Multiple Bonds between Main Group Elements and Transition Metals, LXXXIII[1]

Trioxo(pyrazolyl)rhenium(VII) and [Hydridotris(1-pyrazolyl)borato-*N,N′,N″*]trioxorhenium(VII)

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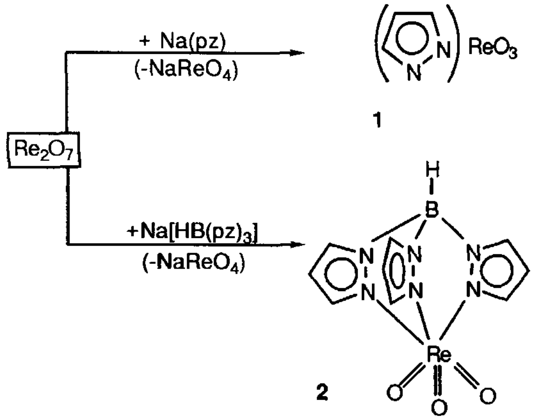
The syntheses of the rhenium(VII) title compounds (pz)ReO$_3$ (**1**) and [HB(pz)$_3$]ReO$_3$ (**2**) (pz = pyrazolyl) are described. An X-ray crystallographic study of **2** shows, that it has a monomeric structure.

The versatile and varied chemistry of the high-oxidation state organorhenium compounds CH$_3$ReO$_3$ and (η^5-C$_5$Me$_5$)ReO$_3$ has been well established in recent years. In particular, these compounds have been shown to exhibit interesting reactivity towards olefins and alkynes[2,3]. In addition, methyltrioxorhenium is an effective catalyst for olefin oxidation and olefin metathesis[2d,4]. We have thought it of interest, therefore, to prepare the potentially analogous compounds (pz)ReO$_3$ (**1**) and [HB(pz)$_3$]ReO$_3$ (**2**) (pz = pyrazolyl ligand). We have found that both of these compounds can easily be synthesized in high yields by treating a solution of Re$_2$O$_7$ in THF with one equivalent of the sodium salt of the ligands, Na(pz) and Na[HB(pz)$_3$][5], respectively. This contrasts with earlier attempts to prepare high-oxidation state organorhenium derivatives by the same procedure which has led only to decomposition products[6].



Trioxo(pyrazolyl)rhenium(VII) (**1**) is a colourless, air-stable, crystalline solid, which is soluble in THF, acetone, and water but insoluble in less polar solvents. So far it has not been possible to obtain crystals of sufficient quality to allow an X-ray structural determination. Therefore its solid state structure is uncertain. The IR spectrum (KBr pellet), however, exhibits a strong ν(Re=O) band at 913 cm^{-1} characteristic of a perrhenate anion. This may indicate that the structure of this compound is more complex than a tetrahedrally substituted monomer. The ^{1}H-NMR spectrum of **1** shows two signals at δ = 8.61 (doublet) and 7.04 (triplet) with relative integrals of 2:1. This result is consistent with either a fluxional pyrazolyl ligand or one that is symmetrically substituted (e.g. bridging). An ionic structure such as [(μ-pz)$_2$Re$_2$O$_4$][ReO$_4$]$_2$ has to be taken into consideration until a definite assignment on the basis of an X-ray diffraction study can be achieved. It is of interest to contrast the stability of this compound with the related compound [(*i*-C$_3$H$_7$)$_2$N]ReO$_3$, which is both air-sensitive and thermally unstable[7].

[Hydridotris(1-pyrazolyl)borato-*N,N′,N″*]trioxorhenium(VII) (**2**) is a colourless, air-stable, involatile solid with low solubility, even in very polar solvents (THF, water). The ^{1}H-NMR spectrum of this compound shows three signals of equal intensities typical of the protons in the pyrazole rings suggesting that all three rings are equivalent in solution. The IR spectrum (KBr pellet) exhibits several bands assignable as ν(Re=O): 944 (m), 924 (s), 911 (s) and 894 (m) cm^{-1}. These bands are found in a similar position in (η^5-C$_5$Me$_5$)-ReO$_3$ [909 (s), 878 (vs)][8].

