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Metal Alkoxides—Models for Metal Oxides. 11.[1] Synthesis and Properties of Mixed Alkyl/Aryl/Benzyl Alkoxides of Formula 1,2-$W_2R_2(OR')_4$ and $W_2R(OR')_5$($M\equiv M$)

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Hydrocarbon solutions of 1,2-$W_2R_2(NMe_2)_4$ compounds (R = Me, Et, *n*- and *i*-Pr, *i*-Bu, CH_2CMe_3, CH_2SiMe_3, Ph, *p*-tolyl, and CH_2Ph) react with alcohols, R′OH, to give initially 1,2-$W_2R_2(OR')_4$ compounds. The latter may be isolated provided the combination of R and R′ has sufficient combined steric bulk to guard against further protolysis with successive elimination of RH and formation of $W_2(OR')_6$ compounds. In the presence of Lewis bases $HNMe_2$ or pyridine, the adducts $W_2Ar_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$, where Ar = Ph and *p*-tolyl, and $W_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$ have been isolated. The former compounds provide rare examples of four-coordinate tungsten atoms united to three-coordinate tungsten atoms by triple bonds: $(i\text{-}PrO)_2(Ar)(HNMe_2)W{\equiv}W(Ar)(O\text{-}i\text{-}Pr)_2$. When R contains β-hydrogen atoms, the initially formed compounds $W_2R_2(OR')_4$ show evidence for reversible β-hydrogen/deuterium abstraction and this can result in an isomerization of the alkyl ligands, e.g., *i*-Pr → *n*-Pr. The compound $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ has been isolated as an air- and heat-sensitive crystalline material and characterized by a single-crystal X-ray study. In the solid state there is a central $W_2C_2O_4$ moiety having virtual C_{2h} symmetry, i.e., the anti rotamer with W–W = 2.309 (1) Å, W–C = 2.141 (9) Å, and W–O = 1.88 (1) Å (averaged) and W–W–C = 100.2 (3)° and W–W–O = 107 (1)° (averaged). The molecule has a crystallographically imposed center of inversion, and the *i*-Bu ligand is arranged such that the W–C–C–H moiety has the anti conformation with the β-hydrogen lying distal to the W≡W bond. In solution the $W_2R_2(OR')_4$ compounds, where R contains β-hydrogen atoms, are reactive toward elimination of alkane and alkene and toward protolysis. In the reactions between $W_2(CH_2CD_3)_2(NMe_2)_4$ and *i*-PrOH (and $W_2(CH_2CH_3)_2(NMe_2)_4$ and *i*-PrOD) there is evidence from ^1H and ^2H NMR spectroscopy for the formation of a $W_2(\mu\text{-}H/D)$ moiety. These observations are compared to previous studies of alcoholyses involving $Mo_2R_2(NMe_2)_4$ compounds with the following conclusions. (1) Reactions proceed faster for M = W relative to Mo. (2) When R = a β-hydrogen containing alkyl, β-hydrogen atom abstraction is reversible for W but not for Mo. (3) Reductive elimination of alkane and alkene occurs more readily for Mo than for W. (4) No reduced W_2^{4+}-containing compounds have been isolated. Crystal data for $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$ at −155 °C: a = 17.836 (8) Å, b = 9.955 (4) Å, c = 19.822 (9) Å, β = 113.72 (2)°, Z = 4, d_{calcd} = 1.714 g cm^{-3}, and space group $P2_1/c$. Crystal data for $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ at −167 °C: a = 9.618 (2) Å, b = 9.077 (2) Å, c = 8.198 (2) Å, α = 99.96 (1)°, β = 92.29 (1)°, γ = 65.52 (1)°, Z = 1, d_{calcd} = 1.860 g cm^{-3}, and space group $P\bar{1}$.

Introduction

Following on from studies of the alcoholysis reactions involving 1,2-$Mo_2R_2(NMe_2)_4$ compounds which yield[1] one of three products, 1,2-$Mo_2R_2(OR')_4$, $Mo_2R''(OR')_5$, or $Mo_2(OR')_4L_4$ compounds (L = HOR′ or $HNMe_2$), depending upon the nature of R and R′, we report here related studies of reactions involving $W_2R_2(NMe_2)_4$ compounds. (R″ is an isomer of R, related by reversible β-hydrogen abstraction/insertion process.)

Results and Discussion

Synthesis. Hydrocarbon solutions of $W_2R_2(NMe_2)_4$ compounds react with alcohols to give initial R′O for NMe_2 substitution, and a variety of $W_2R_2(OR')_4$ compounds have been isolated or at least detected by NMR studies as shown in eq 1.

$$1,2\text{-}W_2R_2(NMe_2)_4 + R'OH\ (\geq 4\ \text{equiv}) \xrightarrow[\text{hexane}]{22\ ^\circ\text{C}} 1,2\text{-}W_2R_2(OR')_4 + 4HNMe_2 \quad (1)$$

R = Et, Pr, and Bu, R′ = *t*-Bu; R = CH_2Ph, CH_2CMe_3, CH_2SiMe_3, R′ = *t*-Bu, *i*-Pr, CH_2-*t*-Bu

The reactions involving the ditungsten compounds proceed differently from those involving $Mo_2R_2(NMe_2)_4$ compounds in two important ways. (1) The reactions involving M = W proceed roughly an order of magnitude faster, and protolysis of the M–C (alkyl/aryl/benzyl) bonds occurs more readily. Thus in the reaction between $M_2(CH_2Ph)_2(NMe_2)_4$ and *i*-PrOH in hexane, the compound $Mo_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ is relatively robust in the presence of excess *i*-PrOH while for the preparation of $W_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ care must be taken to add only 4 equiv of *i*-PrOH in order to suppress formation of $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ and toluene (2 equiv). Similarly attempts to prepare $W_2(CH_2CMe_3)_2(OEt)_4$ failed whereas the molybdenum analogue is readily obtainable. (2) For reactions involving an alkyl group, R, which contains β-hydrogen atoms, the molybdenum compounds $Mo_2R(OR')_5$ are readily prepared but for tungsten, $W_2R_2(OR')_4$ compounds are initially obtained. These are susceptible to elimination of alkane by kinetically competitive routes. One route involves protolysis in the presence of excess R′OH and the other appears to involve β-hydrogen atom transfer from a neighboring alkyl ligand with concomitant reductive elimination of alkane and alkene and subsequent reoxidation of the W_2^{4+} center in a manner analogous to that described for the preparation of $Mo_2R(OR')_5$ compounds.[1]

The first difference between the chemistry of the dimolybdenum and ditungsten compounds is understandable in terms of the greater affinity that $W_2(OR)_6$ compounds show for Lewis bases.[2,3] The compound $W_2Me_2(O\text{-}t\text{-}$

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[1] Chisholm, M. H.; Tatz, R. J. Organometallics, preceding paper in this issue.

[2] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* 1979, *18*, 2266.

[3] Chisholm, M. H. *Polyhedron* 1983, *2*, 681.

