Organometallic Dioxotungsten(VI) Complexes of the Hydrotris(3,5-dimethyl-1-pyrazolyl)borate Ligand

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Summary: Reaction of WO_2Cl_2 with $K\{HB(Me_2pz)_3\}$ [HB-$(Me_2pz)_3^-$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate anion] in *N,N*-dimethylformamide produces *cis*-$\{HB$-$(Me_2pz)_3\}WO_2Cl$ (**1**), which reacts with Grignard reagents in tetrahydrofuran to yield the organometallic dioxo-W(VI) complexes *cis*-$\{HB(Me_2pz)_3\}WO_2(R)$ (R = Me (**2**), Et (**3**), CH_2Ph (**4**), Ph (**5**)). The X-ray structures of **3** and **5** reveal that the monomeric complexes possess distorted-octahedral coordination spheres composed of a facially tridentate $HB(Me_2pz)_3^-$ ligand, two terminal oxo ligands, and an η^1-hydrocarbyl group.

Organometallic oxo complexes are important molecular models for the surface species formed at intermediate stages of metal oxide catalyzed reactions.[2,3] Although the majority are polynuclear cyclopentadienyl, alkyl, or μ_3-oxo carbonyl complexes, research in the 1980s produced a host of remarkably stable mononuclear complexes of oxophilic early transition metals.[3] Organometallic oxo complexes of tungsten[3-7] commonly contain alkyl,[3-7] cyclopentadienyl,[3-5] or 2,2'-bipyridyl (bpy)[3,6] ligands; with the the exception of (bpy)$WO_2(R)_2$ and (bpy)$WO_2(R)X$ complexes, hydrocarbyl ligands containing β-hydrogens generally are not featured in this chemistry. Our recent work has demonstrated the ability of the hydrotris(3,5-di-methyl-1-pyrazolyl)borate ligand, $HB(Me_2pz)_3^-$, to stabilize complexes containing otherwise reactive ligands; these include thio-,[8,9] nitrido-,[10] and hydrosulfido–Mo[9] and

oxo(carbonyl)–[11] and thio–W[12] complexes. It was our conviction that hydrocarbyl oxo–Mo and oxo–W complexes, even those containing β-hydrogens, would be similarly stabilized by this ligand. The accessibility of $Cp'WO_2(R)$ (Cp' = η^5-$C_5H_5^-$, η^5-$C_5Me_5^-$) complexes[4,5] further supports this tenet, as $C_5Me_5^-$ and $HB(Me_2pz)_3^-$ are frequently observed to form analogous metal complexes. Interestingly, $Cp'WO_2(R)$ and related complexes containing hydrocarbyl groups with β-hydrogens have not yet been synthesized. We report herein the synthesis and characterization of the (hydrocarbyl)dioxotungsten(VI) complexes *cis*-$\{HB(Me_2pz)_3\}WO_2(R)$ (R = Me (**2**), Et (**3**), CH_2Ph (**4**), Ph (**5**)) formed in the reactions of Grignard reagents with $\{HB(Me_2pz)_3\}WO_2Cl$ (**1**), a complex also reported here for the first time. The X-ray crystal structures of **3** and **5** confirm the formulation of the complexes as mononuclear, six-coordinate organometallic *cis*-dioxo species; the structure of **3** is only the second reported for an (ethyl)oxotungsten complex. A preliminary account of this work has appeared.[12a]

Experimental Section

General Comments. The compounds WO_2Cl_2[13] and $K\{HB$-$(Me_2pz)_3\}$[14] were prepared according to literature methods. Methylmagnesium chloride (3.0 M in tetrahydrofuran) was used as obtained from Aldrich Chemical Co. All solvents used were carefully dried, distilled, and deoxygenated before use. Unless otherwise stated, all reactions were performed under an atmosphere of pure dinitrogen, employing standard Schlenk line techniques; workups were performed in air. Infrared spectra were obtained on a Perkin-Elmer 1430 ratio recording IR spectrophotometer using pressed KBr disks. The ^1H NMR spectra were recorded on a Bruker AM-400 FT-NMR spectrometer fitted with an Aspect 3000 computer and were referenced against internal $CHCl_3$. Electron impact (70 eV) mass spectra were obtained on a VG-TRIO-1 spectrometer with an ion source temperature of 200 °C. Decomposition temperatures were recorded in air using an Electrothermal melting point apparatus. Microanalyses were performed by Atlantic Microlabs, Norcross, GA.