Despite its low solubility it is possible to obtain small crystals of **2** from a THF solution layered with hexane. These have proven to

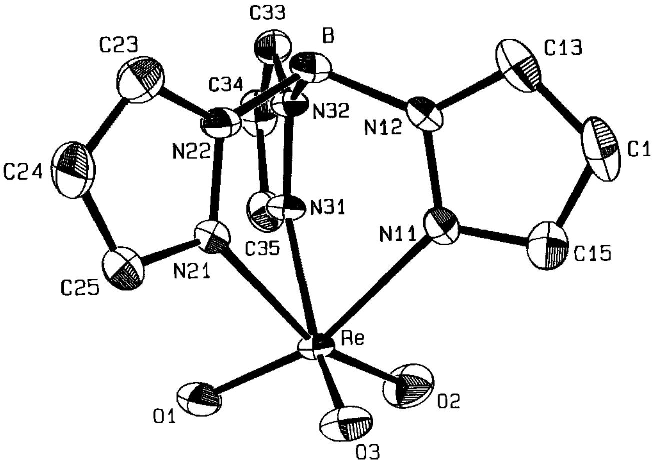


Figure 1. Molecular structure of the Re(VII) complex **2** (ORTEP representation without hydrogen atoms; the thermal ellipsoids are drawn at a 50% probability level)

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be of sufficient quality to allow an X-ray structural determination. The compound has a monomeric structure containing a six-coordinate rhenium atom. A view of this structure is shown in Figure 1.

Table 1. Selected bond distances [Å] and bond angles [°] of **2** with estimated standard deviations in parentheses

Bond Distances			
Re-O(1)	1.708(2)	Re-N(21)	2.225(3)
Re-O(2)	1.707(2)	Re-N(31)	2.229(3)
Re-O(3)	1.720(2)	B-N(12)	1.529(5)
Re-N(11)	2.240(3)	B-N(22)	1.544(5)
		B-N(32)	1.534(5)

Bond Angles			
O(1)-Re-O(2)	104.2(1)	N(11)-Re-N(21)	78.2(1)
O(1)-Re-O(3)	104.3(1)	N(11)-Re-N(31)	77.7(1)
O(2)-Re-O(3)	103.9(1)	N(21)-Re-N(31)	77.0(1)
N(12)-B-N(22)	108.0(3)	O(1)-Re-N(11)	161.6(1)
N(12)-B-N(32)	107.4(3)	O(1)-Re-N(21)	87.4(1)
N(22)-B-N(32)	106.6(3)	O(1)-Re-N(31)	88.0(1)
O(2)-Re-N(11)	87.0(1)	O(3)-Re-N(11)	86.7(1)
O(2)-Re-N(21)	160.8(1)	O(3)-Re-N(21)	87.7(1)
O(2)-Re-N(31)	88.0(1)	O(3)-Re-N(31)	160.0(1)

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations in parentheses[a)]

