order to better understand the relationship between steric bulk and reactivity in Re(0) radicals.

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Synthesis, Structure, and Reactions of 2,2′-Bipyridyl Complexes of Tetramethyloxotungsten(VI) and Dimethyldioxotungsten(VI) and of Related Compounds

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Tetramethyl(2,2′-bipyridyl)oxotungsten(VI), $(CH_3)_4W(O)(bpy)$ (1), and several dialkyl complexes of the composition $R_2W(O)_2(bpy)$, where bpy = 2,2′-bipyridyl and R = CH_3 (2), C_2H_5 (3), n-C_3H_7 (4), and $CH_2C(CH_3)_3$ (5), were synthesized. Complexes 1, 2, and 4 were characterized by X-ray crystallographic analysis. Complex 1, a new seven-coordinate organometallic complex of W(VI), has a distorted pentagonal-bipyramidal coordination geometry with oxygen and one bpy nitrogen in the apexal positions. The W=O bond length is 1.699 (4) Å. The four methyl groups show pairwise nonequivalence at near identical W–C bond lengths of 2.216 (8) Å. The compound hydrolyzes slowly with evolution of CH_4 to yield 2. Complex 2 is isomorphous with the known corresponding molybdenum complex; its mean W=O bond lengths of 1.722 (3) Å are slightly longer, and the mean W–C bond lengths of 2.192 (2) Å are virtually identical with the corresponding bonds in $(CH_3)_2Mo(O)_2(bpy)$. The structural analysis of 4 revealed similar in-plane bond lengths and positional disorder of the n-propyl groups.

In our studies of organometallic derivatives of molybdenum(VI) we previously reported the synthesis, properties, and structures of compounds of composition $R_2Mo(O)_2(bpy)$, where R = alkyl, aralkyl, and aryl and bpy = 2,2′-bipyridyl,[2] by the reactions of $Br_2Mo(O)_2(bpy)$[3] with the corresponding organomagnesium bromides. We have since extended our studies to complexes of oxotungsten(VI), of which still only comparatively few organometallic derivatives are known.[4] The methylation of $W(O)Cl_4$ was previously investigated by several groups,[5,6] but only an unstable monomethyl derivative, $CH_3W(O)Cl_3 \cdot OEt_2$, and several of its adducts with mono- and bidentate ligands were obtained, none of which were structurally characterized. Wilkinson and his school recently demonstrated[7] that all four chloride ions of $W(O)Cl_4$ are displaced on reaction with CH_3MgCl in tetrahydrofuran (THF). The reaction occurs with concomitant reduction of W(VI) to W(V), however, producing the saltlike compound $[(CH_3)_4WO]_2Mg(THF)_4$. In our studies of the methylation of oxobromotungsten(VI) complexes of bpy we have obtained $(CH_3)_4W(O)(bpy)$ (1), a new seven-coordinate organometallic complex of oxotungsten(VI). In addition, we also prepared $(CH_3)_2W(O)_2(bpy)$ (2) and the higher dialkyl derivatives of the type $R_2W(O)_2(bpy)$ with R = C_2H_5 (3), n-C_3H_7 (4), and $CH_2C(CH_3)_3$ (5). The structures of 2 and 4 were determined by X-ray crystallographic methods.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were recorded on a GE QE-300 instrument at 300 MHz (^1H) and on an EM 390 instrument at 90 MHz. UV–vis spectra were measured on a Beckman DU-40 spectrophotometer. Gaseous hydrocarbons formed on thermolysis or photolysis were measured by GLPC as described in ref 2a.

All commercially available inorganic reagents and chemical of "analytical" or "reagent grade" purity were used as received. Alkylmagnesium halides were prepared from freshly distilled alkyl bromides and Mg in dried and distilled THF.

The complex $Br_2W(O)_2(bpy)$ was obtained as a white solid by the reaction of $W(CO)_4(bpy)$ with Br_2 in ethanol as described in ref 3 when moist ethanol, i.e., 95–97% C_2H_5OH, was employed. When the reaction was carried out in highly dried C_2H_5OH, the reaction products were brown-to-yellow insoluble powders that on contact with water converted rapidly into $Br_2W(O)_2(bpy)$. The products approached the composition $Br_4W(O)(bpy)$, but further characterization was precluded due to their insolubility. IR spectra

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[2] (a) Schrauzer, G. N.; Schlemper, E. O.; Liu, N. H.; Wang, Q.; Rubin, K.; Zhang, X.; Long, X.; Chin, C. S. *Organometallics* **1986**, *5*, 2452. (b) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Ross, F.; Ross, D.; Schlemper, E. O. *Organometallics* **1983**, *2*, 481. (c) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Robinson, P. R.; Schlemper, E. O. *Organometallics* **1982**, *1*, 44.

[3] Hull, C. G.; Stiddard, M. H. B. *J. Chem. Soc., A* **1966**, 1633.