Syntheses. $\{HB(Me_2pz)_3\}WO_2Cl$ (**1**). A mixture of finely ground WO_2Cl_2 (1.39 g, 4.85 mmol) and $K\{HB(Me_2pz)_3\}$ (1.64 g, 4.88 mmol) was stirred in *N,N*-dimethylformamide (40 mL) for 20 h. The pale green mixture was then filtered in air, washed

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with acetone and ether, and then purified by Soxhlet extraction with dichloromethane to give the white crystalline product. Yield: 1.82 g (70%). IR (cm⁻¹): 3140 (w), 2965 (w), 2925 (w); ν(B–H) 2560 (m), 1540 (s), 1445 (s), 1415 (s), 1390 (s), 1365 (s), 1210 (s), 1180 (s), 1075 (s), 1065 (s), 1045 (s), 990 (w); $\nu(cis\text{-}WO_2)$ 960 (s) and 915 (s), 880 (m), 865 (s), 815 (s), 790 (m), 690 (m), 640 (m), 470 (m), 380 (m); ν(W–Cl) 345 (s). ¹H NMR (CDCl₃): δ 2.36 (s, 3 H, CH₃), 2.38 (s, 6 H, 2 CH₃), 2.69 (s, 3 H, CH₃), 2.70 (s, 6 H, 2 CH₃), 5.89 (s, 2 H, 2 CH), 5.92 (s, 1 H, CH). Mass spectrum: m/z 548 (8%), [M]⁺.

{HB(Me₂pz)₃}WO₂(Me) (2). A suspension of 1 (0.50 g, 0.91 mmol) in tetrahydrofuran (30 mL) was treated with methylmagnesium chloride (2.73 mmol) and stirred overnight. The resulting mixture was reduced to ca. 8 mL and the substantially pure product removed by filtration. The white compound may be purified by column chromatography (silica gel/dichloromethane) as the second of two UV-active bands. Yield: 0.34 g (71%). Decomposition takes place at 210 °C. IR (cm⁻¹): 3130 (w), 2970 (w), 2930 (m), 2860 (w); ν(B–H) 2550 (m), 1540 (s), 1490 (w), 1445 (s), 1415 (s), 1385 (s), 1365 (s), 1205 (s), 1185 (s), 1070 (s), 1045 (s), 990 (w); $\nu(cis\text{-}WO_2)$ 960 (s) and 915 (s), 880 (w), 865 (s), 815 (m), 790 (m), 735 (w), 695 (m), 645 (m), 515 (w), 470 (w), 380 (m). ¹H NMR (CDCl₃): δ 1.20 (s, 3 H, ¹⁸³W satellites J_{W-H} = 9.8 Hz, CH₃), 2.34 (s, 3 H, CH₃), 2.36 (s, 6 H, 2 CH₃), 2.61 (s, 3 H, CH₃), 2.67 (s, 6 H, 2 CH₃), 5.85 (s, 2 H, 2 CH), 5.86 (s, 1 H, CH). Mass spectrum: m/z 527 (2%), [M – 1]⁺.

{HB(Me₂pz)₃}WO₂(Et) (3). Solid 1 (0.50 g, 0.91 mmol) was treated with ethylmagnesium bromide (2.73 mmol) in tetrahydrofuran (40 mL), the solution was stirred for 1 h and filtered in air, and the filtrate was then evaporated to ca. 8 mL whereupon the white product was collected by filtration. It may be recrystallised from dichloromethane/methanol. Yield: 0.28 g (57%). Decomposition takes place at 205 °C. IR (cm⁻¹): 3120 (w), 2970 (m), 2950 (m), 2930 (m), 2870 (m) ν(B–H); 2550 (m), 1540 (s), 1485 (w), 1445 (s), 1415 (s), 1385 (s), 1355 (s), 1205 (s), 1185 (s), 1070 (s), 1045 (s), 985 (w), 970 (m), 960 (m); $\nu(WO_2)$ 945 (s) and 905 (s), 935 (w), 875 (w), 860 (m), 805 (m), 785 (m), 695 (m), 645 (m), 465 (m), 380 (m). ¹H NMR (CDCl₃): δ 2.07 (2 H, q, J = 7.3 Hz, CH₂CH₃), 2.28 (3 H, t, J = 7.3 Hz, –CH₂CH₃), 2.32 (s, 3 H, CH₃), 2.35 (s, 6 H, 2 CH₃), 2.57 (s, 3 H, CH₃), 2.72 (s, 6 H, 2 CH₃), 5.84 (s, 1 H, CH), 5.87 (s, 2 H, 2 CH). Mass spectrum: m/z 541 (2%), [M – 1]⁺.

