Organometallic Dioxo-, and Oxo-thio- and Dithio-tungsten(VI) Complexes of Hydrotris(3,5-dimethylpyrazolyl)borate

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Reactions of *cis*-[{HB(Me$_2$pz)$_3$}WO$_2$Cl] with Grignard reagents RMgX (R = Me, Et, CH$_2$Ph, Ph; X = Cl or Br) in tetrahydrofuran, or boron sulfide in refluxing 1,2-dichloroethane, result in the formation of organometallic dioxo-W^{VI} complexes, *cis*-[{HB(Me$_2$pz)$_3$}WO$_2$R], and oxo-thio- and dithio-W^{VI} complexes, *cis*-[{HB(Me$_2$pz)$_3$}WE$_2$Cl] (E$_2$ = OS, S$_2$), respectively; the X-ray crystal structure of *cis*-[{HB(Me$_2$pz)$_3$}WO$_2$Et], a rare example of a complex stable towards β-hydrogen elimination, is reported.

The study of high-valent organometallic oxo complexes has intensified in recent years as a result of the intermediacy of such species in metal oxide catalysed reactions.[1,2] The majority of known complexes are polynuclear cyclopentadienyl or alkyl complexes of oxophilic early transition metals or cluster μ$_3$-oxo carbonyls of the group 8 or 9 metals.[1] Few N-donor ligand complexes of this kind have been prepared[3] and while polypyrazolylborate ligands form both oxo[4,5] and organometallic[4,6] complexes, organometallic oxo complexes containing these ligands are restricted to recently reported (carbonyl)oxotungsten(IV) complexes.[7] Considering the ability of the hydrotris(3,5-dimethylpyrazolyl)borate ligand {HB(Me$_2$pz)$_3^-$} to stabilise high-valent mononuclear complexes containing reactive ligands (*e.g.* thio[8] or nitrido[9] ligands) we predicted that oxo-alkyl and oxo-aryl complexes of this ligand would be stable and isolable. Further, we expected that ligands which are normally susceptible to decomposition by β-hydrogen elimination would be stabilised in organometallic oxo complexes of HB(Me$_2$pz)$_3^-$. We describe here the synthesis and properties of the dioxo-W^{VI} complexes [{HB(Me$_2$pz)$_3$}WO$_2$R] (R = Me **1**, Et **2**, CH$_2$Ph **3**, Ph **4** and the X-ray crystal structure of the very stable ethyl complex **2**. Further, we describe the synthesis of the extremely rare[10] pseudo-octahedral oxo-thio-W^{VI} and dithio-W^{VI} complexes [{HB(Me$_2$pz)$_3$}WE$_2$Cl] (E$_2$ = OS or S$_2$) *via* reaction of [{HB(Me$_2$pz)$_3$}WO$_2$Cl] and B$_2$S$_3$. Reduction leads to the isolation of quite different species in analogous molybdenum chemistry (see below).

[{HB(Me$_2$pz)$_3$}WO$_2$R]
1 R = Me
2 R = Et
3 R = CH$_2$Ph
4 R = Ph

Reaction of *cis*-[{HB(Me$_2$pz)$_3$}WO$_2$Cl] with Grignard reagents RMgX (R = Me, Et, CH$_2$Ph, Ph; X = Cl, Br) in tetrahydrofuran results in high yields of the white (R = Me **1**, Et **2**, Ph **4**) or yellow (R = CH_2Ph **3**) *cis*-$[\{HB(Me_2pz)_3\}WO_2R]$ complexes.† These air- and water-stable crystalline solids are reasonably soluble (**1** and **2**) or freely soluble (**3** and **4**) in chlorinated solvents but insoluble in ethers, alcohols and hydrocarbons. The complexes have been characterised by analytical, spectroscopic‡ and X-ray crystallographic data, which are consistent with their formulation as diamagnetic, mononuclear, organometallic dioxo-W^{VI} complexes. The IR spectra of **1**–**4** exhibit bands due to $HB(Me_2pz)_3^-$ and the $[WO_2]^{2+}$ fragment [$\nu(WO_2)/cm^{-1}$ *ca.* 960 and 910]. The ^1H NMR spectra of the complexes are consistent with molecular C_s symmetry, exhibiting pyrazolylborate CH and Me resonances with intensity ratios of 2 : 1 and 6 : 6 : 3 : 3, respectively, as well as resonances assignable to the R group. In complex **1** a singlet W–CH_3 resonance at δ 1.2 [for molecules containing tungsten with I = 0 (85.6%)] is flanked by two resonances produced by coupling of the protons to ^{183}W (I = 1/2, 14.4%). Proton–tungsten coupling is not resolved in **2** but interestingly the CH_2 resonance of **2** is shielded relative to its CH_3 resonance. The CH_2 proton resonance of **3** is also characterised by discernible W–H coupling. With respect to the syntheses described herein, it is interesting to note that reaction of $[\{HB(Me_2pz)_3\}MoO_2Cl]$ with Grignard reagents results in reduction and formation of the mixed-valence complex $[\{HB(Me_2pz)_3\}Mo^{V}OCl(\mu\text{-}O)Mo^{VI}O_2\{HB(Me_2pz)_3\}]$.[11] As well, we note that while related complexes $(C_5Me_5)MO_2R$ (M = Mo, W; R = Me, CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph, CH_2Ph)[12,13] have been reported, decomposition of oxo–C_5Me_5 complexes containing ligands with β-hydrogens prevents their isolation.

