, and O-c-C_6H_{11}, the reactions gave a distribution of products that depended on the specific alkoxide and on whether or not pyridine was present and, if present, then in what concentration.

Reactions Involving $W_2(OR)_6(py)_2$ Compounds, Where R = CH_2-*t*-Bu and *i*-Pr. The compounds $W_2(OR)_6(py)_2$, where R = CH_2-*t*-Bu and *i*-Pr, react with 2 equiv of benzophenone in hydrocarbon solvents at ambient temperatures to form a mixture of products as shown in Scheme I. The relative amounts of the different products depend on R, on the reaction temperature, and on whether or not excess pyridine is present. The ^{13}C NMR spectrum of the reaction mixture derived from an NMR-tube reaction involving $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and $Ph_2{}^{13}CO$ (2 equiv) in toluene-d_8 is shown in Figure 1. The use of the ^{13}C-labeled benzophenone allows the ready identification of products containing the carbonyl carbon atom. The signals arising from the OCH_2-*t*-Bu ligands are identified from proton-coupled spectra. Four significant ^{13}C resonances at δ 56.7, 111.5, 118.5, and 141.5 have been assigned to the compounds $Ph_2CHCHPh_2$, $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$, $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$, and $Ph_2C{=}CPh_2$, respectively. The assignments have been made by either complete isolation and characterization of the compounds or by comparison with authentic samples. A similar distribution of products was obtained in a study of the reaction between $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and $Ph_2{}^{13}CO$.

Scheme I



While we have not been able to isolate the complex responsible for the resonance at δ 271 (Figure 1), we feel confident in assigning this to a compound containing a terminal diphenylalkylidene ligand, $W{=}CPh_2$. This assignment is claimed with confidence on the basis of the observed chemical shift (271 ppm), the magnitude of the ^{183}W-^{13}C coupling constant ($J_{^{183}W-^{13}C}$ = 176 Hz), the relative intensity of the satellites (14%; ^{183}W, $I = {}^1/_2$, 14.5% natural abundance), and a comparison of these data with those for other terminal tungsten alkylidene carbon atoms.[5] A

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[1] Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics*, preceding paper in this issue.

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

[3] (a) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405. (b) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, C. R. *J. Organomet. Chem.* **1978**, *43*, 3255.

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

[5] For listings of chemical shifts and coupling constants involving W-C single, double, and triple bonds, see Table VIII in: Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	7564.1 (2)	3765.4 (3)	7048.0 (2)	11
O(2)	8087 (4)	4754 (5)	7648 (3)	12
C(3)	8295 (8)	5735 (8)	7566 (6)	28
C(4)	7927 (6)	6380 (8)	8156 (5)	20
C(5)	8063 (10)	7433 (10)	7954 (8)	49
C(6)	6965 (10)	6199 (12)	8209 (10)	62
C(7)	8358 (12)	6164 (12)	8893 (7)	66
O(8)	6389 (4)	4035 (5)	7231 (3)	16
C(9)	5856 (6)	3652 (8)	7791 (5)	19
C(10)	4928 (6)	3993 (8)	7643 (6)	23
C(11)	4572 (7)	3609 (10)	6894 (6)	31
C(12)	4402 (6)	3566 (10)	8270 (6)	30
C(13)	4872 (7)	5097 (10)	7656 (7)	32
O(14)	7277 (4)	2750 (5)	6352 (3)	17
C(15)	6522 (6)	2180 (8)	6237 (5)	18
C(16)	6475 (7)	1746 (8)	5454 (5)	19
C(17)	7221 (8)	1059 (9)	5358 (6)	33
C(18)	6468 (8)	2553 (8)	4863 (6)	27
C(19)	5639 (7)	1193 (10)	5378 (6)	32
O(20)	7411 (4)	4742 (5)	6251 (3)	16
C(21)	6655 (6)	5192 (7)	5990 (5)	15
C(22)	6811 (7)	5892 (7)	5324 (5)	18
C(23)	5979 (8)	6379 (9)	5114 (6)	31
C(24)	7476 (8)	6642 (9)	5545 (7)	34
C(25)	7123 (8)	5277 (8)	4672 (6)	28
N(26)	8816 (4)	3774 (6)	6445 (4)	14
C(27)	9543 (6)	4131 (7)	6743 (5)	15
C(28)	10279 (6)	4265 (8)	6349 (6)	21
C(29)	10253 (7)	4006 (8)	5598 (6)	24
C(30)	9508 (6)	3639 (8)	5281 (5)	22
C(31)	8803 (6)	3526 (6)	5715 (5)	16
O(32)	7432 (4)	2930 (4)	7928 (3)	13
C(33)	8260 (6)	2660 (7)	7756 (6)	15
C(34)	8941 (6)	2939 (7)	8310 (5)	12
C(35)	9768 (6)	2591 (7)	8276 (5)	15
C(36)	10401 (7)	2835 (9)	8797 (6)	28
C(37)	10201 (7)	3429 (8)	9395 (6)	26
C(38)	9384 (7)	3788 (9)	9446 (5)	26
C(39)	8753 (6)	3531 (7)	8902 (5)	16
C(40)	8305 (6)	1637 (7)	7445 (5)	50
C(41)	8907 (6)	1362 (8)	6922 (5)	18
C(42)	8944 (7)	404 (8)	6691 (6)	22
C(43)	8377 (7)	−284 (7)	6967 (6)	23
C(44)	7780 (7)	−13 (8)	7469 (6)	22
C(45)	7727 (6)	937 (7)	7699 (6)	18

plausible molecular formula for this compound will be proposed later. It is important to note here, however, that the compound responsible for the resonance at δ 271, which represents a significant sink for the ketonic carbon atom, is a dead-end product in the overall reaction. Once this product is formed, it does not react with further Ph_2CO or decompose to give $Ph_2C{=}CPh_2$ or $Ph_2CHCHPh_2$.

When the reaction between $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and Ph_2CO is carried out in the presence of 20 equiv of pyridine, the rate of reaction slows considerably. The most significant change in the product distribution is that very little $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$ is formed. The retardation in the rate is readily understood as the substrate, Ph_2CO, is forced to compete with pyridine for access to the ditungsten center by the reversible dissociation of pyridine from $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$.

Isolation and Characterization of Products. The organic products $Ph_2C{=}CPh_2$ and $Ph_2CHCHPh_2$ were characterized by comparisons of ^1H and ^{13}C NMR spectra of reaction mixtures containing them with those of authentic samples. Tetraphenylethane was also isolated by chromatography and further characterized by melting point and mass spectrometry. The tungsten-containing products $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$ and $W(OR)_4(OCPh_2CPh_2O)$ were isolated as noted below and were characterized by ^1H and ^{13}C NMR and IR spectroscopies, elemental analysis, and, for $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$, by single-crystal X-ray diffraction.