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Table I. Analytical and Other Characterization Data for Alkyl Alkoxides of Formula $W_2R_2(OR')_4(M{\equiv}M)$

compd	color and form	sublim *T*, °C (10^{-3} torr)	C calcd	C found	H calcd	H found	N calcd	N found
$W_2Me_2(O\text{-}t\text{-}Bu)_4py_2$	red-brown crystals		39.59	39.44	6.29	6.12	3.30	3.32
$W_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$	orange crystals	110	41.97	41.87	7.75	7.59	0.0	0.07
$W_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$	orange crystals	80	35.41	35.41	6.75	6.69	0.0	<0.03
$W_2(CH_2CMe_3)_2(O\text{-}t\text{-}Bu)_4$	red solid		38.92	36.49	7.29	6.67	0.0	<0.02
$W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$	orange crystals		33.44	33.28	6.46	6.32	0.0	0.03
$W_2(Ph)_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$	brown crystals		38.89	38.83	5.65	5.60	1.74	1.84

$Bu)_4(py)_2$ is unstable with respect to loss of pyridine, and even 1:1 Lewis base adducts, $W_2Ar_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$, where Ar = Ph or *p*-tolyl, have been isolated. These are models for $W_2R_2(OR')_4(HOR')_n$ compounds, where $n = 1$ or 2, which are most surely intermediates in reactions leading to successive loss of alkane and $W_2(OR')_6$-containing compounds.

The second difference is both fascinating and puzzling and requires closer scrutiny. When R = a β-hydrogen-containing alkyl, the initially formed $W_2R_2(OR')_4$ compounds show evidence for reversible β-hydrogen atom scrambling. (1) In the reaction between $W_2(CH_2CD_3)_2(NMe_2)_4$ and *t*-BuOH, the compound $W_2(C_2H_2D_3)_2(O\text{-}t\text{-}Bu)_4$ shows, by ^2H NMR spectroscopy, deuteriums in both α- and β-carbon positions in roughly the statistical ratio: $\alpha:\beta = 2:3$. (2) In the reaction between $W_2(i\text{-}Pr)_2(NMe_2)_4$ and *t*-BuOH, it is the *n*-propyl isomer that is formed: $W_2(n\text{-}Pr)_2(O\text{-}t\text{-}Bu)_4$. However, the compounds $W_2R_2(OR')_4$ are kinetically unstable being prone to both a thermal decomposition involving loss of alkane and alkene (alkyl group disproportionation) and protolysis of the W–C(alkyl) bond. The initially formed $W_2R(OR')_5$ compounds are further susceptible to protolysis, and, because of the copresence of $W_2R_2(OR')_4$ compounds and their similar physicochemical properties, not one $W_2R(OR')_5$ compound has been isolated in a pure state. However, NMR studies identify $W_2R(OR')_5$ compounds as analogues of the $Mo_2R(OR')_5$ compounds isolated in the previous work.

Physicochemical Properties. The new compounds are orange-red, hydrocarbon-soluble, crystalline compounds when isolated in a pure state. Elemental analyses and other characterization data for a representitive sample of the compounds are given in Table I. ^1H and ^{13}C NMR data are summarized in Table II. The latter parallel those for 1,2-$Mo_2R_2(OR')_4$ compounds in showing rapidly interconverting mixtures of anti and gauche rotamers at room temperature with rotation about the W≡W bond being frozen out at low temperatures, e.g., below −35 °C, $W_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$ exists as a mixture of gauche to anti rotamers in the concentration ratio ca. 2.5:1. The compounds are less thermally stable than their molybdenum analogues, and purification by sublimation (80–100 °C, 10^{-4} torr) was always accompanied by some decomposition, making recrystallization the preferred method for purification. The compounds did, however, yield molecular ions in the mass spectrometer, $W_2R_2(OR')_4^+$ or $W_2R(OR')_5^+$.

Solid-State and Molecular Structures. Atomic postional parameters for $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ and $W_2(p\text{-}tolyl)_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$ are given in Tables III and IV, respectively. Ortep views of the molecules giving the atomic number schemes used to the tables are given in Figure 1 and 2. Listings of bond distances and bond angles are given in Tables V and VI, and a summary of the crystal data is presented in Table VII.

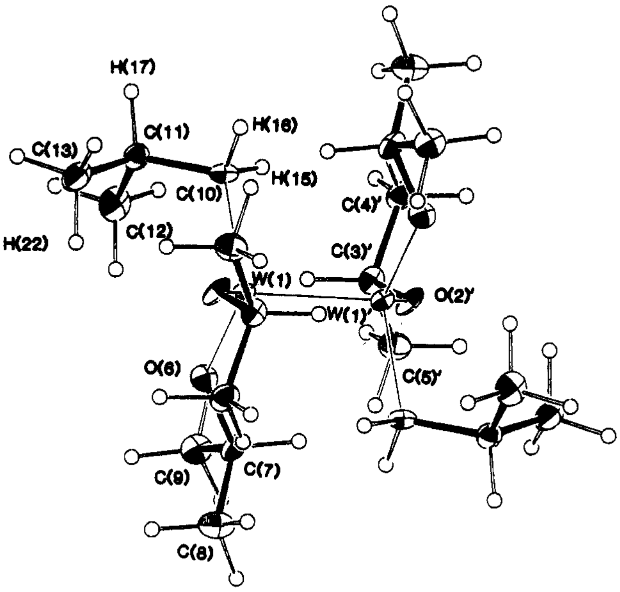

Figure 1. An Ortep view of the $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ molecule giving the atom number scheme used in the tables.

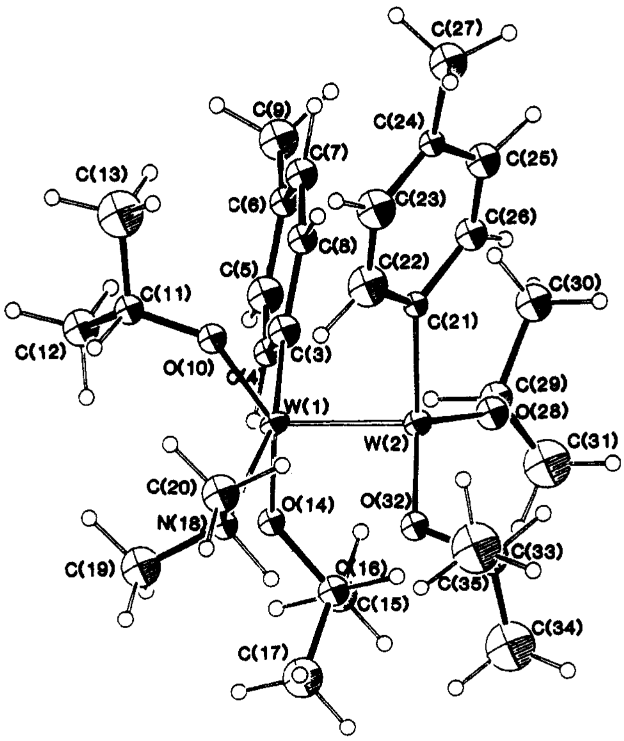

Figure 2. An Ortep view of the $W_2(p\text{-}tolyl)_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$ molecule giving the atom number scheme used in the tables.