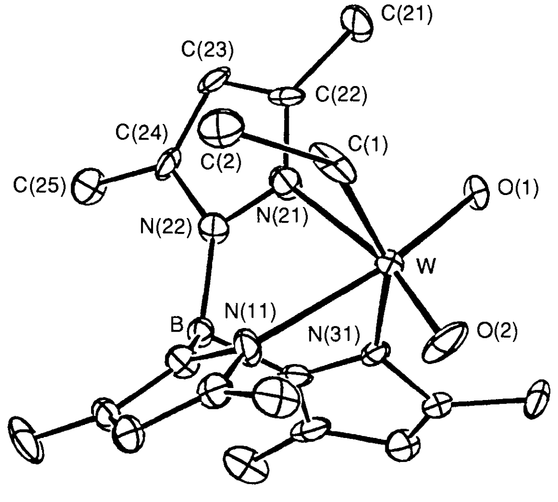

Fig. 1 The structure of **2**, with ellipsoids drawn at the 25% probability level. The numbering schemes for the pyrazolyl rings containing N(11) and N(31) parallel that shown for the ring containing N(21). Selected distances (Å) and angles (degrees) are: W–O(1) 1.721(7), W–O(2) 1.729(6), W–C(1) 2.21(1), W–N(11) 2.331(8), W–N(21) 2.296(8), W–N(31) 2.175(8), C(1)–C(2) 1.55(2), O(1)–W–O(2) 103.6(3), O(1)–W–C(1) 98.0(4), O(1)–W–N(11) 169.2(3), O(1)–W–N(21) 87.8(3), O(1)–W–N(31) 99.4(3), O(2)–W–C(1) 97.2(4), O(2)–W–N(11) 87.1(3), O(2)–W–N(21) 168.4(3), O(2)–W–N(31) 99.3(3), C(1)–W–N(11) 81.6(3), C(1)–W–N(21) 82.9(3), C(1)–W–N(31) 152.4(4), N(11)–W–N(21) 81.5(3), N(11)–W–N(31) 77.3(3), N(21)–W–N(31) 76.6(3).

The molecular structure of **2**§ as determined by single crystal X-ray diffraction is shown in Fig. 1. The coordination sphere of the six-coordinate, mononuclear complex is com-

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† *Syntheses.* *cis*-$[\{HB(Me_2pz)_3\}WO_2Cl]$: a mixture of 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 cm^3) for 20 h. The resultant solid was filtered off in air, washed with acetone and ether, then purified by Soxhlet extraction using dichloromethane. The yield of white solid was 1.82 g (70%).

1 and **2**: Solid $[\{HB(Me_2pz)_3\}WO_2Cl]$ (0.50 g, 0.91 mmol) was treated with MeMgCl or EtMgBr (2.73 mmol) in tetrahydrofuran (40 cm^3). After stirring for 1 h, the mixture was filtered in air and the filtrate was evaporated to *ca.* 8 cm^3. The white product was isolated by filtration and recrystallised from dichloromethane–methanol, further product appearing upon volume reduction. Yields: **1** = 0.34 g (71%), **2** = 0.28 g (57%).

3 and **4**: As above, but after filtration in air the filtrate was evaporated to dryness, redissolved in dichloromethane, washed with 0.1 mol dm^{-3} HCl (3 × 15 cm^3) and dried over sodium sulfate. Upon evaporation the residue was recrystallised from dichloromethane–pentane. Yields: **3** = 0.31 g (48%), **4** = 0.17 g (27%).