Table II. Selected Bond Distances (Å) for $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$

W(1)–O(2)	1.897 (6)	O(8)–C(9)	1.433 (11)
W(1)–O(8)	1.920 (6)	O(14)–C(15)	1.426 (11)
W(1)–O(14)	1.912 (6)	O(20)–C(21)	1.399 (11)
W(1)–O(20)	1.967 (6)	O(32)–C(33)	1.397 (11)
W(1)–O(32)	1.970 (6)	C(40)–C(33)	1.514 (13)
W(1)–N(26)	2.280 (7)	C(40)–C(41)	1.410 (13)
W(1)–C(33)	2.234 (10)	C(40)–C(45)	1.410 (13)
O(2)–C(3)	1.396 (12)		

Table III. Selected Bond Angles (deg) for $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$

O(2)–W(1)–O(8)	99.18 (26)	O(20)–W(1)–N(26)	74.53 (26)
O(2)–W(1)–O(14)	167.50 (27)	O(20)–W(1)–C(33)	156.7 (3)
O(2)–W(1)–O(20)	87.76 (27)	O(32)–W(1)–N(26)	120.32 (26)
O(2)–W(1)–O(32)	91.16 (25)	O(32)–W(1)–C(33)	38.2 (3)
O(2)–W(1)–N(26)	84.57 (27)	N(26)–W(1)–C(33)	82.2 (3)
O(2)–W(1)–C(33)	88.6 (3)	W(1)–O(2)–C(3)	136.8 (7)
O(8)–W(1)–O(14)	92.91 (27)	W(1)–O(8)–C(9)	129.8 (6)
O(8)–W(1)–O(20)	84.46 (25)	W(1)–O(14)–C(15)	131.8 (6)
O(8)–W(1)–O(32)	80.89 (26)	W(1)–O(20)–C(21)	128.4 (6)
O(8)–W(1)–N(26)	158.54 (25)	W(1)–O(32)–C(33)	81.2 (5)
O(8)–W(1)–C(33)	118.9 (3)	W(1)–C(33)–O(32)	60.6 (4)
O(14)–W(1)–O(20)	90.28 (25)	W(1)–C(33)–C(40)	116.8 (7)
O(14)–W(1)–O(32)	93.90 (26)	W(1)–C(33)–C(34)	121.8 (7)
O(14)–W(1)–N(26)	83.0 (3)	O(32)–C(33)–C(40)	112.7 (8)
O(14)–W(1)–C(33)	88.3 (3)	O(32)–C(33)–C(34)	115.7 (8)
O(20)–W(1)–O(32)	164.94 (26)	C(40)–C(33)–C(34)	116.4 (8)

$W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$. When the reaction between benzophenone and $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ is carried out in hexane, a light orange precipitate forms as the reaction proceeds. Recrystallization of the precipitate from toluene gives red-orange crystals of analytically pure $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$. The compound is fluxional in solution at room temperature and exhibits only broad ^1H and ^{13}C NMR signals assignable to $OCH_2\text{-}t\text{-}Bu$ ligands. At −20 °C the ^1H NMR spectrum shows three types of OR ligands in the integral ratio 1:1:2, with those of intensity 2 having diastereotopic methylene protons.

The low-temperature ^{13}C NMR spectrum also has resonances for three different OR ligands as well as a resonance at 117.7 ppm assignable to the Ph_2CO ligand (from ^{13}C labeling), which is invariant with temperature and rather interestingly shows no coupling to ^{183}W. Since these data did not allow a unique structural assignment, we undertook a single-crystal X-ray diffraction study.

A ball-and-stick drawing of the molecular structure of $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$ is shown in Figure 2. Fractional coordinates are given in Table I, and selected bond distances and bond angles are given in Tables II and III, respectively.

The coordination of tungsten may be viewed as pseudooctahedral if the η^2-benzophenone ligand is considered to occupy one coordination site. The low-temperature NMR data that revealed three types of OR ligands in the ratio 1:1:2 are consistent with the solid-state structure.

The η^2-benzophenone ligand is very asymmetrically bonded to tungsten and appears to be a highly reduced (2−) ligand. The W–O(32) bond distance of 1.970 (6) Å is nearly as short as the W–OR distances, 1.92 Å (average),[6] while the W–C(33) distance of 2.234 (10) Å is somewhat longer than a typical $W\text{–}\eta^2\text{-}C_2$ π-bonding distance (cf. W–C = 2.14 (2) Å (average) in $W_2(OCH_2\text{-}t\text{-}Bu)_6(\eta^2\text{-}C_2H_4)_2$).[7] The C–O

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[6] This is suggestive of some oxygen-to-tungsten π-donation; see: Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

[7] Chacon, S. T.; Chisholm, M. H.; Huffman, J. C. Results to be submitted for publication.

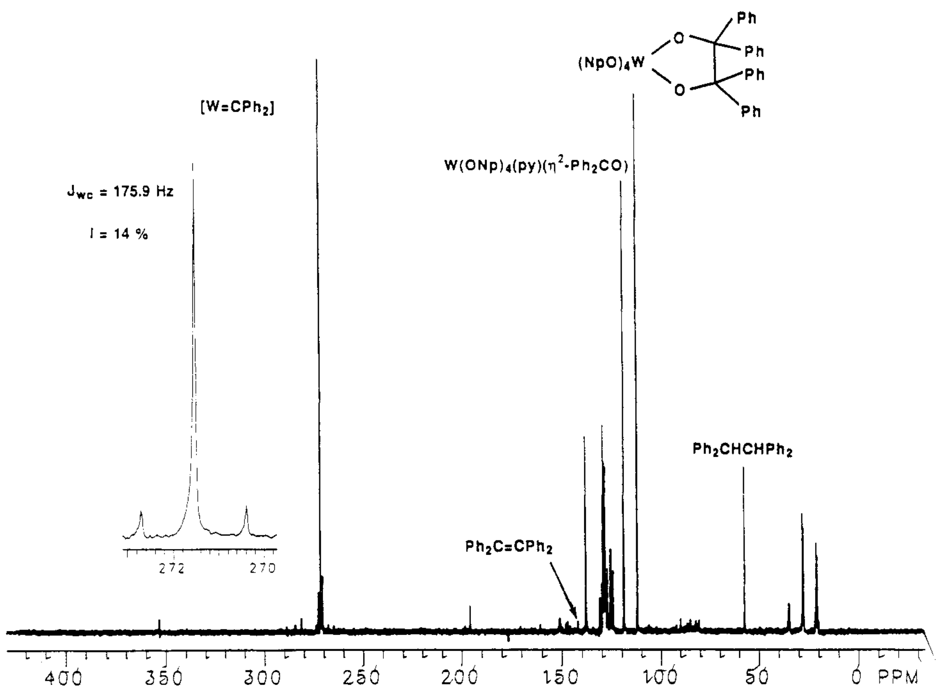


Figure 1. $^{13}C\{^1H\}$ NMR spectrum (toluene-d_8) of the products formed in the reaction between $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and $Ph_2(^{13}CO)$.