$W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ has a crystallographically imposed center of inversion and virtual molecular C_{2h} symmetry. The W–W distance, 2.309 (2) Å, is typical of an unbridged W≡W bond in a W_2^{6+}-containing compound where the metal atoms are coordinated to three ligands.[3,4] The W–O distances, 1.88 (1) Å (averaged), are short and may be

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(4) Cotton, F. A.; Walton, R. A. In *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

Table II. ^1H and ^{13}C NMR Data for Alkyl-Alkoxy Compounds of Formulas $W_2R_2(OR')_4$ and $W_2R(OR')_5(M{\equiv}M)$

compd	^1H chem shift (rel int, multiplicity; J, Hz)[a,b]				^{13}C chem shift (rel int)[a,c]			
	alkyl		alkoxide		alkyl		alkoxide	
$W_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$	α	2.05 (1, s)	β	1.41 (18, s)	α	39.12 (1)	α	77.45 (2)
							β	33.57 (6)
			py: o	8.73 (2, d; 5.5)			py: o	150.31 (2)
			m	7.00 (2, dd; 5.5)			m	135.54 (2)
			p	6.80 (1, t; 5.5)			p	123.16 (1)
$W_2(CH_2CMe_3)_2(O\text{-}t\text{-}Bu)_4$	α	3.45 (2, s)	β	1.59 (18, s)		NR		
	γ	1.11 (9, s)						
$W_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$	α	3.04 (2, s)	α	5.95 (2, sept; 6.1)	α	72.31 (1)	α	88.47 (2)
	γ	1.20 (9, s)	β	1.56 (6, d; 6.1)	β	31.82 (1)	β	27.28 (2)
				1.48 (6, d; 6.1)	γ	34.44 (3)		26.44 (2)
$W_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$	α	3.00 (2, br s)	α	5.25 (2, d; 10.2)	α	73.87 (1)	α	91.30 (2)
	γ	1.07 (9, s)		5.03 (2, d; 10.2)	β	32.49 (1)	β	34.68 (2)
			γ	1.08 (18, s)	γ	34.37 (3)	γ	26.60 (6)
$W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$	α	2.92 (2, d; 6.5)	α	5.90 (2, sept; 6.1)	α	65.38 (1)	α	84.12 (2)
	β	2.22 (1, t-sept; 6.5)	β	1.52 (6, d; 6.1)	β	28.06 (1)	β	27.32 (2)
	γ	0.99 (6, d; 6.5)		1.46 (6, d; 6.1)	γ	26.52 (2)		27.19 (2)
$W_2(Et)_2(O\text{-}t\text{-}Bu)_4$	α	3.05 (2, q; 7.6)	β	1.56 (18, s)		NR		
	β	1.79 (3, t; 7.6)						
$W_2Et(O\text{-}t\text{-}Bu)_5$	α	2.73 (2, q; 7.6)	β	1.52 (18, s)		NR		
	β	1.76 (3, t; 7.6)	β′	1.57 (27, s)				
$W_2(n\text{-}Pr)_2(O\text{-}t\text{-}Bu)_4$	α	2.88 (2, t; 7.6)	β	1.50 (18, s)		NR		
	β	1.96 (2, sext; 7.6)						
	γ	1.30 (3, t; 7.6)						
$W_2(n\text{-}Pr)(O\text{-}t\text{-}Bu)_5$	α	2.58 (2, t; 7.6)	β	1.52 (18, s)		NR		
	β	2.04 (2, sext; 7.6)	β′	1.53 (27, s)				
	γ	1.30 (3, t; 7.6)						
$W_2(n\text{-}Pr)(O\text{-}i\text{-}Pr)_5$	α	2.88 (2, t; 7.6)	α	5.75 (2, sept; 6.0)		NR		
	β	1.74 (2, sext; 7.6)	β	1.58 (6, d; 6.0)		NR		
	γ	1.13 (3, t; 7.6)		1.53 (6, d; 6.0)				
			α′	5.00 (3, sept; 6.0)				
			β′	1.46 (18, d; 6.0)				
$W_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$	α	4.10 (2, s)	α	5.77 (2, sept; 6.1)		NR		
	o	7.14 (2, d; 7.6)	β	1.42 (6, d; 6.1)				
	m	7.07 (2, dd; 7.6)		1.32 (6, d; 6.1)				
	p	6.89 (1, t; 7.6)						
$W_2(Ph)_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$	o	7.89 (4, d; 7.2)	α	5.32 (4, sept; 6.1)		NR		
	m	7.40 (4, dd; 7.2)	β	1.30 (12, d; 6.1)				
	p	7.07 (2, t; 7.2)		1.21 (12, d; 6.1)				
			$HNMe_2$: H	2.78 (1, br)				
			Me	2.31 (6, br)				
$W_2(p\text{-}tolyl)_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$	o	7.88 (4, d; 7.6)	α	5.52 (4, sept; 6.1)		NR		
	m	7.21 (4, d; 7.6)	β	1.36 (12, d; 6.1)				
				1.30 (12, d; 6.1)				
	p-methyl	2.27 (6, s)	$HNMe_2$: H	NO				
			Me	2.29 (6, br)				

[a] All chemical shifts are reported in δ (ppm) relative to Me_4Si. The assignments α, β, and γ are relative to the metal for the alkyl and sept, for the alkoxides. s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = sept, and br = broad. [b] Spectra were recorded at room temperature in toluene-d_8 at 360 MHz. [c] Spectra were recorded at room temperature in benzene-d_6 at 91 MHz. [d] NR = not recorded. [e] NO = not observed.

Table III. Fractional Coordinates and Isotropic Thermal Parameters for $W_2(i\text{-Bu})_2(O\text{-}i\text{-Pr})_4$ Molecule[a–c]

atom	x	y	z	B_{iso}, Å^2
W(1)	514.0 (4)	148.2 (4)	1282.7 (4)	10
O(2)	−997 (6)	1943 (7)	2629 (8)	14
C(3)	−2643 (10)	2875 (11)	2637 (12)	14
C(4)	−3366 (12)	2232 (14)	3790 (14)	19
C(5)	−2985 (12)	4682 (12)	3205 (14)	19
O(6)	1290 (7)	−1928 (7)	1928 (8)	15
C(7)	1263 (10)	−3498 (10)	1385 (12)	15
C(8)	104 (13)	−3654 (14)	2487 (15)	23
C(9)	2861 (11)	−4823 (12)	1443 (15)	18
C(10)	2288 (11)	815 (12)	648 (13)	13
C(11)	3495 (10)	663 (12)	1963 (12)	15
C(12)	4556 (12)	−1126 (13)	2000 (16)	22
C(13)	2772 (13)	1534 (14)	3677 (13)	21
H(1)	−297 (10)	294 (11)	155 (12)	13 (19)
H(2)	−438 (15)	278 (14)	389 (13)	27 (24)
H(3)	−309 (15)	116 (18)	335 (17)	47 (33)
H(4)	−297 (11)	238 (12)	484 (14)	19 (21)
H(5)	−258 (11)	504 (12)	253 (13)	16 (21)
H(6)	−412 (14)	528 (14)	312 (13)	30 (24)
H(7)	−262 (10)	480 (11)	434 (13)	13 (19)
H(8)	94 (9)	−356 (9)	27 (11)	0 (15)
H(9)	−98 (15)	−295 (15)	232 (14)	32 (25)
H(10)	8 (12)	−472 (15)	214 (13)	27 (23)
H(11)	39 (10)	−363 (10)	360 (12)	4 (17)
H(12)	286 (14)	−601 (16)	109 (15)	41 (27)
H(13)	259 (16)	−446 (16)	75 (16)	50 (31)
H(14)	306 (11)	−470 (12)	244 (14)	17 (23)
H(15)	268 (12)	45 (13)	−31 (14)	22 (24)
H(16)	175 (11)	200 (13)	44 (12)	20 (20)
H(17)	428 (9)	121 (10)	174 (10)	3 (15)
H(18)	396 (12)	−166 (13)	249 (13)	25 (23)
H(19)	505 (10)	−168 (11)	99 (12)	6 (18)
H(20)	531 (13)	−127 (13)	268 (13)	23 (23)
H(21)	217 (13)	262 (16)	374 (14)	30 (26)
H(22)	224 (11)	107 (12)	431 (12)	16 (20)
H(23)	357 (14)	160 (15)	456 (15)	39 (27)

[a] Fractional coordinates are $\times 10^{-4}$ for non-hydrogen atoms and $\times 10^{-3}$ for hydrogen atoms. B_{iso} values are X10. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr. 12*, 609. [c] Parameters marked by an asterisk (*) were not varied.

