Table V^a

line	R	A	B	χ^2	σ_A	σ_B	σ
E^b vs. ΔE	0.307287	9×10^{-7}	0.18835	9.38	0.1651	3.2×10^{-2}	0.13504
E vs. $\Delta E_0^{\ddagger}$	0.94727	-2×10^{-2}	0.866336	2.3569	8.2×10^{-2}	1.6×10^{-2}	5×10^{-2}
E vs. E_{p_4}	0.99914	-4×10^{-2}	0.993422	5×10^{-2}	1.2×10^{-2}	2.2×10^{-3}	6×10^{-3}
E vs. E_{Marcus}	0.999096	-4×10^{-2}	0.990536	5×10^{-2}	1.2×10^{-2}	2.3×10^{-3}	7×10^{-3}
X^c vs. X_{p_4}	0.999568	0.2540	0.998808	8.981	0.3809	1.6×10^{-3}	8×10^{-3}
X vs. X_{Miller}	0.987339	0.5574	0.997227	267.2	2.077	9×10^{-3}	4.1×10^{-3}
X vs. $X_{p=2}$	0.999282	0.1646	0.999241	14.94	0.4913	2×10^{-3}	1×10^{-2}
X vs. X_{arccos}	0.999566	9×10^{-2}	0.999552	9.03	0.3821	1.6×10^{-3}	8×10^{-3}
X vs. $X_{p=0.5}$	0.986496	0.238	0.998709	288.13	2.15	9×10^{-3}	4×10^{-2}
X vs. X_{Marcus}	0.998008	-2×10^{-2}	1.00007	41.6	0.819	3.4×10^{-3}	1.7×10^{-2}
theoretically	1.0	0.0	1.0	small	0.0	0.0	0.0

^{a} A statistical fit to the line $y = A + Bx$ has the following associated parameters: A, constant term; B, linear coefficient; σ, standard deviation; σ_A, standard deviation in A; σ_B, standard deviation in B; R, correlation coefficient; and χ^2, chi square. ^{b} $n = 338$ for the E's. ^{c} $n = 338$ for the X's.

of transformations involving Cartesian-based coordinates as well as the relationship between the intrinsic barrier and quantities that form the basis of alternative treatments of chemical reactivity.

Carbon–Carbon Bond Formation in the Reductive Coupling of Ketones by the Doubly Bonded Ditungsten(IV) Alkoxides W₂Cl₄(μ-OR)₂(OR)₂(ROH)₂

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Abstract: Doubly bonded ditungsten(IV) alkoxides of the type W₂Cl₄(μ-OR)₂(OR)₂(ROH)₂ promote the reductive coupling of certain ketones R'R''CO (R' = Me; R'' = Me, Et, or University, to afford ditungsten(V) complexes of the type W₂Cl₄-(μ-OR)₂[R'R''C(O)C(O)R'R'']₂ (where R = Et or *n*-Pr, R' = Me, and R'' = Me or Et) or the complex W₂Cl₄(μ-OEt)₂-(OEt)₂[Me-*n*-PrC(O)C(O)Me-*n*-Pr] depending upon the choice of ketone. These are the first instances where multiply bonded dimetal complexes have been found to reductively couple ketones to form metal alkoxides derived from α-diols. Evidence is presented to support the notion that the role of the dimetal unit is to provide electrons for the reduction of the ketones and to serve as a template for the coupling of the resulting ketyl radicals. In the case of the formation of W₂Cl₄(μ-OR)₂-[R'R''C(O)C(O)R'R'']₂, it is believed that the following stoichiometric equation best explains the reaction course: $2W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2 + 4R'R''CO \rightarrow W_2Cl_4(\mu\text{-}OR)_2[R'R''C(O)C(O)R'R'']_2 + 4OR^- + 4ROH + 2"W^V"$. These complexes, which are derivatives of the singly bonded W_2^{10+} core, have been characterized by using cyclic voltammetry and ¹H NMR spectroscopy and, in the case of W₂Cl₄(μ-OEt)₂[R'R''C(O)C(O)R'R'']₂ (R' = Me; R'' = Me or Et), by X-ray crystallography. For W₂Cl₄(μ-OEt)₂[(CH₃)₂C(O)C(O)(CH₃)₂]₂, crystals belong to the space group $P2_1/n$ with unit cell dimensions $a = 8.681 (2)$ Å, $b = 15.743 (3)$ Å, $c = 9.235 (2)$ Å, $\beta = 90.98 (2)°$, $V = 1261.8 (6)$ Å³, and $Z = 2$. In these centrosymmetric molecules W–W = 2.701 (1) Å, W–OEt = 2.05 [2] Å, W–O_T = 1.82 [1] Å, and W–Cl = 2.364 [7] Å. The conformation of the $\overline{WWOCCO}$ ring is unusual and indicates strain, but nevertheless, it is kinetically inert toward replacement by other RO⁻ groups. W₂Cl₄(μ-OEt)₂[(CH₃)(C₂H₅)C(O)C(O)(CH₃)(C₂H₅)]₂ also forms monoclinic crystals in space group $P2_1/n$ with unit cell dimensions $a = 10.660 (10)$ Å, $b = 12.311 (8)$ Å, $c = 11.268 (9)$ Å, $\beta = 102.23 (2)°$, $V = 1452 (2)$ Å³, and $Z = 2$. The molecular dimensions are very similar to those for the first molecule. The methyl and ethyl groups are disordered in such a way as to indicate that there is little or no stereospecificity in the coupling of the (CH₃)(C₂H₅)CO molecules.

The ditungsten(IV) alkoxides W₂Cl₄(μ-OR)₂(OR)₂(ROH)₂[2,3] constitute the most extensive series of doubly bonded dimetal complexes so far discovered.[4] The most important chemical properties of this class of complexes are (1) the lability of the terminal OR and ROH ligands to exchange by other alcohol ligands,[3] (2) the ready displacement of the ROH ligands by other neutral donors, such as pyridine and other nitrogen donors,[5,6] and (3) their facile oxidation to the singly bonded ditungsten(V) alkoxides W₂Cl₄(μ-OR)₂(OR)₄.[2,3,7] The latter two-electron oxidation proceeds formally with the loss of the two alcohol protons

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and the change in the ground-state electronic configuration from $\sigma^2\pi^2$ to σ^2.

During the course of exploring the reactivity of these complexes toward various classes of nucleophiles, we have discovered a novel reaction with ketones that encompasses the properties 2 and 3 described above. Specifically, we find that the complexes $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$ and $W_2Cl_4(\mu\text{-O-}n\text{-Pr})_2(O\text{-}n\text{-}Pr)_2(n\text{-PrOH})_2$, and by implication other derivatives of the type $W_2Cl_4(\mu\text{-OR})_2(OR)_2(ROH)_2$, bring about the reductive coupling of ketones to form ditungsten(V) alkoxides derived from the α-diol (glycol) ligands. This is the first instance where a multiply bonded dimetal center has served in such a role toward ketones. Full details of this work are described in the present report.[8]

Experimental Section

Materials. All solvents were dried over molecular sieves and purged with nitrogen gas for 30 min prior to use. The starting ditungsten(IV) ethoxide derivative $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$ was prepared from WCl_4 by using a procedure similar to that described by Reagan and Brubaker.[5] The analogous n-propoxide derivative and the mixed ethoxide–isopropoxide of ditungsten(IV), $W_2Cl_4(\mu\text{-OEt})_2(O\text{-}i\text{-Pr})_2(i\text{-PrOH})_2$, were prepared by the previously reported alcohol exchange reactions.[3]

Reaction Procedures. Unless otherwise stated all reactions were carried out under an atmosphere of nitrogen.