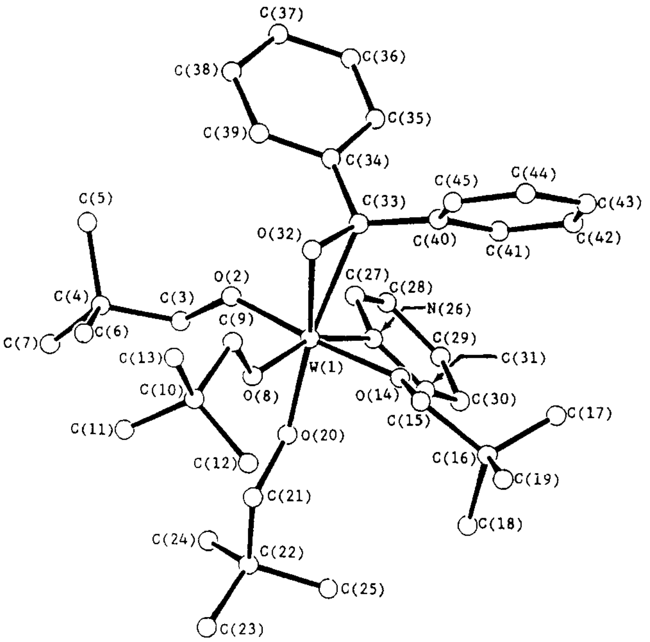
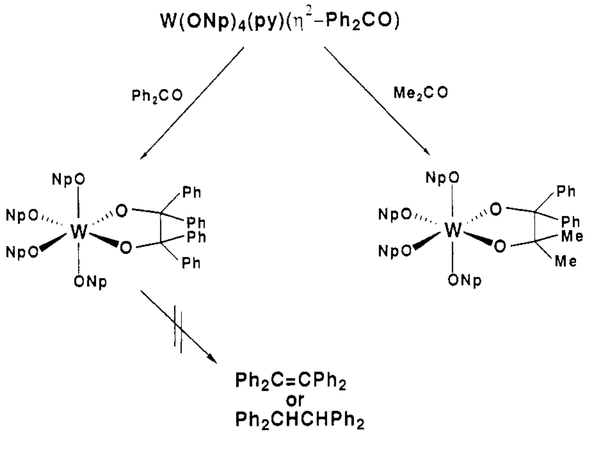


Figure 2. Ball-and-stick drawing of the $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$ molecule showing the numbering scheme used in the tables.

Scheme II



distance in the benzophenone ligand, 1.397 (11) Å, is considerably longer than in free benzophenone, and the carbonyl carbon atom is significantly pyramidalized as evidenced by the sum of the C–C–C and O–C–C angles at C(33), 344.8°. Overall, the coordination of the η^2-$OCPh_2$ ligand is similar to that observed for the η^2-acetone ligands in $WCl_2(PMePh_2)_2(\eta^2\text{-}OCMe_2)_2$[8] and $Os(NH_3)_5(\eta^2\text{-}OCMe_2)^{2+}$.[9]

$W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CR_2O)$ Compounds, Where R = Ph and Me. $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$ reacts with a second equivalent of benzophenone at ambient temperatures in hydrocarbon solvents to form the benzopinacolate (tetraphenylethylene glycolate) complex $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$ (see Scheme II). Comparison of the ^1H and ^{13}C NMR spectra of a prepared sample of the above with the spectra obtained in studies of the reactions between $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and Ph_2CO, such as that shown in Figure 1, confirms its formation in the latter reaction. Specifically, we can identify the resonance at δ 111.5 in Figure 1 as arising from the labeled pinacolate carbon atoms $W(OCH_2\text{-}t\text{-}Bu)_4(O^{13}CPh_2{}^{13}CPh_2O)$. Furthermore, when a reaction mixture such as that shown in Figure 1 is treated with more $Ph_2{}^{13}CO$, the ^{13}C resonance at δ 117.5 of the η^2-$OCPh_2$ complex decreases in intensity as the one at δ 111.5 increases. This strongly suggests that $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$ is an intermediate in the formation of $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$ in the reaction between $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and benzophenone. When the reaction between the labeled η^2-$O^{13}CPh_2$ complexes and unlabeled Ph_2CO (1 equiv) was followed by ^{13}C NMR spectroscopy, no free $Ph_2{}^{13}CO$ was detected. From this we conclude that there is no significant equilibrium involving dissociation of the η^2-$O^{13}CPh_2$ ligand from $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$. The fluxional process probably centers on the ease of py dissociation, and the latter is probably a necessity for pinacolate formation. $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$ and acetone also react in

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[8] Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 7213.

[9] Taube, H.; Harman, W. D.; Fairlie, D. P. *J. Am. Chem. Soc.* **1986**, *108*, 8223.

hydrocarbon solvents to give the mixed pinacolate complex $W(OCH_2\text{-}t\text{-}Bu)_4(OCMe_2CPh_2O)$.

The isopropoxy complex $W(O\text{-}i\text{-}Pr)_4(OCPh_2CPh_2O)$ can be isolated directly from the reaction between $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and benzophenone in a 21% yield. The compounds $W(OR)_4(OCPh_2CPh_2O)$ display very similar variable-temperature NMR behavior. At room temperature there is only one type of time-averated OR signal, but at low temperature (−40 °C, 300 MHz) there are two types of OR groups of equal integral intensity consistent with a pseudooctahedral $W(OR)_4$(pinacolate) molecule having C_{2v} symmetry. The mixed pinacolate (1,1-dimethyl-2,2-diphenylethylene glycolate) complex $W(OCH_2\text{-}t\text{-}Bu)_4(OCMe_2CPh_2O)$ is also fluxional at room temperature but is frozen out on the NMR time scale below −40 °C and shows OR ligands in the ratio 1:1:2.