Table IV. Fractional Coordinates and Isotropic Thermal Parameters for the $W_2(p\text{-tolyl})_2(O\text{-}i\text{-Pr})_4(HNMe_2)$ Molecule

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
W(1)	3144 (1)	2344 (1)	1544 (1)	14
W(2)	1749 (1)	2763 (1)	1001 (1)	15
C(3)	3184 (17)	909 (28)	2363 (16)	21 (6)
C(4)	3460 (16)	−373 (25)	2390 (14)	15 (5)
C(5)	3565 (18)	−1302 (29)	2928 (17)	27 (6)
C(6)	3362 (16)	−972 (25)	3544 (14)	17 (5)
C(7)	3080 (17)	338 (27)	3559 (15)	21 (5)
C(8)	2990 (16)	1217 (26)	2976 (15)	18 (5)
C(9)	3507 (18)	−1963 (32)	4141 (17)	32 (6)
O(10)	3621 (11)	3700 (17)	2285 (10)	17 (3)
C(11)	4395 (16)	3946 (26)	2779 (15)	17 (5)
C(12)	4966 (17)	2634 (29)	2939 (15)	26 (5)
C(13)	4428 (22)	4540 (36)	3480 (20)	42 (8)
O(14)	3286 (10)	1033 (17)	927 (10)	15 (3)
C(15)	2747 (17)	352 (27)	237 (15)	20 (5)
C(16)	2829 (18)	−1159 (29)	339 (16)	25 (6)
C(17)	2998 (20)	778 (32)	−389 (18)	32 (6)
N(18)	3488 (13)	3789 (21)	790 (12)	15 (4)
C(19)	4308 (19)	3498 (31)	798 (17)	31 (6)
C(20)	3396 (19)	4236 (30)	905 (18)	28 (6)
C(21)	1654 (15)	4089 (25)	1786 (14)	12 (5)
C(22)	1997 (20)	5358 (32)	1971 (18)	32 (7)
C(23)	1850 (19)	6191 (32)	2447 (17)	31 (6)
C(24)	1352 (15)	5880 (24)	2790 (14)	14 (5)
C(25)	975 (17)	4597 (28)	2599 (16)	24 (5)
C(26)	1163 (17)	3734 (27)	2164 (15)	21 (5)
C(27)	1115 (18)	6844 (31)	3256 (16)	29 (6)
O(28)	1180 (11)	1196 (18)	967 (10)	22 (4)
C(29)	1264 (17)	−178 (27)	1202 (16)	21 (5)
C(30)	914 (18)	−255 (30)	1811 (17)	27 (6)
C(31)	859 (23)	−1145 (37)	614 (21)	45 (8)
O(32)	1685 (10)	3700 (17)	120 (9)	16 (3)
C(33)	926 (18)	4063 (29)	−422 (16)	25 (6)
C(34)	801 (23)	3329 (40)	−1130 (21)	50 (8)
C(35)	930 (24)	5584 (39)	−455 (22)	48 (8)

Table V. Bond Distances (Å) and Angles (deg) for the $W_2(i\text{-Bu})_2(O\text{-}i\text{-Pr})_4$ Molecule

A	B	dist
W(1)	W(1)	2.309 (1)
W(1)	O(2)	1.878 (6)
W(1)	O(6)	1.880 (6)
W(1)	C(10)	2.141 (9)
O(2)	C(3)	1.453 (11)
O(6)	C(7)	1.428 (11)
C(3)	C(4)	1.516 (14)
C(3)	C(5)	1.522 (13)
C(7)	C(8)	1.528 (14)
C(7)	C(9)	1.515 (13)
C(10)	C(11)	1.535 (13)
C(11)	C(12)	1.524 (14)
C(11)	C(13)	1.524 (14)

A	B	C	angle
W(1)′	W(1)	O(2)	106.9 (2)
W(1)′	W(1)	O(6)	106.5 (2)
W(1)′	W(1)	C(10)	100.2 (3)
O(2)	W(1)	O(6)	119.2 (3)
O(2)	W(1)	C(10)	109.7 (3)
O(6)	W(1)	C(10)	112.4 (3)
W(1)	O(2)	C(3)	137.6 (5)
W(1)	O(6)	C(7)	138.5 (6)
O(2)	C(3)	C(4)	107.8 (8)
O(2)	C(3)	C(5)	107.9 (7)
C(4)	C(3)	C(5)	112.4 (8)
O(6)	C(7)	C(8)	108.2 (8)
O(6)	C(7)	C(9)	109.1 (7)
C(8)	C(7)	C(9)	112.8 (8)
W(1)	C(10)	C(11)	114.4 (6)
C(10)	C(11)	C(12)	111.6 (8)
C(10)	C(11)	C(13)	111.8 (8)
C(12)	C(11)	C(13)	110.5 (9)

taken as W–O double-bond distances;[3] i.e., the i-PrO ligands are both σ^2 and π^2 donors giving each tungsten atom an effective 16-valence-electron count (6e from the $W\equiv W$ bond, 4e per *i*-PrO ligand, 2e per *i*-Bu ligand). The W–C bond distance 2.14 (1) Å is close to that expected for a $W\text{–}C_{sp^3}$ distance based on previous estimates of the covalent radii for W in $(W\equiv W)^{6+}$-containing compounds.[5,6]

A view of the $W_2(i\text{-Bu})_2(O\text{-}i\text{-Pr})_4$ molecule looking down the W–W bond is given in Figure 3. This view of the molecule reveals that the β-hydrogen atom of the *i*-Bu ligand is distal to the $W\equiv W$ bond, and the W–C–C–H moiety has the anti rotameric form. Thus, in the ground-state conformation of the molecule the β-hydrogen of the *i*-Bu ligand is not well disposed for a β-hydrogen-to-metal interaction. Indeed the W···β-H distance is over 4.0 Å. The W to α-carbon hydrogen atom distances involving the *i*-Bu ligand, H(15) and H(16), are 2.62 (5) and 2.63 (5) Å, respectively, and are the shortest W-to-H distances in the molecule.

$W_2(p\text{-tolyl})_2(O\text{-}i\text{-Pr})_4(HNMe_2)$ contains an unbridged $W\equiv W$ bond, 2.317 (2) Å, uniting three-coordinate and four-coordinate metal atoms. This is only the second such

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[5] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Millar, M.; Stults, B. R. *Inorg. Chem.* **1977**, *16*, 320.

[6] Chisholm, M. H.; Corning, J. F.; Folting, K.; Huffman, J. C. *Polyhedron* **1984**, *4*, 383.