[4] (a) Kress, J. R. M.; Russell, M. J. M.; Wesolek, M. G.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 431. (b) Feinstein-Jaffe, I.; Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 7176. (c) Feinstein-Jaffe, I.; Dewn, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 1189. (d) Alt, H. G.; Hayen, H. I. *J. Organomet. Chem.* **1986**, *316*, 105. (e) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1985**, *5*, 398. (f) Legzins, P.; Phillips, E. C.; Rettig, S. J.; Sanchez, L.; Trotter, J.; Yee, V. C. *Organometallics* **1988**, *7*, 1877. (g) Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559.

[5] Fowles, G. W. A.; Frost, J. L. *J. Chem. Soc. (Inorg. Phys. Theoret.)* **1967**, 671.

[6] (a) Santini-Scampucci, C.; Riess, J. G. *J. Chem. Soc., Dalton Trans.* **1976**, 195. (b) Santini-Scampucci, C.; Riess, J. G. *J. Organomet. Chem.* **1974**, *73*, C13. (c) Muetterties, E. L.; Band, E. *J. Am. Chem. Soc.* **1980**, *102*, 6572.

[7] Stavropoulos, P.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1987**, *6*, 1081.

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Table I. Crystallographic Data Collection Parameters of Complexes 1, 2, and 4

	1	2	4
formula	$[(CH_3)_4W(O)(bpy)]_2CH_2Cl_2$	$(CH_3)_2W(O)_2(bpy)$	$(n\text{-}C_3H_7)_2W(O)_2(bpy)$
space group	$C2/c$	$P\bar{1}$	$P2_1/n$
a, Å	28.488 (6)	8.539 (2)	8.432 (3)
b, Å	7.188 (2)	9.890 (2)	13.848 (3)
c, Å	16.586 (3)	8.498 (2)	14.726 (4)
α deg		101.73 (2)	
β, deg	99.87 (2)	116.86 (2)	99.33 (2)
γ, deg		80.12 (2)	
V, Å^3	3346 (1)	624.2 (2)	1696.8 (6)
T, °C	23	23	23
ρ, g/cm^3 (calcd)	1.821 (2)	2.139	1.794
Z	4	2	4
fw	917.3	402.11	458.22
cryst size, mm	0.20 × 0.23 × 0.30	0.15 × 0.22 × 0.25	0.20 × 0.23 × 0.28
abs corr		empirical scan	
range of transmissn	0.786–1.00	0.418–1.00	0.781–1.00
total no. of observns	2634	3524	3234
no. of indepnd observns	2536	2109	2968
no. of variables	178	155	213
λ, Å (Mo Kα)	0.7107	0.7107	0.7107
μ, cm^{-1}	72.1	69.6	94.4
scan width θ, deg	0.75 + 0.35 tan θ	0.70 + 0.35 tan θ	0.75 + 0.35 tan θ
$R(F_o)$	0.040	0.024	0.042
$R_w(F_o)$	0.053	0.040	0.044
S	1.333	0.2482	0.9168

Table II. Selected Geometrical Data for 1

Bond Angles, deg			
O1–W–N1	161.3 (2)	N2–W–C14	144.4 (3)
O1–W–N2	91.6 (2)	C11–W–C12	141.6 (3)
O1–W–C11	89.4 (3)	C11–W–C13	72.6 (4)
O1–W–C12	103.6 (3)	C11–W–C14	143.6 (4)
O1–W–C13	111.7 (3)	C12–W–C13	131.0 (3)
O1–W–C14	92.8 (3)	C12–W–C14	72.6 (4)
N1–W–N2	70.2 (2)	C13–W–C14	73.0 (4)
N1–W–C11	81.0 (2)	W–N1–C6	117.4 (4)
N1–W–C12	75.4 (2)	W–N1–C10	123.1 (4)
N1–W–C13	80.8 (3)	C6–N1–C10	119.4 (6)
N1–W–C14	104.4 (3)	W–N2–C1	120.6 (4)
N2–W–C11	71.7 (3)	W–N2–C5	122.7 (4)
N2–W–C12	72.0 (3)	C1–N2–C5	116.6 (6)
N2–W–C13	136.7 (3)		
Bond Distances, Å			
W–O1	1.699 (4)	W–C13	2.196 (9)
W–N1	2.335 (5)	W–C14	2.222 (8)
W–N2	2.221 (5)	N1–C6	1.346 (8)
W–C11	2.227 (8)	N2–C5	1.369 (8)
W–C12	2.210 (8)	C5–C6	1.484 (9)