{HB(Me₂pz)₃}WO₂(CH₂Ph) (4). Pale-yellow 4 was obtained using benzylmagnesium bromide and a method similar to that employed in the synthesis of 5 (below). Yield: 0.17 g (27%). Decomposition takes place at 235 °C. IR (cm⁻¹): 3130 (w), 3080 (w), 3050 (w), 3030 (w), 2960 (w), 2930 (m), 2860 (w); ν(B–H) 2550 (m), 1595 (m), 1535 (s), 1490 (m), 1445 (s), 1415 (s), 1380 (s), 1365 (s), 1210 (s), 1185 (m), 1070 (s), 1040 (m), 985 (w); $\nu(cis\text{-}WO_2)$ 960 (s) and 915 (s), 880 (w), 865 (m), 820 (m), 790 (m), 735 (m), 695 (m), 645 (m), 465 (w), 440 (w), 375 (w). ¹H NMR (CDCl₃): δ 2.34 (s, 3 H, CH₃), 2.40 (s, 6 H, 2 CH₃), 2.54 (s, 3 H, CH₃), 2.90 (s, 6 H, 2 CH₃), 3.15 (s, 2 H, ¹⁸³W satellites J_{W-H} = 11.7 Hz, CH₂), 5.85 (s, 1 H, CH), 5.94 (s, 2 H, 2 CH), 6.94 (t, 1 H, J_{H-H} = 7.5 Hz, Ph), 7.30 (t, 2 H, J_{H-H} = 7.5 Hz, Ph), 7.46 (d, 2 H, J = 7.5 Hz, Ph). Mass spectrum: m/z 603 (8%), [M – 1]⁺.

{HB(Me₂pz)₃}WO₂(Ph) (5). Solid 1 (0.60 g, 1.09 mmol) was treated with phenylmagnesium bromide (3.33 mmol) in tetrahydrofuran (40 mL) and stirred for 30 min. The dark mixture was filtered in air, reduced to dryness, redissolved in dichloromethane, washed with 0.1 M HCl (3 × 15 mL), dried over sodium suflate, filtered, and evaporated. The white product was obtained by recrystallization from dichloromethane and n-pentane. Further product appears upon volume reduction and refrigeration. Yield: 0.31 g (48%). Decomposition takes place at 285 °C. IR (cm⁻¹): 3120 (w), 3060 (w), 3050 (w), 2960 (w), 2930 (m), 2860 (w); ν(B–H) 2550 (m), 1535 (s), 1445 (s), 1415 (s), 1380 (m), 1365 (s), 1205 (s), 1185 (m), 1065 (s), 1045 (m), 995 (w); $\nu(cis\text{-}WO_2)$ 955 (s) and 910 (s), 880 (w), 860 (m), 815 (m), 800 (m), 785 (m), 730 (m), 695 (m), 645 (m), 470 (w), 380 (w). ¹H NMR (CDCl₃): δ 1.94 (s, 6 H, 2 CH₃), 2.38 (s, 3 H, CH₃), 2.42 (s, 6 H, 2 CH₃), 2.69 (s, 3 H, CH₃), 5.76 (s, 2 H, 2 CH), 5.91 (s, 1 H, CH), 7.09 (5 H, broad, Ph). Mass spectrum: m/z 590 (50%), [M]⁺.

Crystallography. Crystals were grown in air by slow diffusion of n-pentane into dichloromethane solutions of the compounds. Intensity data were measured at 23 °C on an Enraf-Nonius CAD4F

Table I. Crystallographic Data

compd	3·H₂O	5·CH₂Cl₂
formula	C₁₇H₂₉BN₆O₃W	C₂₂H₂₉BCl₂N₆O₂W
fw	560.1	675.1
cryst size, mm	0.13 × 0.16 × 0.60	0.10 × 0.15 × 0.54
cryst syst	triclinic	monoclinic
space group	P1̄ (No. 2)	P2₁/c (No. 14)
a, Å	8.720 (2)	8.006 (1)
b, Å	16.649 (3)	13.957 (1)
c, Å	8.032 (1)	23.788 (3)
α, deg	103.55 (1)	90
β, deg	101.89 (1)	99.31 (1)
γ, deg	98.94 (2)	90
V, Å³	1083.6	2623.1
Z	2	4
ρ_{calcd}, g·cm⁻³	1.717	1.710
F(000)	552	1328
μ, mm⁻¹	5.445	4.694
transm factors	0.465–0.065	0.673–0.349
data collcd	±h,±k,–l	±h,±k,–l
no. of data collcd	3081	4115
no. of unique data	2814	3437
$R_{amal}{}^a$	0.055	0.023
no. of data with $I \geq 2.5\sigma(I)$	2320	2720
R^b	0.044	0.029
g	0.004	0.002
$R_w{}^b$	0.045	0.030
residual density, e·Å⁻³	2.49	1.94