$W_2Cl_4(\mu\text{-OEt})_2[Me_2C(O)C(O)Me_2]_2$. A quantity of freshly recrystallized $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$ (0.1 g) was placed in a flask. To this was added 1.0 mL of acetone and 0.02 mL of glacial acetic acid, and the resulting suspension was stirred for 8 h. Within this time the ethoxide complex dissolved and the solution changed from green to red. The resulting red crystals that slowly separated were filtered off in air and vacuum dried; yield 0.015 g (27%).[9] Anal. Calcd for $C_{16}H_{34}Cl_4O_6W_2$: C, 23.08; H, 4.08. Found: C, 22.76; H, 4.04.

The compound can also be prepared in an analogous manner starting with 0.1 g of $W_2Cl_4(\mu\text{-OEt})_2(O\text{-}i\text{-Pr})_2(i\text{-PrOH})_2$. The reaction time is reduced to 3 h due to the increased solubility of the starting alkoxy complex in acetone; yield 16%.[9]

$W_2Cl_4(\mu\text{-O-}n\text{-Pr})_2[Me_2C(O)C(O)Me_2]_2$. This complex was prepared from $W_2Cl_4(\mu\text{-O-}n\text{-Pr})_2(O\text{-}n\text{-}Pr)_2(n\text{-PrOH})_2$ by a procedure analogous to that described for its ethoxide analogue (vide supra); yield 24%. Anal. Calcd for $C_{18}H_{38}Cl_4O_6W_2$: C, 25.13; H, 4.42. Found: C, 25.67; H, 4.22.

$W_2Cl_4(\mu\text{-OEt})_2[MeEtC(O)C(O)MeEt]_2$. Freshly recrystallized $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$ (0.1 g) was placed in a flask and was admixed with 1.0 mL of methyl ethyl ketone and 0.02 mL of glacial acetic acid. The resulting suspension was stirred for 14 h after which time the red product had separated from the solution. The dark red crystals were filtered off and vacuum dried; yield 0.010 g (18%).[9] Anal. Calcd for $C_{20}H_{42}Cl_4O_6W_2$: C, 27.04; H, 4.73. Found: C, 27.23; H, 4.83.

$W_2Cl_4(\mu\text{-OEt})_2[Me\text{-}n\text{-PrC}(O)C(O)Me\text{-}n\text{-Pr}]$. Freshly recrystallized $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$ (0.1 g) was treated with 1.5 mL of 2-pentanone and 0.02 mL of glacial acetic acid. The mixture was stirred for 6 h, the resulting solution evaporated to dryness, and the residue extracted with CH_2Cl_2. The extract was filtered to remove any blue insoluble materials, and the CH_2Cl_2 was evaporated. A very small volume of EtOH ($\sim$1 mL) was added to dissolve the resulting solid, and the extract was filtered in air. The desired compound was isolated by allowing the ethanol filtrate to evaporate slowly in the air. The product was recrystallized by dissolving it in a minimum volume of acetone, adding an equal volume of EtOH, and evaporating the acetone while the flask was chilled in an ice bath. The red solid was filtered off and vacuum dried; yield 0.025 g (41%). Anal. Calcd for $C_{18}H_{40}Cl_4O_6W_2$: C, 25.06; H, 4.69. Found: C, 24.80; H, 4.87.

Preparation of Single Crystals for Structure Determinations. Crystals of $W_2Cl_4(\mu\text{-OEt})_2[Me_2C(O)C(O)Me_2]_2$ and $W_2Cl_4(\mu\text{-OEt})_2[MeEtC(O)C(O)MeEt]_2$ were grown directly from the reaction mixtures by letting them stand undisturbed following the dissolution of the $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$ starting complex.

X-ray Crystallography. Crystals of $W_2Cl_4(\mu\text{-OEt})_2(C_6H_{12}O_2)_2$, A, and $W_2Cl_4(\mu\text{-OEt})_2(C_8H_{16}O_2)_2$, B, both red with truncated square-bipyramidal habits, were mounted on thin glass fibers for the x-ray diffraction measurements. The same equipment and routine procedures were used for both A and B and are summarized in Table I, along with relevant crystal parameters.

(8) Preliminary details were reported previously; see: Cotton, F. A.; De-Marco, D.; Falvello, L. R.; Walton, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 7375.

(9) Yields are based on the following stoichiometric equation $2W_2Cl_4(\mu\text{-OR})_2(OR)_2(ROH)_2 + 4R'R''CO \rightarrow W_2Cl_4(\mu\text{-OR})_2[R'R''C(O)C(O)R'R'']_2 + 4RO^- + 4ROH + 2$"$W^V$" (see the Results and Discussion).

Table I. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for $W_2Cl_4(\mu\text{-OEt})_2(C_6H_{12}O_2)_2$ and $W_2Cl_4(\mu\text{-OEt})_2(C_8H_{16}O_2)_2$

	$W_2Cl_4C_{16}O_6H_{34}$	$W_2Cl_4C_{20}H_{42}O_6$
formula		
fw	831.95	881.1
space group	$P2_1/n$	$P2_1/n$
systematic absences	$(0k0)$, $k = 2n + 1$; $(h0l)$, $h + l = 2n + 1$	$(0k0)$, $k = 2n + 1$, $(h0l)$, $h + l = 2n + 1$
a, Å	8.681 (2)	10.660 (10)
b, Å	15.743 (3)	12.311 (8)
c, Å	9.235 (2)	11.268 (9)
β, deg	90.98 (2)	102.23 (2)
V, Å^3	1261.8 (6)	1452 (2)
Z	2	2
d_{calcd}, g/cm^3	2.189	2.031
cryst size, mm	0.25 × 0.25 × 0.25	0.23 × 0.20 × 0.15
μ(Mo Kα), cm^{-1}	100.8	87.7
data collectn instrument	Enraf-Nonius CAD-4F	Enraf-Nonius CAD-4F
radiatn (monochromated in incident beam)	Mo Kα (λ_α = 0.710 73 Å)	Mo Kα (λ_α = 0.710 73 Å)
orientatn reflctns, number, range (2θ)	25, 16 < 2θ < 35°	25, 20 < 2θ < 32°
temp, °C	22 ± 2	22 ± 2
scan method	ω scans	ω scans
data col range, 2θ, deg	4 ≤ 2θ ≤ 50	3 ≤ 2θ ≤ 50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1997, 1753	2077, 1603
no. of parameters refined	127	144
trans factors, max, min	0.08, 0.03	0.27, 0.07
R^a	0.0375	0.0364
R_w^b	0.0496	0.0441
quality-of-fit indicator^c	1.416	1.139
largest shift/esd, final cycle	0.02	0.07
largest peak, e/Å^3	2.36	0.60

$^a R = \sum\|F_o\| - |F_c\|/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

Axial photography was used to verify the Laue class ($2/m$) and lattice dimensions for each crystal, prior to collection of intensity data. The crystal of A remained stable through the 34.5 h of X-ray beam time. For B, three intensity-check reflections lost an average of 8.7% of their original intensities during the 52 h of X-ray exposure; so an interpolative decay correction was applied during data reduction.[10] An empirical absorption correction[11] was applied to each data set and was based on azimuthal scans of 7 (compound A) or 8 (compound B) reflections with angle χ (Eulerian) near 90°.