In the McMurry reaction[3] and related reductive couplings of carbonyl compounds[4] the organic products are formed via an intermediate pinacolate. In a number of instances when the reactions are carried out at low temperature and quenched by the addition of water, pinacols and not olefins are the organic products. In our studies, the benzopinacolate complexes $W(OR)_4(O_2CPh_2CPh_2O)$, where R = i-Pr and $CH_2\text{-}t\text{-}Bu$, cannot be the source of $Ph_2C{=}CPh_2$ or $Ph_2CHCHPh_2$. They are stable in solution for weeks at room temperature and do not react with $W_2(OR)_6$ compounds or other species present in the reaction mixtures. They do decompose upon heating to other products that as yet have not been identified. Possible sources of $Ph_2C{=}CPh_2$ and $Ph_2CHCHPh_2$ are discussed later in this paper.

Reactions Involving $W_2(OR)_6$ Compounds, Where R = $CH_2\text{-}t\text{-}Bu$ and $c\text{-}C_6H_{11}$. Reactions involving the Lewis base free $W_2(OR)_6$ compounds, where R = $CH_2\text{-}t\text{-}Bu$ and $c\text{-}C_6H_{11}$, tend to produce tetraphenylethane as the major organic product. In the case of the cyclohexoxide the only isolable tungsten compound appears to be $W_3O(O\text{-}c\text{-}C_6H_{11})_{10}$, which has a ^1H NMR spectrum analogous to that of the fully characterized compound $W_3O(O\text{-}i\text{-}Pr)_{10}$. Presumably this is formed from a comproportionation of $WO(O\text{-}c\text{-}C_6H_{11})_4$ and $W_2(O\text{-}c\text{-}C_6H_{11})_6$. There is also evidence from NMR spectroscopy for the formation of $W(O\text{-}c\text{-}C_6H_{11})_4(OCPh_2CPh_2O)$.

When $W_2(OCH_2\text{-}t\text{-}Bu)_6$ is allowed to react with $Ph_2{}^{13}CO$ at room temperature in toluene-d_8, $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$ and $Ph_2CHCHCPh_2$ are formed in nearly equal amounts as the major products along with a small amount of $Ph_2C{=}CPh_2$. No other $Ph_2{}^{13}C$-containing products are formed, and no intermediate resonances are observed by ^{13}C NMR spectroscopy. When the reaction is carried out on a benchtop scale (ca. 1 g of $W_2(OCH_2\text{-}t\text{-}Bu)_6$), then $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$ can be isolated in 20% yield.

When the reaction is carried out at 0 °C and monitored by ^{13}C NMR spectroscopy, a resonance at δ 162.1 ppm with $J_{^{183}W-^{13}C}$ = 105.6 Hz and integral satellite intensity of 23% is observed. This resonance appears to early reaction times (within 20 min) and before any other new resonances appear. As the reaction proceeds at 0 °C, the δ 162.1 resonance maintains a nearly constant intensity as the δ 111.5 resonance of $W(OCH_2\text{-}t\text{-}Bu)_4(O^{13}CPh_2{}^{13}CPh_2O)$ grows in and that of free $Ph_2{}^{13}CO$ disappears. When the starting material is consumed, the δ 162.1 resonance disappears completely. No detectable $Ph_2{}^{13}C{=}{}^{13}CPh_2$ or $Ph_2{}^{13}CH{-}{}^{13}CHPh_2$ is formed in this reaction. A comparison of the ^{13}C NMR data with those for $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(\mu\text{-}{}^{13}CMe_2)$ leads us to suggest that the transient resonance at δ 162.1 arises from a μ-diphenylalkylidene ($W_2(\mu\text{-}CPh_2)$) containing compound. A proposal as to why this $W_2(\mu\text{-}CPh_2)$ intermediate behaves differently from $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(\mu\text{-}CMe_2)$ and those μ-alkylidene intermediates derived from other ketones will be presented later.

Reactions between $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ and Other Diaryl Ketones. As reported in the preceding paper[1] of this issue, 9-fluorenone and $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ react to yield an isolable μ-alkylidene, $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)(O)(\mu$-9-fluorenylidene), an analogue of the μ-propylidene complex derived from acetone. On the other hand, we have found that two other diaryl ketones, dibenzosubarone (dibenzocycloheptadienone) and $(p\text{-}C_6H_5\text{-}C_6H_4)_2CO$, behave as benzophenone does. These latter reactions have not been fully investigated, but in both cases, the η^2-ketone complexes $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCAr_2)$ have been isolated and identified by ^1H NMR spectroscopy.

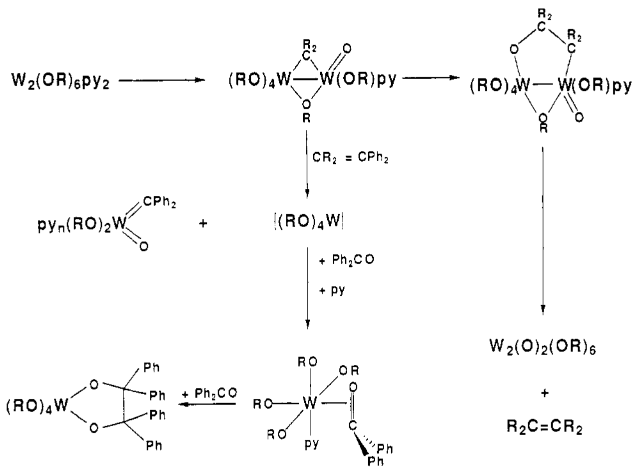
Formation of $Ph_2CHCHPh_2$: Labeling Studies. One of the puzzling aspects of this work in the persistent occurrence of tetraphenylethane as the main organic product rather than tetraphenylethylene. In the McMurry reaction tetraphenylethane is formed preferentially from benzophenone when the $TiCl_3/K$ reducing system is used but the saturated hydrocarbon arises from overreduction of the first-formed olefin.[3b] We have found that tetraphenylethylene does not react with $W_2(OR)_6(py)_2$ complexes in the presence or absence of benzophenone, so this cannot be the source of tetraphenylethane in the present reactions.

To investigate the source of the hydrogen atoms in tetraphenylethane, we chose the reaction between $W_2(O\text{-}c\text{-}C_6H_{11})_6$ and benzophenone because it produces relatively large amounts of tetraphenylethane and because a variety of differently deuterated cyclohexanols are readily available. When the reaction of $W_2(OC_6H_{11})_6$ with $(C_6H_5)_2CO$ is carried out in C_6D_6 or toluene-d_8, there is no detectable deuterium incorporation into the tetraphenylethane that is formed. Likewise, no deuterium can be detected in the tetraphenylethane when benzophenone-d_{10} is used in reactions with $W_2(OCH_2\text{-}t\text{-}Bu)_6$.