$^a R_{amal} = (\sum\{N\sum[w(F_{mean} - |F_o|)^2]\}/\sum[(N - 1)\sum(w|F_o|^2)])^{1/2}$ where the inner summation is over N equivalent reflections averaged to give F_{mean}, the outer summation is over all unique reflections, and the weight, w, is taken as $[\sigma(F_o)]^{-2}$. $^b R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.
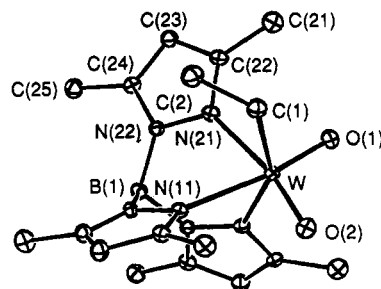
Figure 1. Molecular structure of 3. The labeling of the atoms in the pyrazole rings containing N(11) and N(31) (trans to C(1) but not labeled) parallels that shown for the ring containing N(21).

diffractometer fitted with graphite-monochromated Mo Kα radiation, λ = 0.7107 Å. The ω:2θ scan technique was employed, and data sets were collected up to a maximum Bragg angle of 22.5°. No significant decomposition of 3 occurred during data collection; however, the net intensity values of two standard reflections, monitored after every 7200 s of X-ray exposure time, indicated a linear decrease during the course of the data collection for 5. At the conclusion of the data collection the intensity standards had decreased to 87% of their original values and the data set was scaled accordingly. Lorentz and polarization corrections[15] and analytical absorption corrections[16] were applied in each case. Crystal data are summarized in Table I.

The structures were solved by Patterson and Fourier methods and refined by a full-matrix least-squares procedure based on F.[16] Compound 3 was found to crystallize as the monohydrate, and 5 was characterized as the mono(dichloromethane) solvate. Anisotropic thermal parameters were employed for all non-hydrogen atoms and hydrogen atoms were included in each model at their calculated positions. A weighting scheme of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$ was introduced, and the refinements continued until convergence; final refinement details are listed in Table I.

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Table II. Fractional Atomic Coordinates (×10⁵ for W, ×10⁴ for Other Atoms) and Their Estimated Standard Deviations for 3 • H₂O

atom	x	y	z
W	41624 (5)	20474 (3)	17157 (5)
O(1)	4732 (8)	1343 (5)	144 (9)
O(2)	5585 (8)	2156 (5)	3649 (9)
N(11)	2969 (9)	2975 (5)	3418 (10)
N(12)	1332 (9)	2906 (5)	3047 (10)
N(21)	2012 (10)	2053 (6)	−478 (10)
N(22)	538 (9)	2160 (6)	−212 (9)
N(31)	2192 (9)	1198 (5)	2109 (10)
N(32)	673 (9)	1335 (5)	2012 (9)
B(1)	249 (12)	2140 (8)	1590 (13)
C(1)	5205 (12)	3222 (7)	1165 (13)
C(2)	4151 (13)	3837 (8)	630 (14)
C(11)	5362 (12)	3911 (8)	5705 (13)
C(12)	3595 (11)	3642 (7)	4817 (12)
C(13)	2391 (12)	3995 (7)	5393 (13)
C(14)	994 (11)	3521 (7)	4235 (12)
C(15)	−691 (13)	3601 (9)	4236 (14)
C(21)	3255 (13)	1899 (8)	−3108 (13)
C(22)	1919 (22)	2010 (7)	−2229 (11)
C(23)	388 (12)	2089 (7)	−3027 (12)
C(24)	−443 (12)	2188 (7)	−1714 (12)
C(25)	−2137 (12)	2312 (9)	−1850 (14)
C(31)	3765 (13)	157 (8)	2725 (14)
C(32)	2241 (11)	467 (6)	2474 (12)
C(33)	773 (12)	131 (7)	2602 (12)
C(34)	−202 (12)	673 (7)	2318 (12)
C(35)	−1939 (12)	613 (8)	2319 (14)
O(w)	8460 (10)	4719 (6)	379 (11)
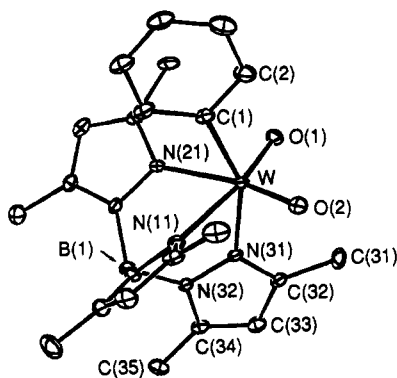
Figure 2. Molecular structure of **5**. The labeling of the atoms in the pyrazole rings containing N(11) and N(21) parallels that shown for the ring containing N(31). The phenyl carbon atoms are labeled C(1) through C(6) in the indicated direction.