Table III. Positional Parameters and Their Estimated Standard Deviations for 1

atom	x	y	z	B, Å^2
W	0.36168 (1)	0.07086 (5)	−0.16777 (2)	3.469 (8)
Cl	0.4809 (2)	0.6879 (7)	0.6620 (3)	14.5 (1)
O1	0.3930 (2)	−0.0712 (9)	−0.2210 (4)	5.0 (2)
N1	0.3361 (2)	0.2252 (9)	−0.0593 (4)	3.4 (1)
N2	0.3931 (3)	−0.0631 (9)	−0.0502 (4)	3.8 (2)
C1	0.4188 (3)	−0.219 (1)	−0.0493 (5)	4.7 (2)
C2	0.4393 (4)	−0.308 (2)	0.0235 (6)	5.7 (2)
C3	0.4320 (4)	−0.236 (2)	0.0960 (6)	6.8 (3)
C4	0.4036 (4)	−0.083 (1)	0.0947 (6)	5.9 (3)
C5	0.3848 (3)	0.000 (1)	0.0240 (5)	3.6 (2)
C6	0.3545 (3)	0.169 (1)	0.0170 (5)	3.7 (2)
C7	0.3429 (4)	0.259 (1)	0.0853 (5)	5.0 (2)
C8	0.3112 (4)	0.402 (1)	0.0762 (7)	5.6 (3)
C9	0.29089 (4)	0.458 (1)	−0.0045 (7)	5.4 (2)
C10	0.3057 (4)	0.366 (1)	−0.0697 (6)	4.8 (2)
C11	0.4289 (4)	0.219 (2)	−0.1171 (7)	6.5 (3)
C12	0.3072 (4)	−0.1151 (1)	−0.1310 (7)	5.5 (2)
C13	0.3561 (4)	0.354 (2)	−0.2181 (7)	7.0 (3)
C14	0.2988 (4)	0.075 (2)	−0.2677 (7)	7.8 (4)
C15	0.500	0.816 (2)	0.750	6.8 (4)

showed broad absorptions in the $\nu_{W=O}$ range (950–1000 cm^{-1}); EI and CI mass spectroscopy was attempted but produced only the molecular ion of bpy. Anal. Calcd for $C_{10}H_8N_2Br_4OW$: C, 17.78; H, 1.19; Br, 47.30, W, 27.21. Found: C, 19.50; H, 1.65; Br, 45.60.

Synthesis of $(CH_3)_4W(O)(bpy)$, 1. To a stirred suspension of 2.50 g (3.7 mmol) of $Br_4W(O)(bpy)$ in 10 cm^3 of THF, 7.0 cm^3 of a 3.0 M solution (21 mmol) of CH_3MgBr in THF was added at 0 °C (water–ice bath) over 5 min. The resulting dark-brown suspension was stirred at room temperature for 12 h. The solid, air-sensitive reaction product was qualitatively shown to contain magnesium, tungsten, and coordinated bpy and was usually not isolated. The reaction suspension was instead added immediately to 100 cm^3 of saturated aqueous NH_4Cl solution and transferred into a separatory funnel. The suspension was extracted aerobically with 100 cm^3 of CH_2Cl_2 under vigorous shaking to effect oxidation, yielding a bright-yellow, homogeneous organic phase. After separation, the organic phase was washed twice with deionized water and dried with $MgSO_4$. After evaporation of most of the CH_2Cl_2, 10 cm^3 of n-hexane was added. A pale yellow, crystalline solid precipitated, which was isolated by vacuum filtration. Recrystallization from CH_2Cl_2/n-hexane yielded 0.5 g (1.2 mmol) of 1, mp 160 °C (dec), corresponding to a yield of 32%, based on $Br_4W(O)(bpy)$. In addition, small amounts—usually about 0.5–0.10 g—of the less soluble byproduct $(CH_3)_2W(O)_2(bpy)$, 2, were isolated as a pale-yellow microcrystalline solid. Anal. Calcd for $C_{14}H_{20}N_2OW$: C, 40.40; H, 4.84; W, 44.18. Found: C, 40.21; H, 4.70; W, 44.32. Complex 1 is stable on dry storage in the dark. Gaseous hydrocarbon products and relative yields formed on thermolysis of 1 at 195 °C: CH_4 (100); C_2H_6 (1.1); C_2H_4 (7.5); C_3H_8 (0.01); C_3H_6 (0.95). Relative yields of gaseous products formed on exposure of 1 to a 150-W tungsten filament lamp in 2 h: CH_4 (100); C_2H_6 (8.75); C_2H_4 (8.67); C_3H_8 (0.73); C_3H_6 (0.1). IR spectrum (Nujol) $\nu_{W=O}$ = 961 cm^{-1}; UV-vis absorptions [nm (ϵ), in CH_2Cl_2]: 384 (9275); 303 (12640); 293 (12100); 250 (1920); mass spectrum (^{184}W), m/z (rel intensity, assignment) 401 (41, M − CH_3), 385 (62, M − 2CH_3), 370 (26, M − 3CH_3), 355 (22, M − 4CH_3); ^1H NMR ($CDCl_3$, numbering of H atoms as for carbon atoms in Figure 1) δ 9.47 [d, J_{CH} = 5.4 Hz, bpy-H(1)], 8.36 [d, J_{CH} = 8.7 Hz, bpy-H(10)], 7.64 [t, J_{CH} = 5.7 Hz, bpy-H(2)], 7.43 [t, J_{CH} = 6.0 Hz, bpy-H(9)], 8.03 [t, J_{CH} = 7.8 Hz, bpy-H(3)], 8.15 (t, J_{CH} = 7.8 Hz, bpy-H(8)], 8.25 (t, J_{CH} = 6.6, bpy-H(4,7)], 0.36 (s, 6 methyl H), 1.33 (s, 6 methyl H).