The deuterium-labeled alkoxide complexes $W_2(O\text{-}\alpha\text{-}DC_6H_{10})_6$ and $W_2(O\text{-}c\text{-}C_6D_{11})_6$ were prepared from $W_2(O\text{-}t\text{-}Bu)_6$ and the corresponding alcohol. Reaction of these with $Ph_2({}^{13}CO)$ in C_6D_6 resulted in the formation of all three possible isotopomers of tetraphenylethane, $Ph_2CHCHPh_2$, $Ph_2CHCDPh_2$, and $Ph_2CDCDPh_2$, as shown by the appearance of eight lines between δ 56.0 and 56.7 in the $^{13}C\{^1H\}$ NMR spectrum. While it is difficult to quantify the relative amounts of the different isotopomers, it is clear that even in the reaction with $W_2(O\text{-}\alpha\text{-}DC_6H_{10})_6$ deuterium is preferentially abstracted. Integration of the ^{13}C–H resonances of $Ph_2CHCHPh_2$ and $Ph_2CHCDPh_2$ reveals a 1:2.4 ratio of d_0 to d_1 tetraphenylethane along with a significant amount of d_2. When $W_2(O\text{-}c\text{-}C_6D_{11})_6$ is employed, the ratio of d_0 to d_1 tetraphenylethanes decreases to 1:6.6 and even more d_2 is formed. Whatever the mechanism of tetraphenylethane formation, it is clear that the alkoxide ligands are by far the major source of the hydrogen atoms.

Mechanism. A mechanism that accounts for the reactivity described in this paper is proposed in Scheme III. The first step of the mechanism is the same as that for dialkyl or alkyl/aryl ketones, namely cleavage of the ketonic C–O bond to form a μ-alkylidene intermediate. Although a μ-diphenylalkylidene has only been observed in one reaction, that of benzophenone with $W_2(OCH_2\text{-}t\text{-}Bu)_6$, we feel confident in proposing that the other reactions presented here also go through such an intermediate. All of the observed products, except tetraphenylethane,

Scheme III



can be rationally derived from a μ-diphenylalkylidene species if a partitioning of reaction pahways from this intermediate occurs.

The predominant reaction path is asymmetric cleavage of the μ-alkylidene to form from half of the dimer $W(OR)_4$ and from the other half $W(OR)_2({=}CPh_2)(O)$. This nicely explains the terminal alkylidene resonance observed in the ^{13}C NMR spectra of reactions between $W_2(OR)_6(py)_2$ and $(C_6H_5)_2{}^{13}CO$. Analogous W(VI) oxo- and imidoalkylidene complexes[8,10] are typically stabilized by coordination of 2 equiv of Lewis base, and so the formula of the complex formed here is likely $W(OR)_2({=}CPh_2)(O)(py)_2$.

Mononuclear $W(OR)_4$ complexes are unknown except when stabilized by bulky aryloxide ligands.[11] The $W(OR)_4$ species formed here with R = OCH_2-*t*-Bu or O-*i*-Pr would be highly unsaturated and would be expected to be very reactive. Coordination of 1 equiv each of benzophenone and pyridine to the $W(OR)_4$ center would provide another of the observed products, $W(OR)_4(py)(Ph_2CO)$. The last of the tungsten-containing products, $W(OR)_4(OCPh_2CPh_2O)$, has already been shown to arise from reaction of $W(OR)_4(py)(Ph_2CO)$ with benzophenone.

The formation of small amounts of tetraphenylethylene is easily explained by a competitive slow reaction between the intermediate alkylidene and another 1 equiv of benzophenone to produce the olefin as happens for other ketones.

The source of tetraphenylethane is more difficult to identify. We know that most, if not all, of the hydrogen atoms come from the alkoxide ligands and are abstracted indiscriminately. We also know that it does not come from hydrogenation of tetraphenylethylene. However, we cannot tell if the hydrogen atom transfer occurs before or after C–C bond formation or what the intermediate leading to C–C bond formation is. Given the nonspecific H atom abstraction and lack of reactivity with the solvent, the intermediacy of radicals that are both formed and react in close proximity to the metal centers seems likely.

In this and the previous paper we have reported two disparate sets of reactions of ketones with $W_2(OR)_6(py)_2$ complexes that for all their seeming dissimilarity proceed via a common intermediate. In attempting to explain these results, it is important to recall that 9-fluorenone behaved like acetone and other dialkyl ketones rather than like its electronic twin, benzophenone. Furthermore, benzophenone and the other diaryl ketones examined reacted more slowly with $W_2(OR)_6(py)_2$ complexes than did acetone; this is exactly the opposite of what one would expect if electron transfer and formation of ketyl radicals were responsible for the way benzophenone reacts. The reduction potential of acetone is 1.0–1.5 V more negative than that of benzophenone or 9-fluorenone.[12]

We believe the difference in reactivity is best explained by steric factors. Apparently, benzophenone is small enough to be able to react with $W_2(OR)_6(py)_2$ complexes to form a μ-alkylidene as other ketones do. However, once the μ-alkylidene is formed, the phenyl rings are large enough that rotations about C(alkylidene)–C(phenyl) bonds cause interactions with alkoxide ligands and exert steric pressure sufficient to cause the dimer to split. Other diaryl ketones would be similar; even dibenzosubarone with its CH_2CH_2 bridge between the phenyl rings would allow considerable motion. Thus, the important difference between benzophenone and 9-fluorenone is that in the latter the phenyl rings are constrained to a single plane and in the μ-alkylidene formed from it lie rigidly perpendicular to the W–W bond axis and well away from any other ligands.