Fractional atomic coordinates are listed in Tables II and III; the numbering schemes employed are shown in Figures 1 and 2 which were drawn with the ORTEP[17] program at 20% probability ellipsoids. Selected interatomic bond distances and angles are listed in Table IV. Scattering factors for neutral W (corrected for f' and f'') were from ref 18, while those for the remaining atoms were those incorporated in SHELX76.[16]

Results and Discussion

Reaction of WO_2Cl_2 and $K\{HB(Me_2pz)_3\}$ in *N,N*-dimethylformamide results in the formation of crude **1** which may be readily purified as a white, air-stable, crystalline solid by Soxhlet extraction. The infrared spectrum of **1** exhibits two strong bands at 955 and 910 cm⁻¹, characteristic of a *cis*-dioxo fragment, a strong W–Cl stretch at 345 cm⁻¹, and bands characteristic of the $HB(Me_2pz)_3^-$ ligand (e.g., $\nu(BH)$ at 2555 cm⁻¹). The ¹H NMR spectrum

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Table III. Fractional Atomic Coordinates (×10⁵ for W, ×10⁴ for Other Atoms) and Their Estimated Standard Deviations for 5 • CH₂Cl₂

atom	x	y	z
W	10264 (3)	9430 (2)	17639 (1)
O(1)	2293 (5)	−51 (3)	1821 (2)
O(2)	−397 (5)	709 (3)	2211 (2)
N(11)	−352 (5)	2384 (3)	1531 (2)
N(12)	−631 (6)	2752 (3)	989 (2)
N(21)	2602 (5)	1523 (3)	1114 (2)
N(22)	1941 (5)	2087 (3)	658 (2)
N(31)	−535 (5)	606 (4)	963 (2)
N(32)	−819 (5)	1199 (3)	493 (2)
C(1)	2687 (7)	1862 (4)	2342 (3)
C(2)	3276 (8)	1517 (6)	2893 (3)
C(3)	4399 (10)	2067 (7)	3273 (3)
C(4)	4953 (8)	2948 (6)	3119 (3)
C(5)	4372 (8)	3291 (6)	2588 (3)
C(6)	3269 (7)	2756 (5)	2205 (3)
C(11)	−1082 (8)	2841 (6)	2478 (3)
C(12)	−1075 (7)	2994 (5)	1864 (3)
C(13)	−1785 (9)	3741 (5)	1525 (3)
C(14)	−1490 (8)	3588 (5)	983 (3)
C(15)	−1982 (12)	4163 (5)	458 (4)
C(21)	5478 (8)	988 (5)	1561 (3)
C(22)	4290 (7)	1535 (5)	1130 (3)
C(23)	4680 (8)	2090 (5)	684 (3)
C(24)	3172 (8)	2433 (4)	401 (3)
C(25)	2878 (9)	3095 (6)	−103 (3)
C(31)	−1437 (10)	−1001 (5)	1249 (3)
C(32)	−1457 (7)	−203 (4)	833 (3)
C(33)	−2327 (7)	−116 (5)	286 (3)
C(34)	−1920 (7)	753 (5)	84 (3)
C(35)	−2552 (9)	1191 (5)	−480 (3)
B(1)	−7 (8)	2204 (5)	511 (3)
C(40)	7934 (11)	419 (7)	3399 (4)
Cl(1)	6781 (4)	−220 (2)	3815 (1)
Cl(2)	9240 (5)	1277 (3)	3780 (1)

Table IV. Selected Bond Distances (Å) and Angles (deg) for 3 and 5[a]