Structural Analysis of $(CH_3)_4W(O)(bpy)$, 1. Complex 1 was recrystallized from CH_2Cl_2/n-hexane, affording crystals of composition $[(CH_3)_4W(O)(bpy)]_2(CH_2Cl_2)$. A crystal of size 0.1 × 0.2 × 0.3 mm was mounted on an Enraf-Nonius CAD-4 automated diffractometer. An empirical ψ scan correction method was employed; the relative range of transmission was 78.6–100%. Crystal decay presumably due to loss of CH_2Cl_2 during data collection was 35% (linear correction). The structure was solved by Patterson and Fourier techniques. Crystallographic data and relevant bond distances and angles are summarized in Tables I–III.

Synthesis of $(CH_3)_2W(O)_2(bpy)$ from 1. Complex **1** (0.020 g, 0.048 mmol) was dissolved in an NMR tube in moist nitromethane-d_3. A slow evolution of CH_4 was observed with parallel changes of the ^1H NMR spectrum. After 2 days of reaction at room temperature in the dark, 0.016 g (0.038 mmol) of pale yellow crystals of **2** was isolated, mp 260 °C (dec), corresponding to a yield of 79%. The crystals were suitable for X-ray analysis. Anal. Calcd for $C_{12}H_{14}N_2O_2W$: C, 35.84; H, 3.52; N, 6.97; O, 7.96; W, 45.72; mol wt 402.11. Found: C, 35.69; H, 3.45; W, 45.65. MS (^{184}W), m/z (rel intensity, assignment) 403 (15, M), 387 (29, M − CH_4). IR $\nu_{W=O}$ (cm^{-1}, in Nujol) 948, 903; UV–vis absorptions [nm (ϵ), in CH_2Cl_2] 350 (776), 306 (12 273), 296 (11 955), 250 (10 133); ^1H NMR (CD_2Cl_2) δ 9.59 [d, J_{CH} = 5.4 Hz, bpy–H(1),(10)], 8.73 [d, J_{CH} = 8.1 Hz, bpy–H(4),(7)], 8.12 [t, J_{CH} = 7.8 Hz, bpy–H(3),(8)], 7.59 [t, J_{CH} = 6.3 Hz, bpy–H(2),(9)], 0.35 [s, W–CH_3 (6)].

Synthesis of 2 from $Br_2W(O)_2(bpy)$. To a stirred suspension of 2.5 g (4.7 mmol) of **2** in 30 cm^3 of the THF was added 18 mmol of methylmagnesium bromide in 6 cm^3 of THF dropwise under argon at 0 °C for a period of 15 min. The reaction suspension was kept at 0 °C for another 15 min and was subsequently allowed to warm to room temperature. After 30 min, the reaction mixture was evaporated in vacuo at room temperature. After addition of 100 cm^3 of water, the suspension was shaken aerobically with portions of 100 cm^3 of CH_2Cl_2 in a separatory funnel. The water extracts were removed and discarded. The pale yellow CH_2Cl_2 solution was dried with anhydrous $MgSO_4$ and concentrated to 10 cm^3. After the addition of 10 cm^3 of n-hexane, a pale-yellow, crystalline solid of composition $C_{12}H_{14}N_2O_2W$ (mp 260 °C (dec)) was obtained, yield 1.5 g, 79% based on $Br_2W(O)_2(bpy)$. The complex prepared by this route was identical with the $(CH_3)_2W(O)_2(bpy)$ formed by the reaction of **1** with H_2O in nitromethane (^1H NMR, IR, and UV–vis spectra). Gaseous hydrocarbon products of anaerobic thermolysis of **2** at 300 °C are as follows: (relative yields in parentheses): CH_4 (100); C_2H_6 (1.90); C_2H_4 (11.3); C_3H_8 (0.14); C_3H_6 (1.90). Gaseous hydrocarbon thermolysis products from $(CH_3)_2Mo(O)_2(bpy)$ at 300 °C are as follows (relative yields in parentheses): CH_4 (100); C_2H_6 (1.45); C_2H_4 (9.60); C_3H_8 (0.14); C_3H_6 (1.42).

Synthesis of $(C_2H_5)_2W(O)_2(bpy)$ (3), $(n\text{-}C_3H_7)_2W(O)_2(bpy)$ (4), and $[(CH_3)_3CCH_2]_2W(O)_2(bpy)$ (5). All were obtained by the reaction of $Br_2W(O)_2(bpy)$ with the corresponding organomagnesium halides in THF in analogy to the synethesis of **2**. Isolated yields ranged from 60 to 70% based on $Br_2W(O)_2(bpy)$; all were recrystallized from CH_2Cl_2/n-hexane.