Table VI. Selected Bond Distances (Å) and Angels (deg) for the $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$

A	B	dist
W(1)	W(2)	2.3170 (19)
W(1)	O(10)	1.922 (17)
W(1)	O(14)	1.874 (17)
W(1)	N(18)	2.328 (21)
W(1)	C(3)	2.14 (3)
W(2)	O(28)	1.848 (18)
W(2)	O(32)	1.942 (17)
W(2)	C(21)	2.100 (25)
O(10)	C(11)	1.36 (3)
O(14)	C(15)	1.48 (3)
O(28)	C(29)	1.43 (3)
O(32)	C(33)	1.40 (3)
N(18)	C(19)	1.48 (4)
N(18)	C(20)	1.48 (4)

A	B	C	angle
W(2)	W(1)	O(10)	106.9 (5)
W(2)	W(1)	O(14)	102.9 (5)
W(2)	W(1)	N(18)	95.8 (5)
W(2)	W(1)	C(3)	100.0 (8)
O(10)	W(1)	O(14)	148.6 (7)
O(10)	W(1)	N(18)	84.6 (7)
O(10)	W(1)	C(3)	91.2 (9)
O(14)	W(1)	N(18)	82.6 (8)
O(14)	W(1)	C(3)	93.4 (9)
N(18)	W(1)	C(3)	164.1 (9)
W(1)	W(2)	O(28)	109.7 (6)
W(1)	W(2)	O(32)	99.7 (5)
W(1)	W(2)	C(21)	99.2 (7)
O(28)	W(2)	O(32)	122.7 (8)
O(28)	W(2)	C(21)	110.5 (9)
O(32)	W(2)	C(21)	111.8 (8)
W(1)	O(10)	C(11)	133.5 (16)
W(1)	O(14)	C(15)	135.6 (15)
W(2)	O(28)	C(29)	144.1 (17)
W(2)	O(32)	C(33)	120.3 (16)
W(1)	N(18)	C(19)	112.7 (16)
W(1)	N(18)	C(20)	115.4 (17)
C(19)	N(18)	C(20)	111.0 (21)
W(1)	C(3)	C(4)	123.7 (21)
W(1)	C(3)	C(8)	123.9 (20)
W(2)	C(21)	C(22)	127.6 (21)
W(2)	C(21)	C(26)	119.3 (18)

Table VII. Summary of Crystal Data[a]

	I	II
empirical formula	$W_2O_4C_{20}H_{46}$	$W_2C_{28}N_{49}NO_4$
color of cryst	yellow to brown	black
cryst dimens, cm	0.04 × 0.04 × 0.04	0.06 × 0.03 × 0.04
space group	$P\bar{1}$	$P2_1/c$
cell dimens		
temp, °C	−167	−155
a, Å	9.618 (2)	17.836 (8)
b, Å	9.077 (2)	9.955 (4)
c, Å	8.198 (2)	19.822 (9)
α, deg	99.96 (1)	
β, deg	92.29 (1)	113.72 (2)
γ, deg	65.52 (1)	
Z molecules/cell	1	4
v, Å^3	641.12	3222.14
D(calcd), g/cm^3	1.860	1.714
wavelength, Å	0.71069	0.71069
mol wt	718.28	831.40
linear abs coeff	91.767	73.168
detector to sample distance, cm	22.5	22.5
sample to source distance, cm	23.5	23.5
av Ω scan width at half-height	0.25	0.25
scan speed, deg/min	4.0	4.0
scan width (deg + dispersion)	1.8	2.0
individual bgd, s	3	8
aperture size, mm	3.0 × 4.0	3.0 × 4.0
2θ range, deg	6–45	6–45
total no. of reflctns collected	2717	4667
no. of unique intensities	1662	4201
no. with $F > 0.0$	1639	
no. with $F > \sigma(F)$	1623	
no. with $F > 2.33\sigma(F)$	1588	
no. with $F > 3.0\sigma(F)$		2876
$R(F)$	0.0308	0.0805
$R_w(F)$	0.0312	0.0727
goodness of fit for the last cycle	1.606	1.173
max Δ/σ for last cycle	0.05	0.05

[a] I = $W_2(i\text{-Bu})_2(O\text{-}i\text{-Pr})_4$; II = $W_2(p\text{-tolyl})_2(O\text{-}i\text{-Pr})_4(HNMe_2)$.

example we have seen.[7] Generally, when Lewis bases add to $(M{\equiv}M)^{6+}$ centers (M = Mo or W), they do so in a cooperative manner such that the bis-ligated compounds are formed, e.g., $M_2(OR)_6L_2$.[3] From solution studies involving the addition of amines, pyridines (4-substituted), and tertiary phosphines, we have found that the equilibrium constant for the formation of monoadducts in the reaction: $M_2(OR)_6 + M_2(OR)_6L_2 \rightleftharpoons 2M_2(OR)_6L$, *K*, is small. The only previous example of a mono-ligated Lewis base adduct was seen for the compound $(i\text{-PrO})_3Mo{\equiv}Mo(benzyl)_2(O\text{-}i\text{-Pr})(PMe_3)$, which was formed in the reaction between $1,2\text{-}Mo_2(benzyl)_2(O\text{-}i\text{-Pr})_4$ and PMe_3 (1 equiv).[7] Our rationale for the preferential isolation of a mono Lewis base adduct was that the benzyl migration to give the 1,1-dibenzyl isomer generated a relatively electron-deficient (14e$^-$) and soft molybdenum center, capable of coordinating and preferentially binding the soft PMe_3 ligand. Our initial reaction to the finding that $W_2(Ar)_2(O\text{-}i\text{-Pr})_4(HNMe_2)$ compounds are formed in the reaction between $W_2(Ar)_2(NMe_2)_4$ compounds and *i*-PrOH was that Ar migration (Ar = Ph or *p*-tolyl) had occurred and that the amine was ligated to a $W(Ar)_2(O\text{-}i\text{-Pr})$ moiety. The ^1H NMR spectra show two types of Ar ligands (see later), but this did not unambiguously identify whether or not we were dealing with a mono-ligated 1,1- or 1,2-isomer. The crystallographic study unambiguously shows the connectivity $(i\text{-PrO})_2(p\text{-tolyl})(HNMe_2)W{\equiv}W(O\text{-}i\text{-Pr})_2(p\text{-tolyl})$, though the quality of the structural determination is not as good as we routinely expect for work from these laboratories. The W–O and W–C distance, associated with the two ends of the molecules, are essentially identical, and the W–N distance, 2.33 (2) Å, is indicative of a relatively weak dative bond, consistent with the solution behavior of the molecule wherein the $HNMe_2$ molecule is reversibly disssociated on the NMR time scale at ambient temperature. The three-coordinate tungsten atom is essentially trigonal, and the four-coordinate tungsten atom square planar with the W–W–O, W–W–C, and W–W–N angles falling in the range 95–107°, as typically seen in $M_2R_2(NMe_2)_4$[8,9] or $M_2(OR)_6L_2$ compounds.[3] The $HNMe_2$ molecule is trans to the W–C(*p*-tolyl) bond as are the py ligands trans to the Mo–C(methyl) bonds in the compound $(t\text{-BuO})_2(Me)(py)Mo{\equiv}Mo(py)(Me)(O\text{-}t\text{-Bu})_2$.[10] A view

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(7) Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1984**, *107*, 5385.

(8) Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046.

(9) Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C.; Janos, J. *J. Am. Chem. Soc.* **1983**, *105*, 1163.

(10) Chisholm, M. H.; Huffman, J. C.; Tatz, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 2075.

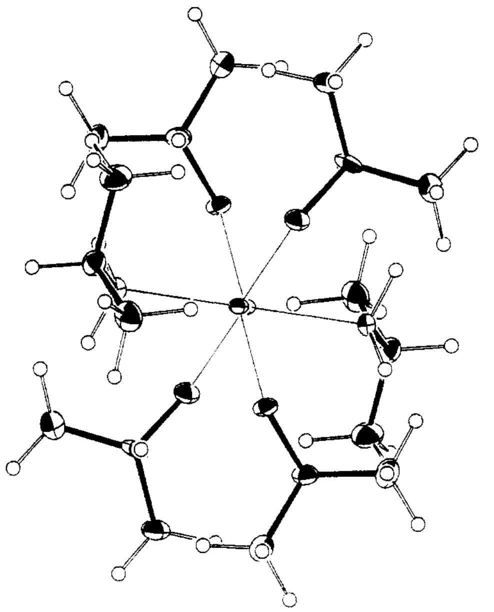

Figure 3. An Ortep view of the $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ molecule looking down the W–W bond and showing the anti –W–C–C–H conformation of the W-*i*-Bu moiety.