	3, R = Et	5, R = Ph
W–O(1)	1.721 (7)	1.711 (4)
W–O(2)	1.729 (6)	1.712 (4)
W–N(11)	2.331 (8)	2.317 (5)
W–N(21)	2.296 (8)	2.295 (4)
W–N(31)	2.175 (8)	2.155 (4)
W–C(1)	2.21 (1)	2.171 (6)
C(1)–C(2)	1.55 (2)	1.40 (1)
O(1)–W–O(2)	103.6 (3)	104.0 (2)
O(1)–W–N(11)	169.2 (3)	167.4 (2)
O(1)–W–N(21)	87.8 (3)	87.5 (2)
O(1)–W–N(31)	99.4 (3)	98.3 (2)
O(1)–W–C(1)	98.0 (4)	97.7 (2)
O(2)–W–N(11)	87.1 (3)	88.5 (2)
O(2)–W–N(21)	168.4 (3)	168.5 (2)
O(2)–W–N(31)	99.3 (3)	99.1 (2)
O(2)–W–C(1)	97.2 (4)	96.9 (2)
N(11)–W–N(21)	81.5 (3)	80.0 (2)
N(11)–W–N(31)	77.3 (3)	78.0 (2)
N(11)–W–C(1)	81.6 (3)	81.8 (2)
N(21)–W–N(31)	76.6 (3)	77.6 (2)
N(21)–W–C(1)	82.9 (3)	82.6 (2)
N(31)–W–C(1)	152.4 (4)	153.8 (2)
W–C(1)–C(2)	121.5 (7)	117.9 (5)
W–C(1)–C(6)		125.1 (5)
C(2)–C(1)–C(6)		116.9 (6)

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

of **1** exhibits six resonances which may be assigned to the methyl and methine protons of the $HB(Me_2pz)_3^-$ ligand in a C_s molecule. A notable feature of the NMR spectrum is the deshielding of the resonance from the unique methine proton relative to that of the two equivalent methine protons. A similar feature is observed in the

spectra of related *cis*-dioxo–Mo(VI) complexes[19] and the organometallic *cis*-dioxo–W(VI) species (vide infra) and appears to be diagnostic of the *cis*-dioxo–M(VI) fragment.

Reaction of **1** with Grignard reagents in tetrahydrofuran results in transmetalation and the formation of the white (**2, 3, 5**) or pale yellow (**4**), air- and water-stable, diamagnetic title compounds. Depending on conditions, various water or dichloromethane solvates are formed when the compounds are recrystallized in air; analytical and spectroscopic results support the ready removal of dichloromethane of solvation when samples are subjected to high vacuum. The infrared spectra of the complexes exhibit two strong bands (ca. 960 and 910 cm^{-1}) characteristic of the *cis*-dioxo fragment and bands typical of the HB-(Me$_2$pz)$_3^-$ ligand (ν(BH) 2550 cm^{-1}). The ^{1}H NMR spectra of the complexes are consistent with molecular C_s symmetry in solution. In all cases, the appropriate pattern of methyl and methine resonances are observed for the HB-(Me$_2$pz)$_3^-$ ligand; the methine resonance pattern is consistent with the presence of a *cis*-dioxo fragment as previously discussed. The methyl derivative **2** exhibits three resonances centered at δ 1.20 which may be assigned to the coordinated methyl group. The large central singlet, due to molecules containing ^{185}W (I = 0, 85.6%), is flanked by satellite resonances produced by coupling (J_{W-H} = 9.8 Hz) of the methyl protons to the ^{183}W nuclei (I = $^1/_2$, 14.4%) in the remainder of the molecules. The chemical shift and the magnitude of the W–H coupling are comparable to those observed for (η^5-C$_5$Me$_5$)WO$_2$(Me) (δ 0.99, J_{W-H} = 10.8 Hz).[5b] The ^{1}H NMR spectrum of ethyl derivative **3** shows the triplet and quartet resonances expected for the coordinated ethyl group, but the quartet resonance is shielded (δ 2.07) with respect to the triplet (δ 2.28). Tungsten–proton coupling was not resolved in the case of **3**. Other ethyltungsten complexes, such as (bpy)WO$_2$(Et)$_2$,[6a] exhibit similar spectral features. Besides well-resolved resonances assignable to the *o-, m-* and *p-*hydrogens of the phenyl group, the NMR spectrum of benzyl derivative **4** exhibited a resonance at δ 3.15, assigned to the benzylic protons, flanked by satellites produced by ^{183}W–H coupling (J_{W-H} = 11.7 Hz). Phenyl derivative **5** is characterized by a single, broad resonance at δ 7.09 in its ^{1}H NMR spectrum. For the alkyl and benzyl complexes **2–4**, mass spectrometry reveals the formation of [M – 1]$^+$ ions whereas the formation of [M]$^+$ ions is indicated in the case of **5**; appropriate isotope patterns were observed in all cases. This observation may arise from initial α-hydrogen loss during ionization of **2–4**, a process which is not possible in the case of **5**. In contrast, but in keeping with the easier reduction of Mo(VI) relative to W(VI),[20] the reaction of Grignard reagents with {HB(Me$_2$pz)$_3$}MoO$_2$Cl leads primarily to the formation of the mixed-valence complex {HB(Me$_2$pz)$_3$}-Mo^{V}O(Cl)(μ-O)Mo^{VI}O$_2${HB(Me$_2$pz)$_3$}.[21]