3: mp 192 °C (dec). Anal. Calcd for $C_{12}H_{18}N_2O_2W$: C, 39.09; H, 4.22; W, 42.74. Found: C, 39.15; H, 4.16; W, 42.62. IR $\nu_{W=O}$ (cm^{-1}, in Nujol) 940, 889; UV–vis absorptions [nm (ϵ), in CH_2Cl_2] 365 (1620), 306 (12 486), 296 (13 126), 251 (10 243); ^1H NMR spectrum [in $CDCl_3$, ppm (intensities)] 7.50–9.65 (8), 1.52 (triplet, J = 0.7 Hz), 1.04 (quartet, J = 0.7 Hz).

4: mp 200 °C (dec). Anal. Calcd for $C_{16}H_{20}N_2O_2W$: C, 41.94; H, 4.84; W, 40.12. Found: C, 41.72; H, 4.90; W, 40.01. IR $\nu_{W=O}$ (cm^{-1}, in Nujol) 941, 890.

5: mp 225 °C (dec). Anal. Calcd for $C_{20}H_{30}N_2O_2W$: C, 46.71; H, 5.88; W, 35.75. Found: C, 46.50; H, 5.76; W, 35.88. IR $\nu_{W=O}$ (cm^{-1}, in Nujol) 942, 891; UV–vis absorptions [in CH_2Cl_2, nm (ϵ)] 370 (1856), 307 (13 196), 296 (13 278), 251 (10 162); ^1H NMR spectrum [in $CDCl_3$, ppm (intensities)] 7.50–9.60 (8, bpy protons), 1.62 (18), 0.95 (4, neopentyl protons).

Structural Analysis of $(CH_3)_2W(O)_2(bpy)$, 2, and of $(n\text{-}C_3H_7)_2W(O)_2(bpy)$, 4. Crystals of **2** were obtained from nitromethane-d_3, and crystals of **4** from CH_2Cl_2/n-hexane. They were mounted on an Enraf-Nonius CAD-4 automated diffractometer. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations. Crystallographic data and results are summarized in Tables II–VII. The n-propyl groups in **4** showed disorder and were modeled for two positions of C(12), C(13), and C(15), i.e., the middle and terminal carbon atoms of one propyl group and the middle carbon atom of the other. For C(12), C(13) and C(12)′, C(13)′ equal occupancies were observed. The occupancy of C(15) is 65%, and of C(15)′, 35%. Because of the disordered structure, the bond distances and angles involving the propyl groups have large standard deviations (see Table V).

Table IV. Selected Geometrical Data for 2

Bond Angles, deg			
O1–W–O2	108.8 (2)	W–N2–C6	120.2 (3)
O1–W–N1	92.9 (1)	W–N2–C10	121.4 (3)
O1–W–N2	161.8 (2)	C6–N2–C10	118.4 (4)
O1–W–C11	97.7 (2)	N1–W–C12	76.8 (2)
O1–W–C12	97.9 (2)	N2–W–C11	78.7 (1)
O2–W–N1	158.3 (1)	N2–W–C12	78.4 (2)
O2–W–N2	89.5 (1)	C11–W–C12	149.6 (2)
O2–W–C11	99.4 (2)	W–N1–C1	120.6 (3)
O2–W–C12	100.1 (2)	W–N1–C5	120.8 (3)
N1–W–N2	68.8 (1)	C1–N1–C5	118.6 (4)
N1–W–C11	76.4 (2)		
Bond Distances, Å			
W–O1	1.715 (3)	N1–C1	1.339 (5)
W–O2	1.728 (3)	N1–C5	1.343 (5)
W–N1	2.302 (4)	N2–C6	1.340 (5)
W–N2	2.333 (3)	N2–C10	1.353 (6)
W–C11	2.195 (4)	C5–C6	1.482 (6)
W–C12	2.194 (5)		