Concluding Remarks

The initial reaction between ketones and $W_2(OR)_6$ compounds is, providing steric factors are favorable, a reductive cleavage of the ketonic C–O double bond to give a ditungsten oxo μ-alkylidene species. This is formally a four-electron reduction of the ketone, and the ditungsten center is oxidized to $W_2{}^{10+}$. This is in keeping with the activation of alkynes, nitriles, and other π-unsaturated systems upon complexation to $(W{\equiv}W)^{6+}$ centers supported by alkoxide ligands.[13] The subsequent reactivity of the $W_2{}^{10+}$–μ-alkylidene complex is apparently very sensitive to the nature of the μ-alkylidene ligand. The formation of the $W(OR)_4(py)(\eta^2\text{-}OCPh_2)$ and $W(OR)_4(OCPh_2CPh_2O)$ complexes reported here can be understood in terms of an asymmetric cleavage of the $W_2{}^{10+}$ center to give "$W(OR)_4$" and "$W(CPh_2)(O)(OR)_2$". This seems to occur in preference to C–C bond formation and olefin elimination only for diaryl ketones and not 9-fluorenone. It seems likely that steric factors are responsible for this subtile divergence in reactivity, given that bulky dialkyl ketones such as $(t\text{-Bu})_2C{=}O$ and $(t\text{-Bu})(Me)C{=}O$ do not react with $W_2(OR)_6$ compounds—presumably because initial coordination is not possible. Similarly, $W_2(O\text{-}t\text{-Bu})_6$ fails to react with either acetone or benzophenone. Finally, it is worth noting that a similar asymmetric cleavage was previously proposed to account for the product distributions in the reactions between $Mo_2(OR)_6$ compounds and dioxygen. The latter is another example of a four-electron oxidation of the $(M{\equiv}M)^{6+}$ center, which when given sufficient O_2 yields only Mo^{6+}-containing products, namely $MoO(OR)_4$ and $Mo(O)_2(OR)_2$.[14]

Experimental Section

General reaction procedures, instrumentation, and preparations of $W_2(OR)_6(py)_2$ and $W_2(OR)_6$ compounds have been described

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elsewhere.[15] The deuterated compound $W_2(O\text{-}c\text{-}C_6D_{11})_6$ was prepared with use of HO-c-C_6D_{11} (98+% D) from Aldrich. The alcohol HO-c-α-DC_6H_{10} was made from the reaction between cyclohexanone and $LiAlD_4$.

Preparation of $W(O\text{-}i\text{-}Pr)_4(OCPh_2CPh_2O)$. A hexane (5 mL) solution of $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ (0.38 g, 0.43 mmol) and $(C_6H_5)_2CO$ (0.157 g, 0.86 mmol) was stirred at ca. 25 °C for 24 h to give a dark red solution with a tan precipitate. The precipitate was collected by filtration and dried in vacuo to provide 140 mg (21% yield) of analytically pure $W(O\text{-}i\text{-}Pr)_4(OCPh_2CPh_2O)$. ^1H NMR (C_6D_6, 22 °C, δ): C_6H_5 7.57 (m, 8 H), 6.98 (m, 12 H); $OCH(CH_3)_2$ 5.39 (sept, 4 H); $OCH(CH_3)_2$ 1.31 (d, 24 H). ^1H NMR (toluene-d_8, −20 °C, δ): C_6H_5 7.51 (m, 8 H), 6.96 (m, 12 H); $OCH(CH_3)_2$ 5.41 (sept, 2 H), 5.40 (sept, 2 H); $OCH(CH_3)_2$ 1.41 (d, J_{HH} = 6.3 Hz, 12 H), 1.28 (d, J_{HH} = 6.3 Hz, 12 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, δ): C_6H_5 146.1 (s), 129.8 (s), 126.6 (s), 126.3 (s); Ph_2CO 109.2 (s); $OCH(CH_3)_2$ 78.5 (br s), 77.4 (br s); $OCH(CH_3)_2$ 25.2 (br s), 24.7 (br s). $^{13}C\{^1H\}$ NMR (toluene-d_8, −20 °C, δ): C_6H_5 145.8 (s), 129.6 (s), 126.5 (s), 126.2 (s); Ph_2CO 109.2 (s); $OCH(CH_3)_2$ 78.6 (s), 77.4 (s); $OCH(CH_3)_2$ 20.4 (s), 20.1 (s). IR (KBr, cm^{-1}): 3040 (m); 2960 (s); 2910 (m); 2835 (m); 1495 (m); 1460 (m); 1445 (m); 1370 (s); 1360 (s); 1315 (s); 1165 (s); 1110 (s); 1055 (s); 1005 (s); 995 (s); 970 (s); 960 (s); 910 (m); 860 (m); 845 (m); 785 (m); 765 (s); 745 (s); 720 (m); 710 (s); 700 (s); 645 (m); 610 (s); 590 (s); 475 (m); 300 (m). Anal. Calcd for $WC_{38}H_{48}O_6$: C, 58.16; H, 6.18. Found: C, 58.07; H, 6.14.

Preparation of $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}Ph_2CO)$. A hexane (10 mL) solution of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ (1.06 g, 1.02 mmol) and $(C_6H_5)_2CO$ (0.37 g, 2.04 mmol) was stirred at ca. 25 °C for 24 h to give a dark red solution containing a microcrystalline orange solid. The volume was reduced to about 5 mL and the mixture cooled to −20 °C for ca. 20 h. The solid was collected by filtration and dried in vacuo to give 384 mg (24% yield) of reasonably pure $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}Ph_2CO)$. Analytically pure material, and crystals suitable for X-ray analysis, were obtained by recrystallization from toluene. ^1H NMR (toluene-d_8, −20 °C, δ): C_6H_5 and py 8.58 (m), 7.14 (s), 6.97 (m), 6.82 (m), 6.70 (m); OCH_2 5.68 (s, 2 H), 4.83 (s, 2 H), 3.70 (d, J_{HH} = 10.9 Hz, 2 H), 3.48 (d, J_{HH} = 10.9 Hz, 2 H); $OCH_2C(CH_3)_3$ 1.36 (s, 9 H), 1.03 (s, 9 H), 0.68 (s, 18 H). $^{13}C\{^1H\}$ NMR (toluene-d_8, −20 °C, δ): C_6H_5 and py 149.9 (s), 146.7 (s), 138.5 (s), 128.8 (s), 126.7 (s), 123.8 (s); $OCPh_2$ 117.7 (s), OCH_2 84.5 (s), 80.5 (s), 79.8 (s); $OCH_2C(CH_3)_3$ 34.4 (s), 34.3 (s), 33.9 (s); $OCH_2C(CH_3)_3$ 27.7 (s), 27.6 (s), 26.8 (s). IR (KBr, cm^{-1}): 2945 (s); 2895 (s); 2880 (s); 1590 (m); 1475 (m); 1460 (m); 1445 (m); 1390 (m); 1360 (m); 1215 (m); 1090 (s); 1070 (s); 1050 (s); 1045 (s); 1015 (s); 950 (m); 935 (m); 695 (s); 650 (s); 640 (s); 450 (m). Anal. Calcd for $WC_{38}H_{59}NO_5$: C, 57.49; H, 7.51; N, 1.76. Found: C, 57.44; H, 7.39; N, 1.74.