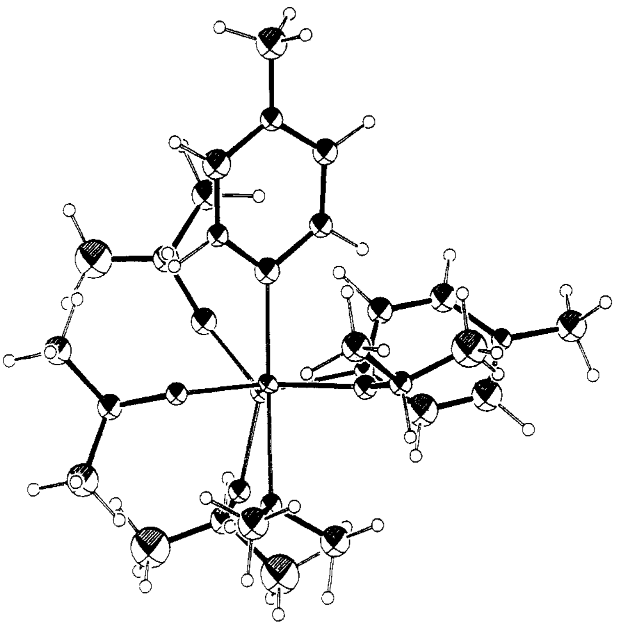

Figure 4. An Ortep view of the $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$ molecule looking down the W–W bond showing the partially staggered orientation of the trigonal and four-coordinate tungsten atoms.

of the $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$ molecule looking down the W–W axis is given in Figure 4. The observed conformation presumably represents a minimum in terms of steric repulsive interactions between the two sets of ligands attached to each tungsten atom.

^{1}H NMR Studies of $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$. The room-temperature ^{1}H NMR spectrum of $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$ in toluene-d_8 is shown in Figure 5 and represents that of the equilibrium shown in eq 2 where free and coordinated amine exchange is fast on the NMR time scale. Note the appearance of one type of *p*-tolyl ligand and one type of O-*i*-Pr ligand with diastereotopic isopropyl methyl signals as expected for 1,2-$W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4$.

$$1,2\text{-}W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2) \rightleftharpoons 1,2\text{-}W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4 + HNMe_2 \quad (2)$$

Upon lowering the temperature the signals arising from the *p*-tolyl group broaden and split into two types for the ortho and meta protons and *p*-methyl groups. The signals associated with the O-*i*-Pr and $HNMe_2$ ligands, however, never reach a sharp low-temperature limiting spectrum. Our interpretation of the latter observation is that rotation about the central W≡W bond is slowed upon cooling but that one conformation is not favored specifically over another. Note that from a consideration of the observed solid-state structure one would predict four types of O-*i*-Pr ligands and one $HNMe_2$ giving rise for the methyl group to 10 doublets since each ligand (O-*i*-Pr and $HNMe_2$) has diastereotopic methyls.

Evidence for a $W_2(\mu\text{-H})$ Moiety. Though the reaction between $Mo_2Et_2(NMe_2)_4$ and *i*-PrOH yields $Mo_2Et(O\text{-}i\text{-}Pr)_5$, the analogous reaction employing $W_2Et_2(NMe_2)_4$ has yielded no isolable compound. When followed by NMR spectroscopy, the formation of ethane, some ethylene, and free and coordinated $HNMe_2$ and i-PrOH ligands can be postulated. The NMR spectra of solutions of these reactants are too complicated for the existence of simple unbridged ethane-like $(W{\equiv}W)^{6+}$-containing compounds. The spectra lead us to believe that we are probably dealing with bridged compounds, possibly confacial bioctahedra, with a hydride in one of the bridging positions. Evidence for the hydride ligand is summarized below.

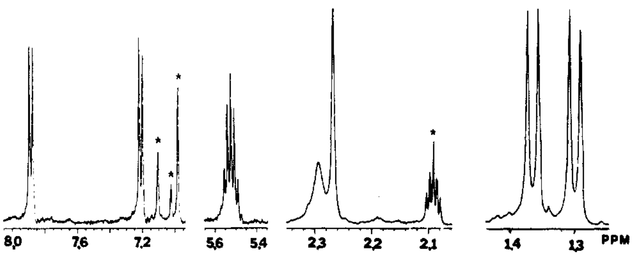

Figure 5. ^{1}H NMR spectrum of $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$ recorded at 360-MHz and 22 °C in toluene-d_8 solvent. Resonances denoted by an asterisk arise from protio impurities in the solvent. Relative peak intensities are not to scale.

(1) When $W_2Et_2(NMe_2)_4$ is allowed to react with *i*-PrOD at room temperature in benzene, there is a signal at δ 0.5 in the ^{2}H NMR spectrum which has satellites due to coupling to ^{183}W, $J_{^{183}W\text{–}^2H}$ = 26 Hz. The relative intensities of the satellites are 16% (i.e., 32% of the total signal) consistent with a deuterium bridging two equivalent (time-averaged or otherwise) tungsten atoms. In the ^{1}H NMR spectrum recorded in toluene-d_8 there is a signal at δ 0.6 flanked by satellites, each of 16% total intensity, due to coupling to ^{183}W, $J_{^{183}W\text{–}^1H}$ = 155 Hz. The ratio of $^1J_{^{183}W\text{–}^1H}$ to $^1J_{^{183}W\text{–}^2H}$ is 6:1 which agrees with that expected from considerations of the relative gyromagnetic ratio of H and D.[11]

(2) When $W_2(CH_2CD_3)_2(NMe_2)_4$ was reacted with *i*-PrOH in either toluene or hexane and the reaction was followed at low temperature, a number of signals were observed in the ^{2}H NMR spectra. Initially a ^{2}H signal at 3.8 ppm was observed along with a singlet at δ 1.06. Speculatively, these are assigned to a coordinated ethylene ligand and a hydride, respectively. In addition there is evidence for the $W\text{–}CH_2CD_3$ moiety at δ 1.4. With time the signal at δ 1.06 decreases in intensity and the signal

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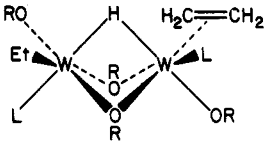
[11] Corio, P. L. In *Structure of High Resolution NMR Spectra*; Academic Press: New York, 1966, pp 140–142.

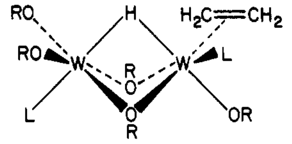
[12] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Leonelli, J.; Little, D. *J. Am. Chem. Soc.* **1981**, *103*, 779.

at δ 3.8 is replaced by one at 4.0 ppm and ethane is liberated, and the ^{2}H signal at 0.5 ppm mentioned previously grows in.