Table V. Positional Parameters and Their Estimated Standard Deviations for 2

atom	x	y	z	B, Å^2
W	0.19895 (2)	0.25628 (2)	0.20483 (2)	2.681 (5)
O1	0.0543 (5)	0.2129 (5)	−0.0134 (5)	4.58 (9)
O2	0.3812 (5)	0.3155 (4)	0.2117 (5)	4.19 (8)
N1	0.0201 (5)	0.1934 (4)	0.3099 (5)	3.04 (8)
N2	0.3254 (5)	0.2919 (4)	0.5157 (5)	2.77 (8)
C1	−0.1344 (7)	0.1434 (6)	0.1966 (7)	3.9 (1)
C2	−0.2519 (7)	0.1158 (6)	0.2543 (7)	4.0 (1)
C3	−0.2057 (6)	0.1348 (6)	0.4333 (7)	3.9 (1)
C4	−0.0478 (6)	0.1841 (5)	0.5535 (6)	3.4 (1)
C5	0.0655 (6)	0.2105 (5)	0.4855 (5)	2.58 (9)
C6	0.2405 (6)	0.2623 (5)	0.6023 (5)	2.70 (9)
C7	0.3119 (6)	0.2789 (6)	0.7881 (5)	2.98 (9)
C8	0.4777 (8)	0.3293 (6)	0.8845 (7)	4.0 (1)
C9	0.5652 (7)	0.3605 (6)	0.7968 (7)	3.8 (1)
C10	0.4866 (7)	0.3393 (5)	0.6128 (7)	3.6 (1)
C11	0.3085 (8)	0.0453 (6)	0.2645 (7)	4.0 (1)
C12	0.058 (1)	0.4542 (6)	0.2592 (9)	5.4 (2)

Table VI. Selected Geometrical Data for 4

Bond Angles, deg			
O1–W–O2	109.4 (2)	N2–W–C11	76.1 (3)
O1–W–N1	90.2 (2)	N2–W–C14	77.6 (4)
O1–W–N2	159.4 (2)	C11–W–C14	147.8 (3)
O1–W–C11	100.2 (3)	W–N1–C1	120.4 (4)
O1–W–C14	97.9 (5)	W–N1–C5	119.8 (5)
O2–W–N1	160.4 (2)	C1–N1–C5	119.8 (5)
O2–W–N2	91.3 (2)	W–N2–C6	120.5 (5)
O2–W–C11	97.3 (3)	W–N2–C10	121.7 (4)
O2–W–W–C14	101.6 (5)	W–C11–C12′	123. (2)
N1–W–N2	69.3 (2)	W–C11–C12	109. (1)
N1–W–C11	76.8 (3)	W–C14–C15	132. (2)
N1–W–C14	76.8 (4)	W–C14–C15′	138. (2)
Bond Distances, Å			
W–O1	1.720 (5)	C5–C6	1.477 (9)
W–O2	1.729 (5)	N1–C1	1.332 (9)
W–N1	2.321 (5)	N1–C5	1.351 (7)
W–N2	2.304 (5)	N2–C6	1.355 (7)
W–C11	2.17 (1)	N2–C10	1.343 (9)
W–C14	2.15 (1)		

Results and Discussion

$(CH_3)_4W(O)(bpy)$, 1. The reaction of $Br_4W(O)(bpy)$ with excess CH_3MgBr in THF at 0 °C results in the formation of a brown, highly oxygen-sensitive insoluble product, presumably the Mg^{2+} salt of an anionic methyl–W^V(bpy) species, from which **1** is generated on aerobic hydrolysis. The yellow, crystalline **1** is itself slowly hydrolyzed further with evolution of CH_4 to yield $(CH_3)_2W$-

Table VII. Positional Parameters and Their Estimated Standard Deviations for 4

atom	*x*	*y*	*z*	*B*,^{a} Å^2
W	0.18533 (4)	0.26660 (3)	0.14826 (3)	6.21 (1)
O1	0.2555 (7)	0.3634 (6)	0.0933 (6)	8.9 (2)
O2	0.3463 (7)	0.1983 (6)	0.2005 (5)	8.3 (2)
N1	−0.0772 (8)	0.3145 (6)	0.0958 (5)	5.5 (2)
N2	0.0059 (8)	0.1627 (6)	0.1998 (5)	5.7 (2)
C1	−0.107 (1)	0.3901 (8)	0.0396 (8)	7.0 (3)
C2	−0.261 (1)	0.4199 (8)	0.0047 (8)	7.3 (3)
C3	−0.388 (1)	0.3680 (8)	0.0296 (8)	6.6 (3)
C4	−0.3586 (9)	0.2899 (7)	0.0884 (7)	5.5 (2)
C5	−0.2006 (9)	0.2637 (6)	0.1200 (6)	5.1 (2)
C6	−0.154 (1)	0.1794 (7)	0.1800 (6)	5.6 (2)
C7	−0.264 (1)	0.1208 (9)	0.2140 (7)	7.3 (3)
C8	−0.208 (1)	0.044 (1)	0.2682 (9)	9.4 (4)
C9	−0.045 (1)	0.0263 (9)	0.2865 (8)	8.7 (3)
C10	0.055 (1)	0.0858 (8)	0.2523 (7)	7.1 (3)
C11	0.111 (1)	0.172 (1)	0.0320 (8)	8.5 (3)
C12′	0.209 (3)	0.154 (2)	−0.038 (2)	8.8 (7)
C12	0.189 (4)	0.211 (2)	−0.053 (2)	11.9 (7)
C13	0.159 (4)	0.142 (2)	−0.129 (2)	11.1 (9)
C13′	0.181 (4)	0.235 (2)	−0.106 (2)	18 (1)
C14	0.121 (2)	0.344 (1)	0.2635 (9)	12.2 (4)
C15	0.183 (3)	0.346 (2)	0.348 (1)	13.6 (8)
C15′	0.155 (5)	0.406 (3)	0.300 (3)	10 (1)*
C16	0.139 (2)	0.425 (1)	0.415 (1)	11.3 (4)