Complexes **2–5** are thermally very stable, as indicated by decomposition points in excess of 200 °C. As expected, even the β-hydrogen-containing ethyl complex is stable toward decomposition until high temperatures are reached. Generally, several conditions must be met in order for decomposition via β-hydrogen elimination to occur; viz., the organic ligand must contain a β-hydrogen atom, a vacant coordination site must be available, and an accessible olefin product must result from the reaction.[22] We
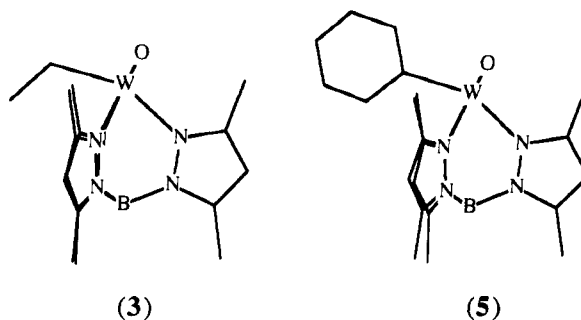
(3)   **(5)**

Figure 3. Comparison of the structures of **3** and **5**. The molecules are viewed perpendicular to the pseudomirror plane containing W, R, and the pyrazole ring containing N(31). Carbon atoms are not labeled.

attribute the stability of **3** to an inhibition of β-hydrogen elimination brought about by the complex's coordinative saturation and the steric bulk of the HB(Me$_2$pz)$_3^-$ ligand, both of which prevent the formation of the requisite four-center transition state. However, we note that Herrmann et al.[23] have provided recent examples of stable *coordinatively unsaturated* oxo–Re(VII) complexes containing β-hydrogen-bearing alkyl ligands, i.e., (R)ReO$_3$ (R = Et, *i*-Bu). The only other tungsten complexes known to be stable toward β-hydrogen elimination are the (bpy)WO$_2$(R)$_2$ (R = Et, *n*-Pr) complexes reported by Schrauzer and co-workers.[6]

The structures of **3** and **5** (Figures 1 and 2, respectively) are very similar and the following discussion applies to both. The molecules possess distorted-octahedral (skewed trapezoidal-bipyramidal) coordination geometries composed of a facial HB(Me$_2$pz)$_3^-$ ligand, two cis terminal oxo ligands, and an η^1-hydrocarbyl group. The trapezoidal plane is defined by atoms O(1), O(2), N(11), and N(21) while atoms N(31) and C(1) constitute the apices of the skewed pyramids. The coordination sphere is characterized by C(1)–W–N(31) angles of ca. 154° and O(1)–W–O(2) angles of ca. 104°, consistent with values found in other *cis*-dioxo–W complexes.[24] Distortion within the trapezoidal plane results from the disparity of the O(1)–W–O(2), O–W–N, and N(11)–W–N(21) angles. The W–C(1) and W–N(31) bonds are inclined away from the imaginary line through W and perpendicular to the trapezoidal plane. This distortion is highlighted in the stick-figures shown in Figure 3. The W atom is displaced toward C(1) by only 0.0247 (5) Å (for **3**) and 0.0197 (2) Å (for **5**) from the least-squares plane through the trapezoidal plane. The cis oxo ligands exhibit bond distances in the range 1.711 (4)–1.729 (6) Å, again consistent with values found in other *cis*-dioxo–W complexes.[24] The O–W–C(1) angles lie within a narrow range of 96.9 (2)–98.0 (4)°. The relationships of the *fac*-O$_2$R ligands can be described with reference to the W⋯B(1) vector. The O–W⋯B(1) and C(1)–W⋯B(1) angles are 123 and 107°, respectively. In contrast, the near-3-fold symmetry of the pyrazolylborato–W fragment is highlighted by a small range of N–W⋯B(1) angles (46.5–47.5°). As a consequence of these structural features, the WO$_2$R