Both structures were solved by Patterson methods and were developed and refined by application of difference Fourier maps and full-matrix least-squares refinement. Refinement converged in final cycles involving data: parameter ratios of 13.8 for A and 11.1 for B. The least-squares residuals are given in Table I.

During the development of the structure of B, we observed a disorder of one of the terminal carbon atoms, C(10), of the bridging diol dianion. This disorder is not imposed by the center of symmetry on which the compound resides. In the final refinement, the two congeneric (but crystallographically independent) carbon atoms C(10) and C(10A) were assigned site occupancies of 0.5 each. The final isotropic thermal parameters are 8.3 (9) for C(10) and 7.1 (7) for C(10A); this indicates that the assignment of site occupancies is accurate. (There was no significant correlation in the refinement.) We can conclude that ligands with the terminal carbon at the position of C(10) are present in the lattice in about the same proportion as those with the terminal carbon atom at the position of C(10A).

Physical Measurements. The ^{1}H NMR spectra of $CDCl_3$ solutions were recorded on a Varian XL-200 spectrometer or a Nicolet NT-470 spectrometer using $CHCl_3$ as the internal reference. Two-dimensional

(10) Data manipulations and crystallographic calculations were done by a PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, Tx, with software from the Enraf-Nonius SDP-PLUS package.

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Reductive Coupling of Ketones by Ditungsten Alkoxides

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J spectroscopy[12] was performed with δ along f_2 and J_{H-H} along f_1. Infrared spectra were recorded on a Beckman Acculab 6 spectrophotometer as Nujol mulls. Electrochemical measurements were made on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. $E_{1/2}$ values were referenced to the saturated potassium chloride calomel electrode (SCE) at room temperature and are uncorrected for junction potentials. All voltammetric measurements were made at a platinum bead electrode in solutions deaerated with a stream of dry nitrogen gas. These cyclic voltammetry experiments were performed by using a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7015B x-y recorder.

Results and Discussion

(a) Synthesis and Preliminary Observations. The reactions of $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2$ and other complexes of this type with ketones originally grew out of studies we had been conducting into the substitutional lability of the ROH ligands. During our attempts to ascertain whether $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2$ could be converted to the carboxylate-bridged ditungsten(IV) complexes $W_2Cl_4(\mu\text{-}OEt)_2(\mu\text{-}O_2CR)_2$, through its reaction in acetone with acetic acid etc., we isolated dark red crystals of an air-stable complex that clearly did not contain acetate, based at least upon its spectroscopic properties. The measurement of the cyclic voltammogram (CV) of a 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane solution of this complex showed that it possessed two accessible one-electron reductions, one of which approached reversibility ($E_{1/2} = -0.75$ V vs. SCE) while the other was clearly electrochemically irreversible ($E_{p,c} = -1.30$ V and $E_{p,a} = -1.10$ V with $i_{p,c} \gg i_{p,a}$). These electrochemical properties are characteristic of alkoxide complexes of ditungsten(V) of the type $W_2Cl_4(\mu\text{-}OR)_2(OR)_4$.[2,3] That we had isolated such a species was confirmed by its electronic absorption spectral properties (λ_{max} at 503 (sh) and 446 nm for a CH_2Cl_2 solution) in accord with corresponding spectral results for $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_4$[7] and other closely allied derivatives.[13] However, the exact identity of this complex still eluded us, although its 90-MHz ^{1}H NMR spectrum (in $CDCl_3$) revealed that while the bridging ethoxide ligands remained, the original terminal ethoxide–ethanol ligands had been displaced. The ^{1}H NMR spectral properties of this complex and others of this type will be discussed in more detail in section d. These preliminary characterizations were followed by the solution of the X-ray crystal structure of this complex which demonstrated that it was the novel pinacol-bridged ditungsten(V) complex $W_2Cl_4(\mu\text{-}OEt)_2[Me_2C\text{-}(O)C(O)Me_2]_2$ (vide infra).

In exploring the scope of this chemistry, we have been able to show that this exact same α-diol product is formed from the reaction of acetone with the mixed alkoxide $W_2Cl_4(\mu\text{-}OEt)_2(O\text{-}i\text{-}Pr)_2(i\text{-}PrOH)_2$. Further examples of the reductive coupling of ketones have been encountered in the formation of $W_2Cl_4(\mu\text{-}OEt)_2[MeEtC(O)C(O)MeEt]_2$ and $W_2Cl_4(\mu\text{-}O\text{-}n\text{-}Pr)_2[Me_2C\text{-}(O)C(O)Me_2]_2$ from the reactions of the appropriate ketones with $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2$ and $W_2Cl_4(\mu\text{-}O\text{-}n\text{-}Pr)_2(O\text{-}n\text{-}Pr)_2(n\text{-}PrOH)_2$, respectively, in the presence of a small amount of acetic acid. These complexes have, as expected, strikingly similar electrochemical and spectroscopic properties to those possessed by $W_2Cl_4(\mu\text{-}OEt)_2[Me_2C(O)C(O)Me_2]_2$,[14] the clear implication being that all three complexes possess closely related structures. As will be discussed later, this conclusion is confirmed by the crystal structure determination of the methyl ethyl ketone product $W_2Cl_4(\mu\text{-}OEt)_2[MeEtC(O)C(O)MeEt]_2$.

One reaction that did not conform to those described above was that between the ditungsten(IV) ethoxide complex and 2-pentanone (Me-*n*-PrCO), in which the major product appeared to be $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2[Me\text{-}n\text{-}PrC(O)C(O)Me\text{-}n\text{-}Pr]$. Although less completely characterized than the other ditungsten(V) complexes, this compound is clearly a derivative of the W_2^{10+} core based upon its CV ($E_{1/2} = -0.71$ V (red.) and $E_{p,c} \simeq -1.42$ V

Table II. Positional Parameters and Isotropic Equivalent Temperature Factors for $W_2Cl_4(\mu\text{-}OEt)_2(C_6H_{12}O_2)_2$[a]

atom	x	y	z	B, Å^2
W(1)	0.09558 (4)	0.04668 (2)	0.41759 (4)	2.363 (7)
Cl(1)	0.0816 (3)	0.1018 (2)	0.1788 (3)	4.10 (6)
Cl(2)	0.3441 (3)	0.1058 (2)	0.4469 (3)	4.09 (6)
O(1)	−0.1217 (7)	−0.0017 (4)	0.3765 (6)	2.6 (1)
O(2)	0.0058 (7)	0.1417 (4)	0.4929 (7)	2.9 (1)
O(3)	−0.1733 (8)	0.0531 (4)	0.6481 (8)	3.1 (1)
C(1)	−0.256 (2)	0.0321 (9)	0.293 (2)	6.0 (4)
C(2)	−0.307 (2)	−0.024 (1)	0.178 (2)	8.8 (5)
C(3)	−0.103 (1)	0.1948 (7)	0.561 (1)	3.9 (2)
C(4)	−0.168 (1)	0.1407 (7)	0.691 (1)	3.6 (2)
C(5)	−0.226 (2)	0.221 (1)	0.449 (2)	6.7 (4)
C(6)	−0.018 (2)	0.2758 (8)	0.610 (1)	5.6 (3)
C(7)	−0.060 (2)	0.1451 (9)	0.830 (1)	7.0 (4)
C(8)	−0.334 (1)	0.1653 (9)	0.734 (2)	6.3 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table III. Positional Parameters and Isotropic Equivalent Temperature Factors for $W_2Cl_4(\mu\text{-}OEt)_2(C_8H_{16}O_2)_2$[a]