Atom	x	y	z	B_{eq} (Å²)
Re	0.27722(2)	0.15202(1)	0.05161(1)	1.581(3)
O(1)	0.1855(4)	0.0336(2)	0.0227(2)	2.65(6)
O(2)	0.1693(4)	0.2340(3)	-0.0367(2)	3.02(6)
O(3)	0.4814(4)	0.1429(2)	0.0115(2)	2.53(6)
N(11)	0.3737(4)	0.2938(2)	0.1399(2)	1.98(7)
N(12)	0.3679(4)	0.3103(3)	0.2434(2)	1.81(6)
N(21)	0.3877(4)	0.0844(2)	0.2027(2)	1.81(6)
N(22)	0.3775(4)	0.1254(3)	0.2981(2)	1.84(6)
N(31)	0.0685(4)	0.1802(3)	0.1543(2)	1.72(6)
N(32)	0.0958(4)	0.2131(3)	0.2544(2)	1.78(6)
C(13)	0.4451(6)	0.4006(3)	0.2700(3)	2.78(9)
C(14)	0.5026(6)	0.4444(3)	0.1812(4)	3.5(1)
C(15)	0.4539(6)	0.3761(3)	0.1033(3)	2.85(9)
C(23)	0.4578(6)	0.0632(4)	0.3696(3)	2.89(9)
C(24)	0.5212(6)	-0.0223(3)	0.3213(3)	3.2(1)
C(25)	0.4754(6)	-0.0058(3)	0.2154(3)	2.38(8)
C(33)	-0.0596(5)	0.2264(3)	0.2908(3)	2.03(8)
C(34)	-0.1877(5)	0.2002(3)	0.2144(3)	2.54(9)
C(35)	-0.1021(5)	0.1711(3)	0.1297(3)	2.15(8)
B	0.2811(6)	0.2293(4)	0.3070(3)	1.93(9)

[a)] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $4/3 \cdot [a^2 \cdot B(1,1) + b^2 \cdot B(2,2) + c^2 \cdot B(3,3) + ac(\cos\beta) \cdot B(1,3)]$.

The average Re=O bond length of 1.712(2) Å is close to the values found for similar compounds (η^5-C_5Me_4Et)ReO_3 [1.696(3) Å][2a,b)] and (σ-mesityl)ReO_3 [1.689(5) Å][6)]. The O–Re–O angles have a mean value of 104.1(1) which compares well with the angles found in the structure of (η^5-C_5Me_4Et)ReO_3 [average 105.2(2)°][2a,b)]. The average value of the N–Re–N angle of 77.6 and the bond angles and lengths associated with the $[HB(pz)_3]^-$ ligand are within the range expected from comparisons with X-ray crystallographic studies of other complexes containing this ligand[9–11)].

It is of particular interest to compare the present structure with that of the cation in Wieghardt's compound $[LReO_3]Cl$ (L = 1,4,7-triazacyclononane)[12)]. Both **2** and $[LReO_3]Cl$ have a similar pseudo-octahedral configuration around the rhenium with a ReN_3O_3 coordination sphere. The average Re–N bond length in **2** is 2.231(3) Å which is close to the value of 2.197(5) Å found for $[LReO_3]Cl$. Both these bond lengths are somewhat longer than those found in the 4-methylpyridine complex $[ReO_2(4\text{-}MePy)_4][ReO_4]$, 2.14(2) Å[13)]. In the case of $[LReO_3]Cl$ this has been attributed to the large *trans* influence of the terminal oxo groups, the interpretation of which would agree with the results of the present study.

Two related high-oxidation state compounds of rhenium have previously been described. Both of the rhenium(V) compounds $[HB(pz)_3]ReOCl_2$ and $[HB(pz)_3]ReSCl_2$ have been found to be stable[14,15)]. However, in **2** the rhenium is in its highest possible oxidation state. Despite this the compound exhibits a surprising degree of thermal stability, showing no melting point or decomposition below 250 °C!

In contrast to CH_3ReO_3[4b)], the title compounds **1** and **2** are not catalytically active in the oxidation of olefins by means of hydrogen peroxide. On the other hand, an interesting and versatile reactivity of these compounds is developing. We will report on further chemistry of **1** and **2** shortly.

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Experimental

The preparations were carried out under dry nitrogen, and all solvents were dried and distilled prior to use. For further details of experimental techniques, see previous publications of this series[1,16)].