Preparation of $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$. From $W_2(OCH_2\text{-}t\text{-}Bu)_6$. A hexane (9 mL) solution of $W_2(OCH_2\text{-}t\text{-}Bu)_6$ (0.80 g, 0.90 mmol) and $(C_6H_5)_2CO$ (0.326 g, 1.79 mmol) was stirred at ca. 25 °C for 22 h. A small amount of red solid that had formed was filtered off and discarded. The volume of the filtrate was reduced to ca. 4 mL, and the solution was cooled to −20 °C for 6 days to form tan microcrystalline $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$ (0.315 g, 19.6% yield).

From $W(OCH_2\text{-}t\text{-}Bu)_4(py)((C_6H_5)_2CO)$. A hexane (5 mL) solution of $W(OCH_2\text{-}t\text{-}Bu)_4(py)((C_6H_5)_2CO)$ (0.299 g, 0.377 mmol) and $(C_6H_5)_2CO$ (0.068 g, 0.377 mmol) was stirred at ca. 25 °C for 2 days to give a clear, nearly colorless solution. The volume was reduced by ca. half and the solution cooled to −20 °C for 1 week to form off-white platelike crystals of $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$ (115 mg, 35% yield).

$W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CPh_2O)$. ^1H NMR (C_6D_6, 22 °C, δ): C_6H_5 7.55 (m, 8 H), 6.99 (m, 12 H); OCH_2 4.77 (s, 8 H); $OCH_2C(CH_3)_3$ 1.06 (s, 36 H). ^1H NMR (toluene-d_8, −40 °C, δ): C_6H_5 7.37 (m, 8 H), 6.82 (m, 12 H); OCH_2 4.64 (s, 4 H), 4.54 (s, 4 H); $OCH_2C(CH_3)_3$ 1.01 (s, 18 H), 0.79 (s, 18 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, δ): C_6H_5 145.4 (s), 129.7 (s), 126.8 (s), 126.6 (s); $OCPh_2$ 111.4 (s), OCH_2 84.5 (br s); $OCH_2C(CH_3)_3$ 34.0 (s); $OCH_2C(CH_3)_3$ 26.5 (s). IR (KBr, cm^{-1}): 2960 (s); 2900 (m); 2890 (m); 1480 (m); 1470 (m); 1450 (m); 1395 (m); 1365 (m); 1050 (s); 1025 (s); 965 (m); 780 (m); 755 (m); 710 (s); 665 (s). A satisfactory analysis was not obtained.

Preparation of $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2{}^{13}CMe_2O)$. To a C_6D_6 (0.40 mL) solution of $W(OCH_2\text{-}t\text{-}Bu)_4(py)(Ph_2CO)$ (0.03 g, 0.038 mmol) in a 5-mm NMR tube was added $(CH_3)_2{}^{13}CO$ (5.6 mg, 0.094 mmol) via syringe. The NMR tube was then frozen in liquid N_2, evacuated, and sealed. The mixture was warmed to ambient temperature and monitored by ^1H and ^{13}C NMR spectroscopies. After 12 h the starting material had been consumed, so the solution was transferred to a Schlenk flask and the volatiles removed in vacuo to leave an off-white solid, which was shown to be essentially pure $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2{}^{13}CMe_2O)$ by ^1H and ^{13}C NMR spectroscopies.

$W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2CMe_2O)$. ^1H NMR (toluene-d_8, −40 °C, δ): C_6H_5 7.72 (m, 4 H), 7.17 (m, 4 H), 7.07 (m, 2 H); OCH_2 4.90 (s, 2 H); 4.77 (s, 2 H), 4.61 (d, J_{HH} = 11.3 Hz, 2 H), 4.29 (d, J_{HH} = 10.9 Hz, 2 H); CMe_2 1.49 (s, 6 H); $C(CH_3)_3$ 1.15 (s, 9 H), 1.04 (s, 18 H), 1.00 (s, 9 H).

$W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2{}^{13}CMe_2O)$. $^{13}C\{^1H\}$ NMR (toluene-d_8, −60 °C, δ): C_6H_5 143.8 (s), 130.9 (s), 127.3 (s); $C(C_6H_5)_2$ 102.9 (d, J_{CC} = 33.2 Hz); $C(CH_3)_2$ 96.5 (s); OCH_2 84.6 (s), 83.8 (s), 83.7 (s); $C(CH_3)_3$ 34.8 (s), 34.7 (s), 34.5 (s); $^{13}C(CH_3)_2$ 28.7 (d, J_{CC} = 43.7 Hz); $C(CH_3)_3$ 27.1 (s), 26.8 (s).

Reactions of $W_2(OR)_6(py)_2$ (R = $OCH_2\text{-}t\text{-}Bu$, O-*i*-Pr) with $Ph_2{}^{13}CO$. In the glovebox, 50 mg of $W_2(OR)_6(py)_2$ and 2.0 equiv of $Ph_2{}^{13}CO$ were weighed out and dissolved in toluene-d_8 (ca. 0.4 mL) in an extended-length 5-mm NMR tube. After removal from the glovebox the NMR tube was cooled in liquid N_2, evacuated, and sealed with a flame. The mixture was then warmed to and stood at ambient temperature as the reaction went to completion over ca. 2 days. Reactions of $Ph_2{}^{13}CO$ with $W_2(O\text{-}c\text{-}C_6H_{11})_6$ and $W_2(OCH_2\text{-}t\text{-}Bu)_6$ were done similarly.

Reaction of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ with Dibenzosubarone (Dibenzocycloheptadienone). A toluene (3 mL) solution of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ (0.50 g, 0.48 mmol) and dibenzosubarone (0.208 g, 1.0 mmol) was stirred at ambient temperature for 2.5 days to give a homogeneous dark red solution. The volatile components were removed in vacuo; the residue was dissolved in 3 mL of hexane and the solution cooled to −20 °C. After approximately 6 weeks red platelike crystals of $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-dibenzosubarone})$ (95 mg, 12% yield) were isolated by filtration and dried in vacuo. ^1H NMR (C_6D_6, 23 °C, δ): py and C_6H_4 8.37 (m, 2 H), 7.79 (m, 2 H), 7.22 (m, 2 H), 6.97 (m, 2 H), 6.95 (m, 1 H), 6.82 (m, 2 H), 6.61 (m, 2 H); OCH_2 4.39 (br, 8 H); CH_2CH_2 2.92 (m, 2 H), 2.78 (m, 2 H); $C(CH_3)_3$ 0.94 (br s, 36 H). ^1H NMR (toluene-d_8, −44 °C, δ): py and C_6H_4 7.99 (m, 2 H), 7.95 (m, 2 H); 7.29 (m, 2 H), 6.90 (m, 4 H), 6.79 (m, 1 H), 6.48 (m, 2 H); OCH_2 5.54 (s, 2 H), 4.79 (s, 2 H), 3.87 (d, J_{HH} = 10.9 Hz, 2 H), 3.73 (d, J_{HH} = 11.3 Hz, 2 H); CH_2CH_2 2.55 (m, 2 H), 2.35 (m, 2 H); $C(CH_3)_3$ 1.35 (s, 9 H), 1.07 (s, 9 H), 0.74 (s, 18 H).