atom	x	y	z	B, Å^2
W(1)	0.02905 (4)	0.05923 (4)	0.10250 (4)	3.628 (8)
Cl(1)	−0.0794 (3)	0.1920 (3)	0.1945 (3)	6.48 (8)
Cl(2)	0.2051 (3)	0.0756 (3)	0.2677 (3)	6.09 (8)
O(1)	−0.1330 (6)	0.0539 (6)	−0.0326 (6)	3.9 (2)
O(2)	−0.0424 (7)	−0.0497 (6)	0.1755 (6)	4.5 (2)
O(3)	−0.0934 (6)	−0.1611 (6)	−0.0158 (6)	4.2 (2)
C(1)	−0.221 (1)	0.138 (1)	−0.090 (1)	5.5 (3)
C(2)	−0.358 (1)	0.112 (1)	−0.088 (2)	7.5 (4)
C(3)	−0.137 (1)	−0.132 (1)	0.181 (1)	5.3 (3)
C(4)	−0.128 (1)	−0.218 (1)	0.083 (1)	5.3 (3)
C(5)	−0.270 (1)	−0.071 (1)	0.156 (1)	6.1 (3)
C(6)	−0.104 (1)	−0.179 (1)	0.312 (1)	7.1 (4)
C(7)	−0.120 (2)	−0.099 (2)	0.410 (1)	9.9 (5)
C(8)	−0.023 (1)	−0.305 (1)	0.127 (1)	7.7 (4)
C(9)	−0.260 (1)	−0.272 (1)	0.032 (1)	6.5 (3)
C(10)	−0.235 (3)	−0.358 (3)	−0.047 (3)	8.3 (9)*
C(10A)	−0.024 (3)	−0.384 (2)	0.016 (3)	7.1 (7)*

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

vs. SCE at $\nu = 200$ mV/s for 0.2 M TBAH–CH_2Cl_2 solutions using a Pt bead electrode). Whereas the complexes that contain two α-diol ligands (i.e., those of the type $W_2Cl_4(\mu\text{-}OR)_2\text{-}[R'R''C(O)C(O)R'R'']_2$) have poor solubility in organic solvents (although they do display limited solubility in $CHCl_3$ and CH_2Cl_2), the complex $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2[Me\text{-}n\text{-}PrC(O)C(O)Me\text{-}n\text{-}Pr]$ is soluble in acetone, $CHCl_3$, and CH_2Cl_2. The ^{1}H NMR spectrum of this complex in $CDCl_3$ displays quartets at δ +5.89 and +4.50 (intensity 1:1) that can be confidently assigned to the bridging and terminal ethoxide ligands, respectively.[2,3] The corresponding methyl resonances occur in the region between δ +1.55 and +0.85 where they are overlapped by a complex pattern arising from the CH_3 and *n*-C_3H_7 groups of the 4,5-dimethyl-4,5-octanediol dianionic ligand.[15]

Our attempts to prepare ditungsten(V) complexes through the reductive coupling of ketones R_2CO in cases where $R \neq Me$ (e.g., $R = Et$) were unsuccessful. Likewise, we have not yet been able to prepare such derivatives starting from MePhCO or Ph_2CO, the latter (solid) ketone being reacted with $W_2Cl_4(\mu\text{-}OEt)_2\text{-}(OEt)_2(EtOH)_2$ using dichloromethane as solvent.

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(14) A comparison of the electrochemical properties of these three complexes is given in ref 13.
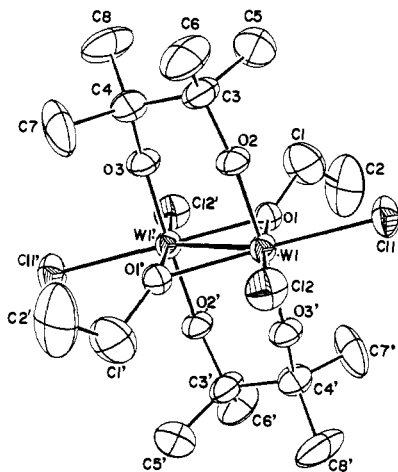
(15) The ^{1}H NMR spectrum of $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2[Me\text{-}n\text{-}PrC(O)C\text{-}(O)Me\text{-}n\text{-}Pr]$ in the region between δ +1.55 and +0.85 resembled quite closely that of the mixed alkoxide complex of stoichiometry $W_2Cl_4(\mu\text{-}OEt)_2\text{-}(OCHMe\text{-}n\text{-}Pr)_4$, i.e., containing the 2-pentoxide ligand. The latter complex was prepared from $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2$ by first generating the ditungsten(IV) complex of $W_2Cl_4(\mu\text{-}OEt)_2(OCHMe\text{-}n\text{-}Pr)_2(Me\text{-}n\text{-}PrCHOH)_2$ by the typical alcohol exchange reaction[3] and subsequently oxidizing the latter species using $AgNO_3$ as the oxidant.[3]

Figure 1. A view of the $W_2Cl_4(\mu\text{-OEt})_2[(CH_3)_2C(O)C(O)(CH_3)_2]_2$ molecule showing the atom labeling. Each atom is represented by its ellipsoid of thermal vibration at the 50% probability level.
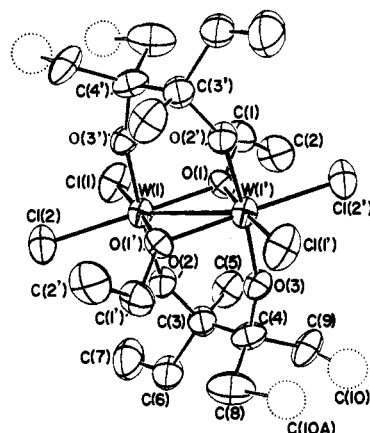

Figure 2. A view of the $W_2Cl_4(\mu\text{-OEt})_2[(CH_3)(C_2H_5)C(O)C(O)\text{-}(CH_3)(C_2H_5)]_2$ molecule showing the atom labeling. All atoms except C(10) and C(10A), the disordered β-carbon atoms, are represented by their thermal vibration ellipsoids at the 40% probability level. C(10) and C(10A) were refined isotropically at 0.5 occupancy.