5: A suspension of $[\{HB(Me_2pz)_3\}WO_2Cl]$ (1.00 g, 1.82 mmol) and boron sulfide (0.19 g, 1.6 mmol) in 1,2-dichloroethane (50 cm^3) was refluxed for 7 days, filtered, reduced to *ca.* 10 cm^3 and eluted on a silica column with dichloromethane. Compound **5** was collected as the second pink band. Yield: 0.1 g, 10%. A mixture of **5** and **6** is the other major fraction isolated by this method.

6: A suspension of $[\{HB(Me_2pz)_3\}WO_2Cl]$ (1.00 g, 1.82 mmol) and boron sulfide (1.00 g, 8.5 mmol) in 1,2-dichloroethane (50 cm^3) was refluxed for 7 days, filtered, reduced to *ca.* 10 cm^3 and eluted on a silica column with dichloromethane. Compound **6** was collected as the first green band. Yield: 0.19 g, 18%.

‡ Satisfactory microanalyses have been obtained for all compounds **1–6**.

Selected spectroscopic data: IR data (KBr; ν/cm^{-1}), assignment, NMR data, ^1H 400 MHz, as δ relative to $CHCl_3$ (δ 7.24) in $CDCl_3$, relative intensity, coupling constant (J, in Hz) and assignment. Mass spectrum: *m*/*z* [ion] (expected isotope pattern observed).

1: IR: ν(BH) 2550m, $\nu(WO_2)$ 960s and 915s. ^1H NMR: 1.20 (3H, $J_{W\text{-}H}$ = 9.8, W–CH_3), 2.34 (3H), 2.36 (6H), 2.61 (3H), 2.67 (6H) [6 × CH_3 of $HB(Me_2pz)_3^-$], 5.85 (2H), 5.86 (1H) [3 × CH of $HB(Me_2pz)_3^-$]. Mass spectrum: *m*/*z* 527 $[M - 1]^+$.

2: IR: ν(BH) 2550m, $\nu(WO_2)$ 945s and 905s. ^1H NMR: 2.07 (2H, q, J = 7.3, W–CH_2–CH_3), 2.28 (3H, d, J = 7.3, W–CH_2–CH_3), 2.32 (3H), 2.35 (6H), 2.57(3H), 2.72 (6H) [6 × CH_3 of $HB(Me_2pz)_3^-$], 5.84 (1H), 5.87 (2H) [3 × CH of $HB(Me_2pz)_3^-$]. Mass spectrum: *m*/*z* 542 $[M - 1]^+$.

3: IR: ν(BH) 2550m, $\nu(WO_2)$ 960s and 915s. ^1H NMR: 2.34 (3H), 2.40 (6H), 2.54 (3H), 2.90 (6H) [6 × CH_3 of $HB(Me_2pz)_3^-$], 3.15 (2H, $J_{W\text{-}H}$ = 11.7, W–CH_2–Ph), 5.84 (1H), 5.94 (2H) [3 × CH of $HB(Me_2pz)_3^-$], 6.94 (1H, t, J = 7.5, p-CH of Ph), 7.30 (2H, t, J = 7.5, 2 × m-CH of Ph), 7.46 (2H, d, J = 7.5, 2 × *o*-CH of Ph). Mass spectrum: *m*/*z* 603 $[M - 1]^+$.

4: IR: ν(BH) 2550m, $\nu(WO_2)$ 955s and 910s. ^1H NMR: 1.94 (6H), 2.38 (3H), 2.42 (6H), 2.69 (3H) [6 × CH_3 of $HB(Me_2pz)_3^-$], 5.76 (2H), 5.91 (1H) [3 × CH of $HB(Me_2pz)_3^-$], 7.09 (5H, broad, C_6H_5). Mass spectrum: *m*/*z* 590 $[M]^+$.

5: IR: ν(BH) 2560m, ν(W=O) 940s, ν(W=S) 480s, ν(W–Cl) 340s. ^1H NMR: 2.33 (3H), 2.37 (3H), 2.41 (3H), 2.59 (3H), 2.68 (3H), 2.93 (3H), 5.81 (1H), 5.95 (1H), 5.98 (1H) [inequivalent protonic groups of $HB(Me_2pz)_3^-$]. Mass spectrum: *m*/*z* 565 $[M]^+$.

6: IR: ν(BH) 2550w, ν(*cis*-WS_2) 495m and 475s, ν(W–Cl) 325m. ^1H NMR: 2.36 (6H), 2.39 (3H), 2.76 (3H), 2.81 (6H), [6 × CH_3 of $HB(Me_2pz)_3^-$], 5.89 (2H), 6.02 (1H) [3 × CH of $HB(Me_2pz)_3^-$]. Mass spectrum: *m*/*z* 580 $[M - 1]^+$.