^{a}The starred value indicates that the atom was refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

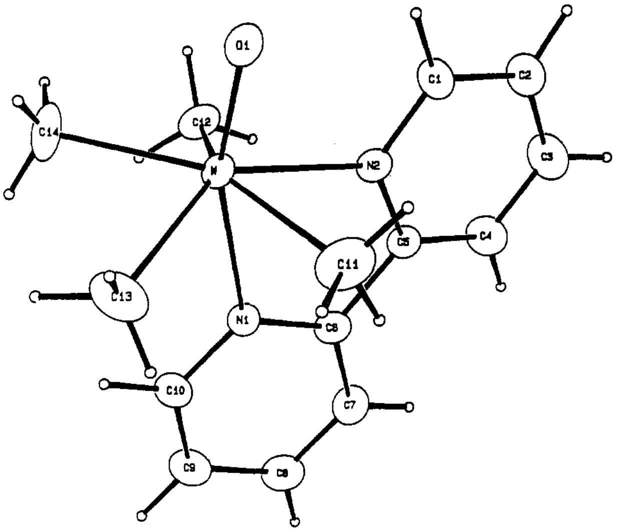

Figure 1. Perspective view of $(CH_3)_4W(O)(bpy)$, **1**, and numbering of atoms as mentioned in the text. The hydrogen atoms are shown as small spheres.

$(O)_2(bpy)$, **2** (eq 1), and hence complex **2** is invariably formed as a byproduct of the synthesis of **1**.

$$(CH_3)_4W(O)(bpy) + H_2O = (CH_3)_2W(O)_2(bpy) + 2CH_4 \quad (1)$$

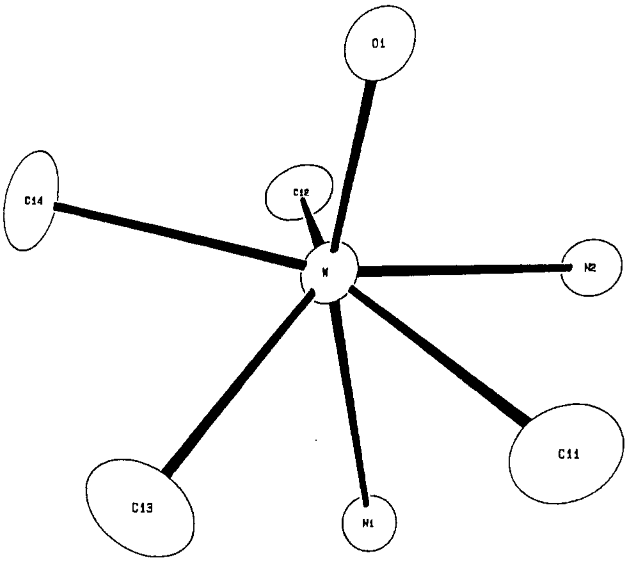

Figure 2. Coordination geometry of W(VI) in **1**.

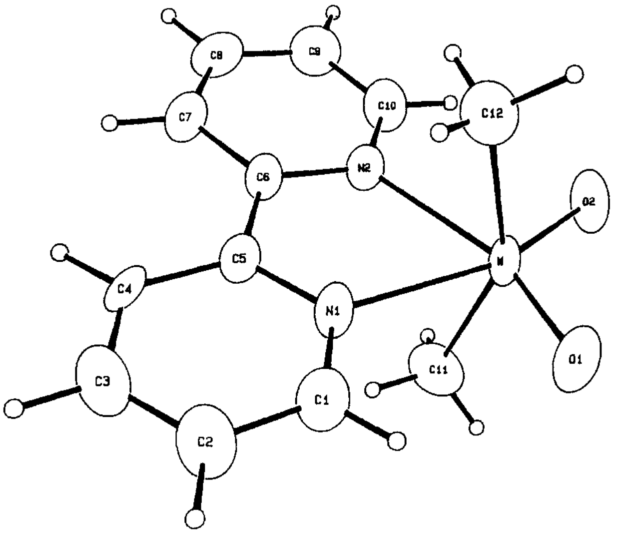

Figure 3. Perspective view of $(CH_3)_2W(O)_2(bpy)$, **2**.