(b) Crystal Structures of $W_2Cl_4(\mu\text{-OEt})_2[Me_2C(O)C(O)Me_2]_2$ (A) and $W_2Cl_4(\mu\text{-OEt})_2[MeEtC(O)C(O)MeEt]_2$ (B). The atomic positional parameters are listed for A and B in Tables II and III, respectively. The molecules and their atom labeling schemes are shown in Figure 1 and 2. Tables IV and V list the bond lengths and angles, respectively, for the two molecules. It can be seen that corresponding pairs of distances and angles are virtually identical, within the esd's in the two cases. In each case the dinuclear molecule resides on a crystallographic inversion center. For compound A this is consistent with the composition of the molecule and all atoms were refined anisotropically without difficulty. With compound B, however, one $(CH_3)(C_2H_5)C$ moiety (and, of course, the one related to it by inversion) showed a disorder such that, in effect, the β-carbon atom of the ethyl group appears at reduced occupancy at two sites. A satisfactory refinement was achieved (vide supra) by assigning an occupancy factor of 0.5 to each site. It must be recognized, however, that this 1:1 ratio is subject to some uncertainty and might deviate by as much as 10%, i.e., to occupation factors of 0.45 and 0.55. As will be discussed in detail later, we attribute this crystallographic observation to the presence of two or more diastereoisomers in the crystal, randomly disordered.

The mean W–W distance in the two molecules, 2.696 [3] Å, is fully consistent with the existence of a single bond between two W^V atoms as in the previously characterized[7] $W_2Cl_4(\mu\text{-OEt})_2$-(OEt)$_4$ molecule. The WWOCCO rings, however, have unusual conformations that are indicative of steric strain. Thus, the W–O–C angles are large, 155–160°, and the torsional angles about

Table IV. Table of Bond Distances (Å) for $W_2Cl_4(\mu\text{-OEt})_2(C_6H_{12}O_2)_2$ (A) and $W_2Cl_4(\mu\text{-OEt})_2(C_8H_{16}O_2)_2$ (B)[a]

		A	B
W(1)	W(1')	2.701 (1)	2.691 (1)
W(1)	Cl(1)	2.359 (2)	2.365 (3)
W(1)	Cl(2)	2.368 (2)	2.355 (3)
W(1)	O(1)	2.062 (5)	2.048 (6)
W(1)	O(1)'	2.036 (5)	2.039 (7)
W(1)	O(2)	1.827 (5)	1.822 (7)
W(1)	O(3)'	1.815 (5)	1.812 (7)
O(1)	C(1)	1.485 (12)	1.450 (13)
O(2)	C(3)	1.416 (10)	1.437 (13)
O(3)	C(4)	1.432 (10)	1.423 (13)
C(1)	C(2)	1.45 (2)	1.51 (2)
C(3)	C(4)	1.582 (13)	1.56 (2)
C(3)	C(5)	1.523 (15)	1.57 (2)
C(3)	C(6)	1.539 (14)	1.55 (2)
C(4)	C(7)	1.580 (13)	
C(4)	C(8)	1.549 (13)	1.55 (2)
C(4)	C(9)		1.55 (2)
C(6)	C(7)		1.51 (2)
C(8)	C(10A)		1.58 (3)
C(9)	C(10)		1.45 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Table of Bond Angles (deg) and Their Estimated Standard Deviations for $W_2Cl_4(\mu\text{-OEt})_2(C_6H_{12}O_2)_2$, A, and $W_2Cl_4(\mu\text{-OEt})_2(C_8H_{16}O_2)_2$, B
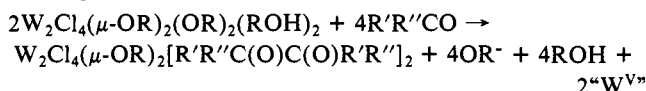
	A	B
W(1')-W(1)-Cl(1)	134.40 (6)	134.92 (9)
-Cl(2)	135.87 (6)	136.46 (9)
-O(1)	48.4 (2)	48.7 (2)
-O(1')	49.2 (2)	49.0 (2)
-O(2)	87.8 (2)	86.9 (2)
-O(3')	87.3 (2)	87.5 (2)
Cl(1)-W(1)-Cl(2)	89.72 (8)	88.6 (1)
-O(1)	86.1 (2)	86.2 (2)
-O(1')	176.4 (2)	176.1 (2)
-O(2)	92.2 (2)	91.2 (3)
-O(3')	91.1 (2)	92.0 (3)
Cl(2)-W(1)-O(1)	175.8 (2)	174.8 (2)
-O(1')	86.7 (2)	87.5 (2)
-O(2)	91.6 (2)	92.6 (2)
-O(3')	92.0 (2)	92.1 (2)
O(1)-W(1)-O(1')	97.5 (2)	97.6 (2)
-O(2)	88.7 (2)	86.8 (3)
-O(3')	87.9 (2)	88.7 (3)
O(1')-W(1)-O(2)	88.4 (2)	89.2 (3)
-O(3')	88.5 (2)	88.0 (3)
O(2)-W(1)-O(3')	175.1 (3)	174.3 (3)
W(1)-O(1)-W(1')	82.5 (2)	82.4 (2)
-C(1)	132.1 (6)	132.2 (7)
W(1')-O(1)-C(1)	133.1 (6)	131.6 (7)
W(1)-O(2)-C(3)	160.4 (6)	154.4 (7)
W(1')-O(3)-C(4)	155.9 (6)	161.7 (7)
O(1)-C(1)-C(2)	113 (1)	112 (1)
O(2)-C(3)-C(4)	105.5 (7)	107.2 (9)
-C(5)	108.9 (8)	106 (1)
-C(6)	107.2 (8)	107 (1)
C(4)-C(3)-C(5)	113.9 (9)	113 (1)
-C(6)	113.3 (8)	113 (1)
C(5)-C(3)-C(6)	108 (1)	111 (1)
O(3)-C(4)-C(3)	108.6 (7)	106.8 (9)
O(3)-C(4)-C(7)	106.2 (8)	
-C(8)	106.7 (8)	
C(3)-C(4)-C(7)	112.0 (8)	
-C(8)	113.8 (8)	
C(7)-C(4)-C(8)	109 (1)	
O(3)-C(4)-C(8)		108 (1)
-C(9)		107 (1)
C(3)-C(4)-C(8)		113 (1)
-C(9)		111 (1)
C(8)-C(4)-C(9)		111 (1)
C(3)-C(6)-C(7)		114 (1)
C(4)-C(8)-C(10A)		107 (2)
C(4)-C(9)-C(10)		105 (2)

the C(3)–C(4) bonds are only about 33°, instead of ca. 60°. However, as discussed below, this does not lead to lability of the bridging ligands.

(c) Significance of the Reactions and Mechanistic Considerations. The reductive coupling of ketones by the ditungsten(IV) complexes to afford ditungsten(V) species containing the α-diol ligands constitutes an interesting and significant use of these complexes as reagents for organic reactions. Historically, α-diols have been prepared from ketones by electrochemical[16] and photochemical[17] means and through the use of active metals such as sodium and aluminum.[18] The present results provide the first examples of the use of *multiply bonded dinuclear complexes* to promote carbon–carbon bond formation through the reductive coupling of ketones. A somewhat related reaction involving the reductive coupling of methyl pyruvate by the bifunctional complex [Co(salen)Na(THF)], where salen = the dianion of *N,N'*-ethylenebis(salicylideneiminato), has recently been described,[19] but few details have yet been published.