§ Crystals of **2**·H_2O were grown in air from dichloromethane layered with n-pentane. *Crystal data* for **2**·H_2O: $C_{17}H_{29}BN_6O_3W$, M = 560.1, triclinic, space group $P\bar{1}$, a = 8.720(2), b = 16.649(3), c = 8.032(1) Å, α = 103.55(1), β = 101.89(1), γ = 98.94(2)°, U = 1083.6 Å^3, D_c = 1.717 Mg m^{-3}, Z = 2. Monochromatised Mo-Kα radiation, λ = 0.7107 Å, μ = 54.45 cm^{-1}, T = 293 K, analytical absorption correction (max./min. transmission factors: 0.465, 0.065, respectively). Total of 3081 reflections measured ($1.5 \leqslant \theta \leqslant 22.5°$) on a CAD4 diffractometer; 2814 were unique and 2320 satisfied $I \geqslant 2.5\sigma(I)$. The structure was solved using Patterson and Fourier methods and refined by full-matrix least-squares techniques (SHELX).[14] Anisotropic thermal parameters for non-H atoms, and H-atoms included in their calculated positions. Refinement converged with R = 0.044 and R_w = 0.045 for weighting scheme $w = [\sigma^2(F) + 0.004\,|F|^2]^{-1}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

posed of a facially tridentate $HB(Me_2pz)_3^-$ ligand, two oxo ligands and an ethyl ligand. The average distance of the W=O bonds is 1.725(7) Å while the W–C(1) and C(1)–C(2) distances characterising the ethyl ligand are 2.21(1) and 1.55(2) Å, respectively; the W–C(1)–C(2) angle of 121.5(7)° is considerably larger than the angle expected for an sp^3 hybridised carbon atom. Consistent with a *trans* influence associated with the oxo ligands, the W–N(31) bond *trans* to the ethyl group is the shortest of the W–N bonds in the molecule. Considerable trigonal elongation and compression, respectively, characterise the faces occupied by the N_3 and O_2C donor atom sets; this is reflected in large O(1)–W–O(2) and O–W–C(1) angles (average 99.6°) and small N–W–N angles (average 78.5°). There is no indication of interactions involving ethyl C–H bonds and the tungsten centre. The phenyl complex **4** possesses a similar molecular structure (determined by X-ray diffraction) with two oxo ligands and a η^1-Ph ligand occupying facial coordination sites opposite the tridentate $HB(Me_2pz)_3^-$ ligand.

$[\{HB(Me_2pz)_3\}WE_2Cl]$
5 $E_2 = OS$
6 $E_2 = S_2$

Reaction of $[\{HB(Me_2pz)_3\}WO_2Cl]$ with boron sulfide in refluxing 1,2-dichloroethane results in the formation of the pink $[\{HB(Me_2pz)_3\}WOSCl]$ or green $[\{HB(Me_2pz)_3\}WS_2Cl]$† characterised by analytical and spectroscopic data.‡ These crystalline complexes are produced in reliable but low yields, are air- and water-stable and exhibit solubilities similar to **3** and **4**. Along with bands characteristic of the pyrazolylborate ligand, the IR spectrum of **5** exhibits ν(W=O), ν(W=S) and ν(W–Cl) bands at 940, 480 and 340 cm^{-1} respectively. The ^1H NMR spectrum of the complex reveals that all CH and methyl groups are inequivalent, consistent with a chiral molecule. The IR spectrum of **6** exhibits bands at 495 and 475, and 325 cm^{-1}, assigned to bands associated with *cis*-WS_2 and W–Cl moieties, respectively. This compound produces an ^1H NMR spectrum consistent with C_s molecular symmetry. In contrast, the reaction of *cis*-$[\{HB(Me_2pz)_3\}MoO_2X]$ and B_2S_3 under similar conditions results in reduction and the formation of $[\{HB(Me_2pz)_3\}MoX(S_4)]$[15] complexes. We have been unable to isolate organometallic derivatives $[\{HB(Me_2pz)_3\}WE_2R]$ from related reactions involving $[\{HB(Me_2pz)_3\}WO_2R]$, which contrasts with the reported synthesis of analogous $[(C_5Me_5)MOSR]$ (M = Mo, W; R = Me, CH_2SiMe_3) complexes.[16]

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