The structure of **1** as determined by X-ray crystallographic methods is shown in Figure 1. The seven-coordinate coordination geometry of W(VI) in Figure 2 reveals a distorted pentagonal bipyramid in which the apical positions are occupied by the oxygen atom and one of the bpy nitrogen atoms, N(1). It thus differs fundamentally from that of $Cl_4W(O)(diars)$,[8] where diars = *o*-phenylenebis(dimethylarsine), in which diars occupies equatorial sites and the pentagonal bipyramidal coordination geometry is less distorted. The W–O bond length of 1.699 (4) Å is typical for W–O bonds in monooxo derivatives shortened by d_π–p_π interactions.[9] The N(1)–W distance of 2.335 (5) Å exceeds that of W–N(2) by 0.114 (5) Å, and the N(1)–W–O(1) angle is 161.3 (2)°. The carbon atoms of the four methyl groups and the bpy N atom N(2) occupy the base of an idealized pentagonal bipyramid with nearly equal equatorial bond distances of 2.220 (8) Å and bond angles of 72.0 (4)°. Two of the methyl groups (i.e., C(11) and C(14) and N(2) are coplanar with W and in a plane perpendicular to the W–O bond axis. The bonds from W to C(12) and C(13) are bent downward by 13.6 (3)° and 21.7 (3)°, respectively, but their angles with W–N(1) of 80.9 (3)° are both identical. Although the angles C(12)–W–N(1) and C(13)–W–N(1) of 75.4 (2)° and 80.8 (3)° differ, two pairs of the methyl groups, i.e., C(11),C(12) and C(13),C(14), may be regarded as equivalent. This is consistent with the ^1H NMR spectrum in $CDCl_3$, which, in addition to the signals of the bpy protons in the range 7.37–9.48 ppm, shows two signals of equal intensity at 0.36 and 1.33 ppm. These signals remain unchanged from −50 to +50 °C; they broaden

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[8] Drew, M. G. B.; Mandyczewsky, R. *J. Chem. Soc., Chem. Commun.* **1970**, 292.

[9] Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899.

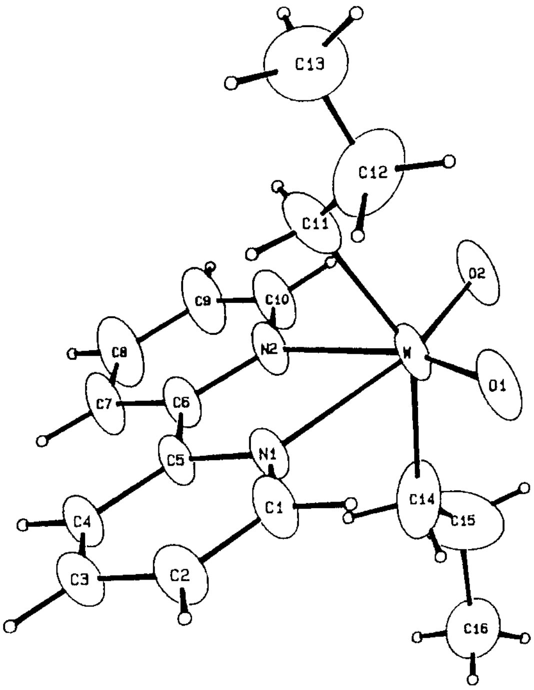

Figure 4. Perspective view of $(n\text{-}C_3H_7)_2W(O)_2(bpy)$, **4**, showing one configuration of the *n*-propyl groups.

slightly at 80 °C in CD_3NO_2 solution without changing their chemical shifts.

The dimethyl derivative **2** was found to be isomorphous with the corresponding molybdenum complex.[2c] The structure of **2** is shown in Figure 3. The mean W–O bond lengths of 1.72 (1) Å are slightly longer than the mean Mo–O bonds of 1.708 (2) Å, and the mean W–N bonds of 2.32 (2) Å are shorter than the Mo–N bonds of 3.22 (2) Å; the W–C and Mo–C bond lengths are essentially identical. There are no consistent differences of any bond angles in the molecules of **2** and its molybdenum analogue. Although **2** (mp 260 °C (dec)) is more stable thermally than its molybdenum analogue (mp 230 °C (dec)), both complexes produce the same gaseous hydrocarbons on thermolysis at 300 °C at virtually the same relative yields (see Experimental Section).

The X-ray crystallographic analysis of **4** revealed a disordered orientation of the *n*-propyl groups. A structure of **4** with one configuration of the propyl groups is shown in Figure 4. The in-plane bond distances and angles of **4** were also found to be essentially identical with those of **2**. The W–C distances appear shorter, but this may be an artifact due to the positional disorder of the propyl groups. The ^1H NMR signals of the alkyl group protons of the complexes are also observed as chemical shifts closely similar to those of the Mo derivatives, indicating the virtual identity of the chemical environments. In the infrared spectra, the two $\nu_{W=O}$ absorptions are observed at somewhat higher frequencies than expected from the reduced mass difference, indicating a higher W=O bond order due to stronger tungsten–oxygen orbital interactions.

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Supplementary Material Available: Tables of equivalent positions, scattering factors, least-squares parameters, positional parameters, torsion angles, and least-squares planes for complexes 1, 2, and 4 (36 pages); listings of observed and calculated structure factors for complexes 1, 2, and 4 (41 pages). Ordering information is given on any current masthead page.