While we do not as yet have a full understanding of the mechanism of these reactions, we certainly have sufficient information to propose some reasonable and logical steps in the reaction pathway. First, the reaction between $W_2Cl_4(\mu\text{-OEt})_2$-$(OEt)_2(EtOH)_2$ and acetone-d_6 in chloroform was followed by ^1H NMR spectroscopy that clearly established that free ethanol (δ +3.67 for CH_2) is liberated within minutes of the addition of acetone. At the same time, there is a corresponding decrease in the intensity of signals attributable to the bound terminal ethoxide–ethanol ligands (δ +4.54). This process is apparently enhanced by the addition of acid (CH_3CO_2H, HCO_2H, or H_2SO_4) whose role seems to be protonating and labilizing the terminal ethanol ligands. Unfortunately, we have not been able to isolate the ketone adducts $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(\text{ketone})_2$, although complexes of this general type have been prepared in the case of pyridine and related nitrogen donors.[5,6] Following the coordination of the ketone molecules, electron transfer evidently ensues to generate ketyl radicals and the oxidized W^V–W^V unit; the former moieties then couple to give the stable coordinated diol ligand. Up to this point at least, it seems probable that the mechanism resembles that in which the reduction of acetone and acetophenone by $(\eta^5\text{-}C_5H_5)TiX_2$ (X = Cl or Br) leads to the titanium(IV) complexes $\{(\eta^5\text{-}C_5H_5)Ti^{IV}X_2\}_2(\mu\text{-RR'C(O)C(O)RR'})$.[20] However, it differs from the mechanism that has been proposed for the reductive coupling of methyl pyruvate by [Co(salen)Na(THF)].[19]

The fashion in which the ditungsten systems differ quite dramatically from any others is that *two* α-diol ligands end up bound to each ditungsten(V) unit. Since a total of four electrons are required to reduce four ketone molecules (to give two α-diols), this implies that 2 mol of ditungsten(IV) are needed to produce 1 mol of ditungsten(V). Indeed, yields of the product never exceeded 50%, in accord with the supposition that only half of the starting tungsten atoms go to form the product while the other half simply supply electrons and end up in some oxidized form.[21] Accordingly, we suggest that the following stoichiometric equation best explains these facts:

$$2W_2Cl_4(\mu\text{-OR})_2(OR)_2(ROH)_2 + 4R'R''CO \rightarrow$$
$$W_2Cl_4(\mu\text{-OR})_2[R'R''C(O)C(O)R'R'']_2 + 4OR^- + 4ROH +$$
$$2\text{``}W^V\text{''}$$

Of additional note is the observation that $W_2Cl_4(\mu\text{-OEt})_2$-$(OEt)_2(EtOH)_2$ and $W_2Cl_4(\mu\text{-OEt})_2(O\text{-}i\text{-Pr})_2(i\text{-PrOH})_2$ both react with acetone to give $W_2Cl_4(\mu\text{-OEt})_2[Me_2C(O)C(O)Me_2]_2$. This

proves that there is no exchange of alkoxide ligands during the course of the reaction and that the original $[W_2Cl_4(\mu\text{-OR})_2]$ unit remains intact.

Upon monitoring the course of the reaction by ^1H NMR spectroscopy (using acetone-d_6 in $CDCl_3$) we obtained no evidence for the presence of significant levels of free pinacol or the dianion $C_6H_{12}O_2^{2-}$ in solution. Neither have we been able to isolate or detect such species by workup of the reaction solution prior to the crystallization of the diol products $W_2Cl_4(\mu\text{-OR})_2[R'R''C\text{-}(O)C(O)R'R'']_2$.[22] Furthermore, we find that neither W_2Cl_4-$(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$ nor $W_2Cl_4(\mu\text{-OEt})_2(OEt)_4$ react with pinacol or the salt $Li_2C_6H_{12}O_2$. The latter observation is not surprising in view of the strained nature of the $\overline{WWOCCO}$ rings that are known to be present in the diol products. However, this strain in turn suggests that these compounds should be thermodynamically unstable toward reaction with an alcohol (ROH) to generate pinacol and $W_2Cl_4(\mu\text{-OEt})_2(OR)_4$. While we find that reaction between $W_2Cl_4(\mu\text{-OEt})_2[Me_2C(O)C(O)Me_2]_2$ and EtOH does not occur owing to the insolubility of this complex, it does dissolve in refluxing *n*-BuOH but can be recovered unchanged from the solution. This reflects the quite remarkable kinetic stability of these complexes and, indeed, all others of the type $W_2Cl_4(\mu\text{-OR})_2(OR)_4$. Of further note is the observation that $W_2Cl_4(\mu\text{-OEt})_2[Me_2C(O)C(O)Me_2]_2$ does not hydrolyze even when a suspension of it is stirred in water for 24 h.

Our isolation of the ditungsten(V) complex $W_2Cl_4(\mu\text{-OEt})_2$-$(OEt)_2[Me\text{-}n\text{-PrC}(O)C(O)Me\text{-}n\text{-Pr}]$ suggests that such compounds are formed as intermediates on the way to $W_2Cl_4(\mu\text{-}OR)_2[R'R''C(O)C(O)R'R'']_2$.[23] Accordingly, we suggest the following sequence of reaction steps. (1) Initial displacement of two ROH ligands to form a highly reactive ketone adduct $W_2Cl_4(\mu\text{-OR})_2(OR)_2(R'R''CO)_2$. (2) A two-electron-transfer step converting W^{IV}≡W^{IV} to W^V—W^V and generating two ketyl radicals that then couple to give $W_2Cl_4(\mu\text{-OR})_2(OR)_2[R'R''C\text{-}(O)C(O)R'R'']$. (3) An intermolecular electron-transfer reaction between this "intermediate" and some lower-valent tungsten species that is present in solution, leading to its reduction back to a derivative of ditungsten(IV). (4) The process of coordination of two $R'R''CO$ molecules and their subsequent reductive coupling can then be repeated to give the final product containing two α-diol ligands. Thus, the role of the dimetal unit is as a source of electrons for the reduction and as a template for the coupling of the ketyl radicals. While this sequence of reactions is in accord with the experimental observations, other interpretations are presumably possible. Indeed, at the present time, we do not have a satisfactory explanation as to why the reactions of $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$ with Et_2CO and $MePhCO$ have failed to produce analogous reductively coupled products. Presumably, there is a subtle interplay of stereochemical restrictions and electronic factors that we do not as yet understand.

The reductive coupling of ketones that we have observed here in the case of the ditungsten(IV) complexes bears an interesting relationship to some recent results of Chisholm and co-workers[24] concerning the reduction of α-diketones. The ditungsten(III) alkoxides $W_2(OR)_6$ (R = *t*-Bu and *i*-Pr) react with $R'C(O)C\text{-}(O)R'$ (R' = Me, Ph, and *p*-tol) to give the ditungsten(V) complexes $W_2(OR)_6[R'C(O)C(O)R']_2$. This corresponds to a net four-electron reduction of two diketone molecules to give products that contain two coordinated $[R'C(O)=C(O)R']^{2-}$ ligands. Here

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(21) When the reaction filtrates are set aside following the isolation of $W_2Cl_4(\mu\text{-OR})_2[R'R''C(O)C(O)R'R'']_2$, a blue amorphous solid precipitates over a period of several hours. The latter materials were insoluble in all solvents, and their IR spectra were indicative of tungsten blue species.