A possible interpretation for the above is that the initial low-temperature alcoholysis of $W_2Et_2(NMe_2)_4$ yields a confacial bioctahedral molecule of the type shown in I, where L = a site occupied by $HNMe_2$ or *i*-PrOH. Subsequently a protolysis of the ethyl ligand yields ethane and II. The suggestion for the $W_2(\mu\text{-}H)$ moiety finds at least support in the hydride signals of $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$ $W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_8Na\cdot$diglyme[13] and $W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_6(I)(H_2NMe)$[13] which occur at ca. δ 8 with $J_{^{183}W-^{1}H}$ in the range 98–145 Hz.



I



II

Concluding Remarks

The alcoholyses of 1,2-$W_2R_2(NMe_2)_4$ compounds proceed similarly to related reactions involving 1,2-$Mo_2R_2(NMe_2)_4$ to give 1,2-$M_2R_2(OR')_4$ compounds. The latter for M = W are more susceptible to protolysis of the M–C(alkyl) bonds. The $W_2R_2(OR')_4$ compounds also bind Lewis bases more strongly, and in the cases where R = Ph or *p*-tolyl 1:1 adducts $(i\text{-}PrO)_2(Ar)W{\equiv}W(Ar)(O\text{-}i\text{-}Pr)_2(HNMe_2)$ are formed. These are rare examples of compounds containing M≡M bonds united by three- and four-coordinated metal atoms. When R contains β-hydrogen atoms, the $W_2R_2(OR')_4$ compounds reveal that reversible β-hydrogen elimination has occurred during the alcoholysis. Reductive elimination of alkane and alkene occurs notably slower from the W_2^{6+} center, and, unlike the chemistry of molybdenum, W_2^{4+}-containing compounds $W_2(OR')_4L_4$ (L = $HNMe_2$ or R'OH) have not been detected or isolated. Finally during the reaction between $W_2Et_2(NMe_2)_4$ and *i*-PrOH, there is evidence for the formation of a $W_2(\mu\text{-}H)$-containing species.

Further studies of these reactions are clearly warranted.

Experimental Section

General Procedures. Throughout the syntheses, care was taken to maintain dry and oxygen-free atmospheres (nitrogen) and solvents. Standard Schlenk procedures were coupled with the use of Vacuum Atmospheres Co. Dri-Lab Systems.

^{1}H and ^{2}H NMR spectra were recorded by using either a Varian HR-220 or a Nicolet NT-360 spectrometer. Infrared spectra were obtained from Nujol Mulls Between CsI plates with the use of a Perkin-Elmer 283 spectrophotometer and data were calibrated with polystyrene. Mass spectra were obtained, courtesy of Mr. Peter Cook, by the method of direct insertion using an AE1 MS902 spectrometer. Elemental analyses were performed by Alfred Bernhardt Analytical Laboratories, West Germany, using drybox sampling techniques.

Chemicals. $W_2R_2(NMe_2)_4$ compounds were made by the published procedure involving the reaction of $W_2Cl_2(NMe_2)_4$ with organolithium reagents.[8,9] CD_3CH_2Li was synthesized from CD_3CH_2Br which was purchased from Merck, Sharp and Dohme.

The alcohols were commercially available. Ethanol and 2-propanol were distilled over calcium hydride and sodium, respectively. Neopentyl alcohol was dissolved in toluene and stored over molecular sieves. *tert*-Butyl alcohol was distilled from benzene as an azeotrope and stored over molecular sieves.

Preparation of $W_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$. $W_2Me_2(NMe_2)_4$ (0.69 g, 1.2 mmol) was dissolved in 20 mL of hexane at 0 °C to give a bright yellow solution. *tert*-Butyl alcohol (1.2 mL, 5.0 mmol, 4.3 equiv) was added via microsyringe. The solution immediately turned dark red-brown, and the solvent and other volatile compounds were removed in vacuo at 0 °C. The sticky dark red residue was then redissolved in hexane (5 mL), and pyridine 0.40 mL, 5.0 mmol) was added to give a dark red solution. Red-brown crystals form upon cooling to −20 °C; yield ca. 70% based on W.

Analytical data and ^{1}H NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull, CsI plates): 480 (w), 545 (w), 570 (w), 692 (m), 718 (w), 750 (m), 771 (m), 780 (m), 938 (br), 984 (s, br), 1022 (m), 1035 (m), 1062 (w), 1171 (s), 1225 (m), 1260 (2), 1350 (s), 1360 (s), 1600 (m) cm^{-1}.

Preparation of $W_2(CH_2CMe_3)_2(O\text{-}t\text{-}Bu)_4$. $W_2(CH_2CMe_3)_2(NMe_2)_4$ (0.61 g, 0.87 mmol) was dissolved in hexane (20 mL) to give a bright yellow solution. *tert*-Butyl alcohol (1.0 mL, 4.2 mmol) was added while the solution was stirred. The solution was stirred for 8 h and then evaporated to dryness in vacuo. The crude product was sublimed at 80 °C (10^{-4} mmHg) to give a bright red solid. Analytical data and NMR data for this compound are reported in Tables I and II, respectively. The analysis was not satisfactory which is probably due to the presence of $W_2(O\text{-}t\text{-}Bu)_6$.

Preparation of $W_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$. *i*-PrOH (0.35 mL, 4.6 mmol) was added via microsyringe to a solution of $W_2(CH_2CMe_3)_2(NMe_2)_4$ (0.700 g, 1.00 mmol) in hexane (15 mL). The solution was evaporated to dryness after 2 h under a dynamic vacuum, and the yellow solid was sublimed at 70 °C (10^{-4} mmHg) to yield $W_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$ as an orange crystalline solid (79% yield). Analytical data and ^{1}H NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 300 (w), 460 (w, br), 550 (w), 618 (s), 632 (m), 720 (w), 735 (2), 851 (s), 978 (vs), 990 (s), 1110 (s), 1124 (m), 1128 (m), 1162 (m), 1227 (m), 1258 (w), 1320 (s), 1353 (m), 1366 (s) cm^{-1}.

Preparation of $W_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$. Similar procedure as for $W_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$ was used, but with Me_3CCH_2OH. Reaction time equaled 1.5 h. The residue was recrystallized from hexane to yield orange-red crystalline $W_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$ (83%). Analytical data and NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 368 (w), 400 (w), 455 (w, br), 690 (m), 720 (w), 750 (w), 800 (w, br), 902 (w), 1022 (s), 1060 (vs, br), 1216 (w), 1258 (w), 1360 (s), 1390 (s) cm^{-1}.

Preparation of $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$. $W_2(i\text{-}Bu)_2(NMe_2)_4$ (0.70 g, 1.1 mmol) was dissolved in hexane (30 mL) to give a bright yellow solution. Addition of *i*-PrOH (340 μL, 4.5 mmol) caused the solution to darken slightly. The reaction was evaporated to dryness at reduced pressure after 45 min to give a yellow-brown solid which was recrystallized from hexane (3 mL). It is necessary to store $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ at −20 °C to prevent decomposition. Analytical data and NMR data are reported in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 399 (w), 430 (m), 458 (w), 618 (s), 720 (w), 852 (s), 988 (vs), 1111 (s), 1127 (m), 1163 (m), 1298 (m), 1318 (s), 1362 (s) cm^{-1}.