Reaction of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ with $(p\text{-}C_6H_5\text{-}C_6H_4)_2CO$. A toluene (5 mL) solution of $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$ (0.50 mg, 0.48 mmol) and $(p\text{-}C_6H_5\text{-}C_6H_4)_2CO$ (0.321 g, 0.96 mmol) was stirred at ambient temperature for 6 days to give a red solution containing some white solid. The solid (unreacted ketone) was filtered off and the filtrate reduced to dryness in vacuo. The residue was extracted with 2 × 4 mL of hexane to leave behind orange, insoluble $W(OCH_2\text{-}t\text{-}Bu)_4(py)((p\text{-}C_6H_5\text{-}C_6H_4)_2CO)$ (167 mg, 19% yield). ^1H NMR (toluene-d_8, −30 °C, δ): py and phenyl 8.66 (m, 2 H), 7.73 (m, 2 H), 7.46–7.00 (m's, 17 H), 6.82 (m, 2 H); OCH_2 5.75 (s, 2 H), 4.87 (s, 2 H), 3.78 (d, J_{HH} = 10.8 Hz, 2 H), 3.50 (d, J_{HH} = 10.9 Hz, 2 H), 1.40 (s, 9 H), 1.06 (s, 9 H), 0.68 (s, 18 H).

Crystal and Molecular Structure of $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$. General operating procedures at the Indiana University Molecular Structure Center have been described previously.[16] A summary of crystal data is given in Table IV. A suitable small crystal was selected from the bulk sample and transferred to the goniostat, where it was cooled to −144 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of centered

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[15] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266. Chisholm, M. H.; Hampden-Smith, M. J.; Martin, J. D. *Inorg. Synth.*, in press.

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Table IV. Summary of Crystal Data for $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}OCPh_2)$

empirical formula	$C_{38}H_{58}NO_5W_1$
color of cryst	black
cryst dimens, mm	0.16 × 0.12 × 0.16
space group	$P2_1/c$
cell dimens	
temp, °C	−144
a, Å	15.675 (1)
b, Å	13.736 (1)
c, Å	17.936 (2)
β, deg	92.39 (0)
Z (molecules/cell)	4
V, Å^3	3858.46
calcd density, g/cm^3	1.365
wavelength, Å	0.710 69
mol wt	792.73
linear abs coeff, cm^{-1}	30.942
detector to sample dist, cm	22.5
sample to source dist, cm	23.5
average ω-scan width at half height	0.25
scan speed deg/min	6.0
scan width (+-dispersion), deg	1.8
individual bkgd, s	6
aperture size, mm	3.0 × 4.0
2θ range, deg	6–45
total no. of rflns collected	6084
no. of unique intens	5029
no. with $F > 0.0$	4511
no. with $F > 3.0\sigma(F)$	3927
$R(F)$	0.0452
$R_w(F)$	0.0431
goodness of fit for the last cycle	1.091
max δ/σ for last cycle	0.05

reflections that exhibited monoclinic diffraction symmetry ($2/m$). The systematic extinction of $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$ uniquely identified the space group as $P2_1/c$. Data collection was carried out in the usual manner with use of the parameters given in Table IV. A total of 6084 reflections (including standards and extinctions) were collected. Following the usual data reduction, Lp corrections, and averaging of redundant data, a unique set of 5029 reflections remained. The *R* value for the averaging was 0.034 for 670 redundant data. A total of 3927 reflections were considered observed by the criterion $F > 3.0\sigma(F)$. No correction for absorption was carried out.

The structure was solved by locating the W atom by direct methods (MULTAN); the remaining non-hydrogen atoms were located in a difference Fourier phased by the W atom. Almost all of the hydrogen atoms were located in a difference map following initial refinement of the structure. The hydrogen positions were idealized, and the positions for the missing hydrogen atoms were calculated. The full-matrix least-squares refinement was completed by using anisotropic thermal parameters on the non-hydrogen atoms and leaving the hydrogen atoms fixed, with thermal parameters equal to the equivalent isotropic thermal parameter for the parent atom plus 1 Å^2. The final *R* value was 0.045.

The final difference map was essentially featureless, the largest peak being 1.4 e/Å^3 within 0.1 Å of the W atom.

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Registry No. $W_2(O\text{-}i\text{-}Pr)_6(py)_2$, 70178-75-5; $W(O\text{-}i\text{-}Pr)_4(OCPh_2CPh_2O)$, 125076-33-7; $(C_6H_5)_2CO$, 119-61-9; $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2\text{-}Ph_2CO)$, 125050-54-6; $W(OCH_2\text{-}t\text{-}Bu)_4(COPh_2CPh_2O)$, 125108-02-3; $W(OCH_2\text{-}t\text{-}Bu)_4(OCPh_2{}^{13}CMe_2O)$, 125050-53-5; $W(OCH_2\text{-}t\text{-}Bu)_4(py)(\eta^2$-dibenzosuberone), 125076-34-8; $W(OCH_2\text{-}t\text{-}Bu)_4(py)((p\text{-}C_6H_5\text{-}C_6H_4)_2CO)$, 125050-55-7; $W_2(OCH_2\text{-}t\text{-}Bu)_6(py)_2$, 88608-50-8; $W_2(OCH_2\text{-}t\text{-}Bu)_6$, 110116-70-6; $W_2(O\text{-}c\text{-}C_6H_{11})_6$, 111835-58-6; $(p\text{-}C_6H_5\text{-}C_6H_4)_2CO$, 3478-90-8; $Ph_2CHCHPh_2$, 632-50-8; $Ph_2C{=}CPh_2$, 632-51-9; dibenzosuberone, 1210-35-1.

Supplementary Material Available: A table of anisotropic thermal parameters and complete listings of bond distances and bond angles (4 pages); listings of F_o and F_c values (11 pages). Ordering information is given on any current masthead page.