(22) Our attempts to monitor the complete course of these reactions using ^1H NMR spectroscopy were thwarted by a variety of problems that included the following: (a) the formation of "contaminants" such as $W_2Cl_4(\mu\text{-OR})_2$-$(OR)_4$ from competing side reactions (i.e., involving oxidation of the ditungsten(IV) species without the coordination and concomitant reduction of the ketone molecules); (b) precipitation of the rather insoluble $W_2Cl_4(\mu\text{-}OR)_2[R'R''C(O)C(O)R'R'']_2$ as the reactions proceeded; (c) the presence of several isomers in the case of the MeEtCO products (see section d of the Results and Discussion).

(23) In this connection the chemistry of $W_2Cl_4(OEt)_2[Me\text{-}n\text{-PrC}(O)C\text{-}(O)Me\text{-}n\text{-Pr}]$ is being further studied. It does not readily react further, perhaps for steric reasons.

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is an example where a ditungsten species serves as a reductant toward an organic ketonic substrate without concomitant C–C bond formation.

(d) ¹H NMR Spectroscopic Results and Their Interpretation in Terms of Stereochemical Features Associated with the α-Diol Ligands. As already alluded to in ref 20, ¹H NMR spectroscopy did not prove to be a satisfactory means of monitoring the reaction course within the reaction mixtures. Furthermore, the poor solubility of the complexes $W_2Cl_4(\mu\text{-}OR)_2[R'R''C(O)C(O)R'R'']_2$ has frustrated our attempts to obtain high quality spectral data. However, the data we have at hand for $W_2Cl_4(\mu\text{-}OEt)_2[Me_2C(O)C(O)Me_2]_2$ and $W_2Cl_4(\mu\text{-}OEt)_2[MeEtC(O)C(O)MeEt]_2$ will be presented here and, in the case of the latter of these two complexes, will be discussed in terms of various isomeric possibilities.

(i) $W_2Cl_4(\mu\text{-}OEt)_2[Me_2C(O)C(O)Me_2]_2$. The 200-MHz ¹H NMR spectrum of this compound in $CDCl_3$ solution shows a quartet at δ +5.89 ($J_{CH_2\text{-}CH_3}$ = 7 Hz) and a triplet at δ +1.89 ($J_{CH_3\text{-}CH_2}$ = 7 Hz) that correspond to the methylene and methyl groups, respectively, of the bridging ethoxide ligands. A singlet at δ +1.15 is assigned to the methyl groups of the pinacol ligands.

(ii) $W_2Cl_4(\mu\text{-}OEt)_2[MeEtC(O)C(O)MeEt]_2$. The presence of a total of four chiral carbon atoms in the two $[MeEtC(O)C(O)MeEt]^{2-}$ ligands gives a number of isomeric possibilities. Based on purely statistical grounds, five types of isomers can be expected. If the distribution of R and S configurations about each chiral center is random, then the following isomers would be present.

isomer type	1	2	3	4	5
example	RS	RS RS	RS	RR	RR SS
	RS	SS RR	SR	SS	RR SS
number	2	8	2	2	2

One example of each type of isomer is given, and below each is the number of permutations corresponding to that example.

The structure of crystalline $W_2Cl_4(\mu\text{-}OEt)_2[MeEtC(O)C(O)MeEt]_2$ shows half of the molecule to be ordered and to contain a center of inversion. This necessitates the configuration at carbon atoms C(3) and C(3') to be R and S, respectively. However, for C(4) the ethyl and methyl groups are equally distributed over the two available positions. This means that there must be as many C(4)–R as C(4)–S sites and, also, as many C(4')–R as C(4')–S sites. it is not necessary that the configurations at the C(4) and C(4') sites in *one molecule* be enantiomeric. It is, therefore, possible that as many as four arrangements occur in these crystals. The four arrangements (A–D) are shown below, where the two upper symbols pertain to C(4') and C(3') and the two lower ones to C(3) and C(4), on the left and right, respectively.

isomer	A	B	C	D
	RS	SS	SS	RS
	RS	RR	RS	RR

Arrangement A corresponds to previous isomer type 1, B to 4, and C and D to 2; isomers of types 3 and 5 are excluded entirely. To satisfy the crystallographic criteria, it is required that if A or B is present, $N_A = N_B$ (i.e., they must be present in equal numbers) and that if C or D is present, $N_C = N_D$. The relative amounts of A/B and C/D pairs is unrestricted. It is possible that there might be no A/B pairs (i.e., only C's and D's) or no C/D pairs (i.e., only A's and B's) or any intermediate mixture.

The 200-MHz ¹H NMR spectrum of a sample of the crystalline $W_2Cl_4(\mu\text{-}OEt)_2[MeEtC(O)C(O)MeEt]_2$ is consistent with the presence of more than one isomer. We see resonances between δ +5.44 and +5.62 and in the region between δ +1.92 and +1.86 due to the methylene and methyl protons of the bridging ethoxide ligands. The methylene resonance appears as a distorted quartet, a feature that accords with the presence of more than one isomer in solution (vide infra). Through the use of two-dimensional J spectroscopy, the complex methyl portion of the spectrum (δ +1.92 to +1.86) has been resolved into three overlapping triplets, each with a coupling constant of 6–7 Hz; a 470-MHz ¹H NMR spectrum also shows three partially overlapping triplets. Three such separate resonances may indicate the presence of three isomers in solution.

Turning now to the ¹H NMR spectral properties of the diol ligands $[R'R''C(O)C(O)R'R'']^{2-}$, the Et groups (R'') have resonances from δ +1.65 to +1.46 (methylene) and δ +1.04 to +0.93 (methyl). The methylene region should be a series of quartets, and the methyl protons should appear as a set of triplets. We actually observe complex overlapping patterns in each of these regions of the spectrum. The Me protons (R') of the diols appear in the region between δ +1.22 and +1.09 as singlets. Due to this relatively uncomplicated portion of the spectrum, these resonances can be used to identify the number of isomers present in solution. In isomers A and B (vide supra), all of the Me groups are equivalent, and therefore a singlet for each set of protons is expected. Isomers C and D have four chemically inequivalent Me groups. In this case then, four methyl singlets are predicted. If all three isomer types (i.e. 1, 2, and 4) are present in solution, then there should be six methyl singlets. The 470-MHz ¹H NMR spectrum together with the two-dimensional J experiment supports there being six such singlets between δ +1.22 and +1.09. Two of these are coincident such that there is a 1:1:2:1:1 intensity ratio for resonances at δ +1.22, +1.21, +1.17, +1.14, and +1.09.

The preceding, and admittedly tentative, interpretations of the ¹H NMR spectra, along with the crystallographic results, demonstrate that there is no strict steric control of the reductive coupling reaction (eq 1) since both RS and RR (or SS) type

$$2MeEtCO + 2e^- \rightarrow [MeEtC(O)C(O)MeEt]^{2-} \qquad (1)$$

α-diols are present. On the other hand, the crystal does not contain an entirely random distribution of coupling products either. There is no unambiguous explanation for this situation, but the following two hypotheses might be considered, if we were to assume that coupling occurs randomly. (1) The bulk crystalline material is not homogeneous, and in addition to crystals of the type we happened to have selected for structure work, there are others that contain different isomers. However, the 200-MHz ¹H NMR spectra of several different preparative samples of the reductively coupled methyl ethyl ketone product yield the same resonances possessing the same relative intensities. (2) The type of crystal we have studied is formed preferentially, for either kinetic or thermodynamic reasons. This would mean that the remaining supernatant solution would contain an excess of other isomers, especially types 3 and 5 that are entirely excluded from these crystals. While the 200-MHz ¹H NMR spectrum of the residue from the supernatant solution is clearly more complex than that of the crystals which had been removed by filtration, we are unable to prove or disprove that isomer types 3 and 5 are present.