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unit is compressed while the WN_3 unit is elongated; the W atom lies ca. 0.86 Å out of the plane defined by O(1), O(2), and C(1) and ca. 1.54 Å out of the plane defined by the three N atoms. Consistent with previous observations in other oxo polypyrazolylborate complexes, the W–N(11) and W–N(21) bonds which are trans to the oxo ligands are significantly longer than the remaining W–N(31) bond. The pyrazole rings containing N(11) and N(21) are slightly splayed as a result of the occupation of the cleft between them by the R group. The atoms of the R groups lie on or close to the pseudomirror plane of the molecules, thus minimizing steric interactions. The dihedral angles in the C(2)–C(1)–W–N(31) fragments of 3 and 5 are 7.2 and 1°, respectively. The W–C(1) distances for 3 and 5 are 2.21 (1) and 2.271 (6) Å, respectively, the C(1)–C(2) distance in the ethyl ligand is 1.55 (1) Å, and the phenyl group is planar with C–C distances averaging 1.385 Å.

The structures of 3 and 5 can be compared with those established by Schrauzer et al.[6] for members of the series (bpy)WO$_2$(R)$_2$ (R = Me,[6a] n-Pr,[6a] and Ph[6b]); a distinct structural similarity is noted. The (bpy)WO$_2$(R)$_2$ complexes exhibit skewed-trapezoidal-bipyramidal geometries in which oxo and N-donor atoms define the trapezoidal plane and the R groups occupy apical positions. The W=O bond distances range from 1.710 (5) to 1.729 (5) Å while the O—W—O bond angles range from 107.8 (3) to 109.4 (2)°. The C—W—C angles associated with the trans R groups range from 147.8 (3) to 161.0 (4)°. The complex (bpy)MoO$_2$(Et)$_2$ has also been structurally characterized[25] and exhibits a structure and ethyl ligand geometrical parameters consistent with those observed for 3. Similar metrical parameters have been observed in other (alkyl)-oxo–W complexes, e.g. (η^5-C$_5$H$_5$)WO$_2$(CH$_2$SiMe$_3$).[5a]

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Practical Synthesis of Tris(trimethylsilyl)methyl Bromide and Its Conversion to the Corresponding Grignard Reagent and (Tris(trimethylsilyl)methyl)lithium

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Summary: A practical synthesis of tris(trimethylsilyl)-methyl bromide in 75% yield by photobromination of neat tris(trimethylsilyl)methane at 180–190 °C in less than 5 h is reported. The bromide was converted to (tris(trimethylsilyl)methyl)lithium in over 75% yield by reaction with lithium metal in diethyl ether and THF and via facile halogen–metal interconversion with phenyllithium. The first synthesis of the Grignard reagent (tris(trimethylsilyl)-methyl)magnesium bromide in 75–90% yield from the corresponding bromide and magnesium metal in diethyl ether also is described.

In 1970, Eaborn et al. reported the synthesis of (tris-(trimethylsilyl)methyl)lithium (hereafter referred to as trisyllithium) in high yield by metalation of tris(trimethylsilyl)methane with methyllithium in THF,[1] and improvements in this procedure were published in 1984.[2] To date, trisyllithium has proven to be a useful reagent for the preparation of many unique molecules, especially those in which the bulky (Me$_3$Si)$_3$C group is attached to metals or metalloids. The major impetus for interest in this area is due to findings that organometallic compounds bearing the trisyl moiety possess unique properties and often have novel structures.[3,4]

In routine laboratory practice, organolithium and Grignard reagents are most often prepared from organic halogen compounds and the appropriate metal. However, to date the preferred route to trisyllithium involves the accessible tris(trimethylsilyl)methane because practical routes to the trisyl halides have yet to be reported.[1,5] For example, two methods have been reported for the preparation of tris(trimethylsilyl)methyl bromide (hereafter referred to as trisyl bromide): (1) an indirect procedure involving a halogen–metal exchange between bis(trimethylsilyl)dibromomethane and butyllithium followed by a reaction of the intermediate (bis(trimethylsilyl)-bromomethyl)lithium with chlorotrimethylsilane[6] and (2) a direct route in which a mixture of N-bromosuccinimide, benzoyl peroxide, and tris(trimethylsilyl)methane was refluxed for 5 days.[7]

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