Preparation of $W_2(Et)_2(O\text{-}t\text{-}Bu)_4$. *tert*-Butyl Alcohol (4.17 M benzene azeotrope, 3.3 mL, 6.0 mmol) was added to a solution of $W_2Et_2(NMe_2)_4$ (0.70 g, 1.2 mmol) in hexane (20 mL). The solution immediately changed from yellow to bright red. The solution was evaporated to dryness under a dynamic vacuum after 30 min to give an oily red solid. The major product is $W_2Et_2(O\text{-}t\text{-}Bu)_4$ with some $W_2Et(O\text{-}t\text{-}Bu)_5$ as evidenced by ^{1}H NMR spectroscopy. Attempts to sublime the crude product at 80 °C leads to decomposition and does not result in separation of the two compounds. Addition of pyridine to the crude product causes the solution to turn brown; no crystalline material was obtained.

Preparation of $W_2(Pr)_2(O\text{-}t\text{-}Bu)_4$. Similar procedure as for $W_2Et_2(O\text{-}t\text{-}Bu)_4$ was used except employing $W_2(i\text{-}Pr)_2(NMe_2)_4$, and reaction time equaled 1 h. The major product formed was $W_2(n\text{-}Pr)_2(O\text{-}t\text{-}Bu)_4$.

$W_2(Ph)_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$. In a Schlenk reaction vessel, $W_2(C_6H_5)_2(NMe_2)_4$ (0.815 g, 1.17 mmol) was dissolved in hexane (15 mL) and cooled to 0 °C. Four and one-tenth equiv of isopropyl

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(13) Chisholm, M. H.; Huffman, J. C.; Smith, C. A. *J. Am. Chem. Soc.* **1986**, *106*, 222.

alcohol (370 μL, 4.80 mmol) was syringed into the reaction mixture. The solution was stirred at 0 °C for 1 h during which time the color gradually changed from orange to brown. The solution was evaporated to dryness in vacuo; the brown residue was extracted into hexane (5 mL) and cooled to −15 °C. After 24 h, large brown cubic crystals were isolated by filtration and dried in vacuo. A second crop of crystals was collected by reducing the volume of the filtrate and cooling to −15 °C (total crystalline yield 0.447 g, 48%). Analytical and NMR data are given in Tables I and II, respectively.

Infrared data (Nujol mull between CsI plates): 1569 (w), 1418 (vw), 1362 (m), 1318 (m), 1259 (vw), 1165 (m), 1129 (m), 1119 (s), 1110 (vs), 1000 (m), 981 (vs), 897 (w), 858 (m), 725 (sh), 695 (m), 620 (m), 450 (w), 300 (vw) cm^{-1}.

$W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$ was prepared similarly employing $W_2(p\text{-tolyl})_2(NMe_2)_4$. NMR data are recorded in Table II.

$W_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$. In a Schlenk reaction vessel, $W_2(CH_2Ph)_2(NMe_2)_4$ (260 mg, 0.36 mmol) was dissolved in pentane (20 mL). Four and one-tenth equiv of *i*-PrOH (0.11 mL, 1.48 mmol) was added at room temperature and the mixture stirred for 1.0 h. The solution was then evaporated to dryness in vacuo; the residue was extracted into pentane (ca. 2 mL) and cooled to −15 °C. After 24 h, brown crystalline $W_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$ was harvested by filtration and drying in vacuo (yield 180 mg, 63%).

Crystallographic Studies. General operating procedures and listings of programs have been previously described.[14] A summary of crystal data is given in Table VII.

$W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$. The crystal used for characterization and data collection was an irregular fragment cleaved from a larger crystal. The air-sensitive sample was transferred to the goniostat by using inert-atmosphere handling techniques and cooled to −167 °C. A search of a limited hemisphere of reciprocal space yielded a set of reflections that showed no evidence of symmetry or systematic extinctions. The unit cell was identified as triclinic, space group $P\bar{1}$. This choice was confirmed by the subsequent solution and refinement of the structure.

The structure was solved by means of Patterson and Fourier methods. The hydrogen atoms were locatable and were included in the least-squares refinements with isotropic thermal parameters, while all non-hydrogen atoms were assigned anisotropic thermal parameters. An absorption correction was carried out. In the least-squares refinement a total of 211 parameters were varied. A total of 1605 reflections having F greater than $3\sigma(F)$ were used. The final difference map was essentially featureless with a few peaks in the vicinity of the W atoms.

$W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$. A suitable crystal was located and transferred to the goniostat by using inert-atmosphere handling techniques and cooled to −155 °C for characterization and data collection.

A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and systematic extinctions corresponding to the unique space group $P2_1/c$. This choice was confirmed by the subsequent solution and refinement of the structure.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least squares. Numerous atoms converged to nonpositive definite thermal parameters when allowed to vary anisotropically, and an examination of ψ scans of several reflections indicated an absorption correction was necessary. Unfortunately, the crystal was very poorly shaped, and the absorption correction, while improving the overall residuals, did not improve the anisotropic refinement. For this reason, and due to the low parameter to observation ratio, only the two metal atoms were assigned anisotropic thermal parameters. Hydrogen atoms were placed in fixed idealized positions for the final cycles of refinement.

A final difference Fourier was essentially featureless, with the two largest peaks being 1.84 and 1.59 e/Å^3, each located near a metal site.

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Registry No. $W_2Me_2(O\text{-}t\text{-}Bu)_4(py)_2$, 101860-11-1; $W_2Me_2(NMe_2)_4$, 72286-64-7; $W_2(CH_2CMe_3)_2(O\text{-}t\text{-}Bu)_4$, 101860-12-2; $W_2(CH_2CMe_3)_2(NMe_2)_4$, 72286-69-2; $W_2(CH_2CMe_3)_2(O\text{-}i\text{-}Pr)_4$, 101860-13-3; *i*-PrOH, 67-63-0; *t*-BuOH, 75-65-0; $W_2(CH_2CMe_3)_2(OCH_2CMe_3)_4$, 101860-14-4; Me_3CCH_2OH, 75-84-3; $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$, 101860-15-5; $W_2(i\text{-}Bu)_2(NMe_2)_4$, 101860-16-6; $W_2(Et)_2(O\text{-}t\text{-}Bu)_4$, 101860-17-7; $W_2(Et)_2(NMe_2)_4$, 72286-65-8; $W_2(Et)(O\text{-}t\text{-}Bu)_5$, 101860-18-8; $W_2(Pr)_2(O\text{-}t\text{-}Bu)_4$, 101860-19-9; $W_2(i\text{-}Pr)_2(NMe_2)_4$, 72286-68-1; $W_2(Ph)_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$, 101915-85-9; $W_2(Ph)_2(NMe_2e_4$, 84417-25-4; $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$, 101915-86-0; $W_2(p\text{-tolyl})_2(NMe_2e_4$, 84417-28-7; $W_2(CH_2Ph)_2(O\text{-}i\text{-}Pr)_4$, 99639-27-7; $W_2(CH_2Ph)_2(NMe_2)_4$, 82555-52-0; W, 7440-33-7; $W_2(n\text{-}Pr)(O\text{-}t\text{-}Bu)_5$, 101860-20-2; $W_2(n\text{-}Pr)(O\text{-}i\text{-}Pr)_5$, 101860-21-3.

Supplementary Material Available: Tables of anisotropic thermal parameters, complete listings of bond distances and angles, stereoviews, and listings of F_o and F_c for $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ and $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$ (20 pages). Ordering information is given on any current masthead page. The complete structural reports are available in microfiche form only, from the Indiana University Chemistry Library at a cost of $2.50 per copy. Request MSC Reports Nos. 83017 and 85101 for $W_2(i\text{-}Bu)_2(O\text{-}i\text{-}Pr)_4$ and $W_2(p\text{-tolyl})_2(O\text{-}i\text{-}Pr)_4(HNMe_2)$, respectively.

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[14] Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.