(e) Concluding Remarks. Those reactions between complexes of the type $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$ and certain ketones that lead to the formation of stable crystalline $W_2Cl_4(\mu\text{-}OR)_2[R'R''C(O)C(O)R'R'']_2$ represent a novel use of multiply bonded dimetal complexes[4] as reagents for the transformation of organic chemicals. The present study is also noteworthy in that the isolated products contain two α-diol ligands, thereby implying the existence of a mechanism that has not previously been encountered for the reductive coupling of ketones. Furthermore, the stability of the products has permitted us the opportunity to carry out their full structural characterization. As far as we are aware, a structural characterization of this type of bridged α-diol complex has not been reported previously. Further studies are underway to expand the scope of this chemistry to include other carbonyl containing organics.[25]

(25) These studies currently include reactions with aldehydes. We find that acetals are formed in high yield from the reactions between $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(EtOH)_2$ and certain secondary aldehydes R'R''CHCHO (Anderson, L. B.; Walton, R. A., unpublished results).
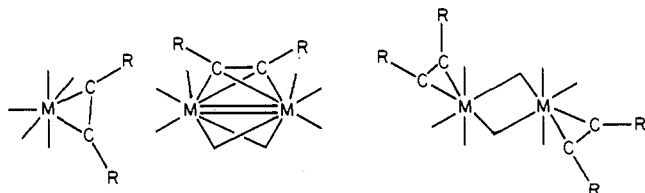
A New Double Bond Metathesis Reaction: Conversion of an Nb=Nb and an N=N Bond into Two Nb=N Bonds

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Abstract: $Nb_2Cl_6(Me_2S)_3$ reacts readily with azobenzene, $C_6H_5N{=}NC_6H_5$, to afford a red crystalline product, [$NbCl_2$-$(Me_2S)(NC_6H_5)$]$_2(\mu\text{-}Cl)_2$, in 50–60% yields. This compound has been characterized by NMR, IR, mass spectrometry, and X-ray crystallography. It is a centrosymmetric molecule in which each of two niobium(V) atoms have distorted octahedral coordination, with the ligand set consisting of two bridging Cl atoms, with one normal (2.462 (2) Å) and one long (2.762 (2) Å) bond, two mutually cis terminal chlorine atoms with Nb–Cl distances of 2.325 (3) Å and 2.344 (3) Å, one Nb–SMe₂ bond, 2.654 (3) Å, and one Nb=NC_6H_5 bond, 1.733 (7) Å. The long Nb–Cl bridge bond is trans to the Nb=NC_6H_5 bond. The dinuclear molecule can be regarded as the product of an inorganic double bond metathesis reaction in which Nb=Nb and N=N bonds react to yield two Nb=N bonds. The Nb=N—C group is practically linear, 175.1 (7)°. The compound crystallizes in space group *C2/c* with unit cell dimensions of *a* = 20.736 (4) Å, *b* = 7.671 (1) Å, *c* = 16.780 (3) Å, β = 96.86 (2)°, *V* = 2650 (2) Å³, and *Z* = 4. Refinement, using a data to parameter ratio of 9.4, converged with an unweighted discrepancy index of 4.89%.

Metal–metal multiple bonds constitute a source of remarkable reactivity.[1] In the case of the chemistry of doubly bonded niobium and tantalum, in their oxidation states of III, this extensive reactivity is perhaps best demonstrated by the reactions of the $Cl_2(R_2S)M(\mu\text{-}Cl)_2(\mu\text{-}R_2S)M(R_2S)Cl_2$ molecules (where R_2S represents tetrahydrothiophene or dimethyl sulfide) with unsaturated organic molecules such as isocyanides,[2] nitriles,[3-5] and acetylenes.[6-9] With *tert*-butyl isocyanide, $Nb_2Cl_6(SMe_2)_3$ has been shown to afford two novel complexes,[2] $Nb_3Cl_8(t\text{-}BuNC)_5$ and $Nb_2Cl_6(t\text{-}BuNC)_6$, whereas with nitriles, the $M_2Cl_6(SC_4H_8)_3$ compounds reductively couple two molecules of the nitrile with concomitant oxidation of the metal atoms.[3-5] The reactivity of our dinuclear, doubly bonded M^{III} starting materials towards acetylenes is manifested in several ways, which include (1) the formation of complexes of the following general types

(2) dimerization to give molecules with new carbon–carbon bonds which further react with the metal to form unusual structures containing metallocycles, (3) oligomerization to substituted benzenes, or (4) polymerization to substituted, high molecular weight polyolefins.

We now wish to report a new and unprecedented form of chemical behavior for the niobium–niobium double bond, namely, a double bond metathesis reaction with azobenzene, $C_6H_5N{=}NC_6H_5$, whereby Nb=Nb + N=N affords 2Nb=N, i.e., a product containing metal–imide linkages.

Experimental Section

All operations were performed under an atmosphere of argon by using standard Schlenk techniques and a double-manifold vacuum line. Toluene and hexane were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless cannulae and/or syringes. Azobenzene was deaerated under vacuum at 25 °C. $Nb_2Cl_6(SMe_2)_3$ was prepared according to the published procedure[10] for $Nb_2Cl_6(THT)_3$ by using dimethyl sulfide instead of tetrahydrothiophene. The ¹H NMR spectrum was obtained on a Varian XL 200 spectrometer. The IR spectrum was recorded on a Perkin-Elmer 783 spectrophotometer. Mass spectra were measured (direct insertion probe, 70 eV; the probe temperature increased steadily from 25 to 230 °C) on a Hewlett-Packard 5980A mass spectrometer equipped with a 5933A data system.

[$NbCl_2(SMe_2)(NC_6H_5)$]$_2(\mu\text{-}Cl)_2$. A solution of $Nb_2Cl_6(SMe_2)_3$ (0.50 g, 0.85 mmol) in 20 mL of benzene was filtered and to the filtrate azobenzene (0.25 g, 1.4 mmol) was added. Upon stirring, the color of the reaction mixture changed from purple to red within several minutes. Stirring of the mixture was continued at room temperature for 12 h, after which it was filtered into a flask, leaving a red solid behind. A total of 60 mL of hexane was carefully added on top of this filtrate and the flask was placed in a refrigerator. After a period of 1–2 days, a red crystalline solid was obtained. The red solids were combined and washed 3 times with 10 mL of fresh hexane. Yield: 58%, 0.35 g. ¹H NMR (C_6D_6): δ 1.73 (s, 12 H), 7.13 (m, 10 H). IR (Nujol), cm⁻¹: 1320 (m), 1300 (w), 1278 (w), 1255 (w), 1165 (w), 1153 (w), 1090 (w), 1065 (m), 1030 (m), 1020 (m), 1000 (w), 982 (m), 975 (m), 915 (vw), 910 (w), 832 (w), 760

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