Trioxo(pyrazolyl)rhenium (**1**): To a frozen solution of Re_2O_7 (1.14 g, 2.35 mmol) in THF (10 ml) was added solid Na(pz)[5b)] (0.21 g, 2.35 mmol). The mixture was allowed to warm to room temp. with stirring. After 1 h the resulting colourless suspension was filtered. The filtrate was concentrated, mixed with *n*-hexane (2 ml), and stored at −30 °C for ca. 12 h. The colourless microcrystalline solid obtained was isolated by filtration and dried in vacuo, yield 0.52 g (73%), m.p. 168–170 °C. – ^{1}H NMR [$(CD_3)_2CO$, 400 MHz, 25 °C]: δ = 7.04 (t, $J_{H,H}$ = 3 Hz, 1H, CH), 8.61 (d, $J_{H,H}$ = 3 Hz, 2H, NCH). – IR (KBr): $\tilde{\nu}$ = 3114–2825 cm^{-1} m br, 1539 m, 1453 w, 1410 w, 1313 w, 1107 m, 1048 m, 913 s br, 794 s, 611 m.

$C_3H_3N_2O_3Re$ (301.3) Calcd. C 11.96 H 1.00 N 9.30
Found C 11.73 H 1.64 N 8.91

[Hydridotris(1-pyrazolyl)borato-N,N′,N″]trioxorhenium (**2**): To a frozen solution of Re_2O_7 (0.78 g, 1.61 mmol) in THF (20 ml) was added solid $Na[HB(pz)_3]$[5a)] (0.38 g, 1.61 mmol). The mixture was allowed to warm to room temp. and stirred for 1 h. The resulting colourless suspension was filtered, and the solid thus obtained was washed with hot water (2 × 10 ml) and acetone (2 × 10 ml). The resulting white powder was dried in vacuo, yield 0.56 g (78%), m.p. >250 °C. – ^{1}H NMR [$(CD_3)_2CO$, 400 MHz, 25 °C]: δ = 6.48 (s, 1H, CH), 8.04 (s, 1H, CH), 8.32 (s, 1H, CH). – IR (KBr): $\tilde{\nu}$ = 3128 cm^{-1} w, 2530 w, 1502 w, 1405 m, 1317 m, 1228 s, 1122 m, 1056 s, 944 m, 924 s, 911 s, 894 m, 879 w, 857 w, 782 m, 764 m, 716 m, 658 w, 614 w.

$C_9H_{10}BN_6O_3Re$ (447.2) Calcd. C 24.17 H 2.25 N 18.8 Re 41.64
Found C 24.21 H 2.35 N 19.2 Re 41.86

X-ray Structure Determination of **2**[17)]: The data were collected using an Enraf-Nonius CAD4 four-circle diffractometer with graphite-monochromated Cu-K_α radiation ($2\Theta_{max}$ = 65°). Orientation matrix and cell dimensions were obtained from least squares refinement[18)] using a set of 25 reflections, $2\Theta \geq 80.6°$. During the data collection no decay was detected. The data were corrected for Lorentz and polarisation effects, and an empirical absorption correction based upon six reflections was applied. 4711 reflections were measured of which 2148 ($I \geq 0.0$) were taken as independent. The rhenium atom position was determined from Patterson maps, and the remaining atoms were located using successive Fourier syntheses. Refinement minimized the function $\Sigma w(F_o - F_c)^2$ where $w = 1/\sigma^2(F_o)$. Hydrogen atoms were placed in ideal positions (C–H, 0.95 Å) and added to the calculations with isotropic temperature factors, but not refined. Anomalous dispersion corrections were applied to all non-hydrogen atoms[19]. Refinements converged with weighted and unweighted agreement factors of $R = 0.024$ and $R_w = 0.021$. The calculations were performed on VAX 11/730 and VAX-8200 computers using the STRUX-II[20] and SDP[18] systems. Selected bond lengths and angles are listed in Table 1 and the atomic coordinates in Table 2.

Space group $P2_1/n_1$ (Int. Tab. No. 14), unit cell with $a = 7.742(<1)$, $b = 12.892(<1)$, $c = 12.935(1)$ Å, $\beta = 96.18(<1)°$, $V = 1284$ Å^3, $Z = 4$, $\rho = 2.313$ g cm^{-3}.

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