

Figure 1. Drawing of the $\text{Pt}(\text{OTeF}_5)_2(\text{NBD})$ molecule (50% probability ellipsoids).

discussed.⁸⁻¹² For example, the Te-O stretching frequencies are 824 and 804 cm^{-1} for $\text{Pt}(\text{OTeF}_5)_2(\text{NBD})$ and 800 cm^{-1} ($\nu(\text{TeO})_{\text{asym}}$) for $\text{Pd}(\text{OTeF}_5)_2(\text{C}_6\text{H}_5\text{CN})_2$.²⁰ These values are consistent with metal-oxygen bonds with a large degree of covalent character, in contrast to the "ionic" metal-oxygen bonds in $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ (848 cm^{-1})¹⁰ and $\text{Fe}(\text{TPP})(\text{OTeF}_5)$ (849 cm^{-1})²¹ (cf. $[\text{N}(\text{n-Bu})_4]^+[\text{OTeF}_5]^-$, 867 cm^{-1}).^{8,9}) Similarly, the ^{19}F NMR chemical shifts of the axial fluorine atom in our metal teflates, $\delta_A -33.2$ for $\text{Pt}(\text{OTeF}_5)_2(\text{NBD})$ and $\delta_A -33.9$ for $\text{Pd}(\text{OTeF}_5)_2(\text{C}_6\text{H}_5\text{CN})_2$, are midway between the extremes for ionic OTeF_5^- ($\delta_A -19.0$ for $[\text{N}(\text{n-Bu})_4]^+[\text{OTeF}_5]^-$)⁸ and a covalent teflate group ($\delta_A -42.4$ for HOTeF_5).⁸ No coupling between ^{195}Pt and ^{125}Te was observed in the ^{195}Pt or ^{125}Te NMR spectra of $\text{Pt}(\text{OTeF}_5)_2(\text{NBD})$; the bandwidths of the ^{125}Te resonances suggest that $^2J_{\text{TePt}}$ must be less than 50 Hz. This lack of coupling may be due to intermolecular exchange of OTeF_5^- ligands that is fast on the NMR time scale. Two-bond coupling between tellurium and the central atom, M, in $\text{M}(\text{OTeF}_5)_x$ compounds is generally quite large: $^2J_{\text{TeTe}} = 1302$ Hz in $\text{Te}(\text{OTeF}_5)_6$,²² $^2J_{\text{TeXe}} = 1,008$ Hz in $\text{Xe}(\text{OTeF}_5)_4$,²³ $^2J_{\text{TeAs}} = 420$ Hz in $\text{As}(\text{OTeF}_5)_6$.²⁴

The molecular structure of $\text{Pt}(\text{OTeF}_5)_2(\text{NBD})$ is shown in Figure 1. The teflate oxygen atoms and the centroids of the NBD double bonds adopt a planar arrangement about the platinum atom: the maximum deviation from the least-squares plane through O1, O2, Pt, and the two centroids is experienced by the Pt atom (0.016 Å). The small centroid-Pt-centroid bond angle of 70.7° is expected from the small bite of the NBD ligand.²⁵ However, the O1-Pt-O2 bond angle of 83.0 (2)° is surprisingly acute for two bulky, monodentate ligands. For example, the Cl-Pt-Cl bond angle in $\text{MCl}_2(\text{diolefin})$ complexes (M = Pt(II) or Pd(II)) varies from 90 to 95°. ²⁵⁻²⁷ Intermolecular contacts could conceivably be severe enough to be the cause of the small O1-Pt-O2 angle: the closest are F8...H3 (2.415 Å) and F1...C6

(2.894 Å). Both of these are shorter than the sum of the appropriate van der Waals radii, which are 1.20 Å for H, 1.70 Å for C, and 1.40 Å for F.²⁸ The closest intramolecular nonbonded contacts are also shorter than the sum of appropriate van der Waals radii: the closest are F10...H3 (2.250 Å) and F5...H5 (2.455 Å). Nevertheless, a stereoview of the unit cell packing (Figure S-1) suggests that the teflate groups could rotate away from these interactions without encountering other, more severe steric interactions. Thus, the small O-Pt-O angle is probably the result of an electronic effect, but steric effects cannot be ruled out and may contribute to this unusual structural feature.

The platinum-oxygen bond distances of 2.065 (5) and 2.042 (6) Å are near the high end of the recently reported range of 1.98-2.06 Å (a survey of 10 structures),²⁹ consistent with the accumulating evidence that teflate is a weak ligand (i.e. weaker than chloride but stronger than perchlorate or triflate).¹⁰⁻¹² When $\text{Pt}(\text{OTeF}_5)_2(\text{NBD})$ is dissolved in donor solvents such as acetone, acetonitrile, or nitromethane, OTeF_5^- , observed in IR and ^{19}F NMR spectra, dissociates from the metal complex to yield, presumably, $\text{Pt}(\text{OTeF}_5)(\text{NBD})(\text{solvent})^+$. The metal-carbon bond lengths, all equal to within experimental error (average 2.145 Å), are slightly shorter than those in $\text{PtCl}_2(\text{COD})$ (average 2.170 Å)²⁷ and $\text{PdCl}_2(\text{NBD})$ (average 2.162 Å).²⁵ Slightly stronger metal-olefin bonding in $\text{Pt}(\text{OTeF}_5)_2(\text{NBD})$ as compared with the bonding in these other complexes is also in harmony with metal-anion bonding being weaker for teflate than for chloride.

In summary, four-coordinate d^8 complexes of Pd(II) and Pt(II) with OTeF_5^- ligands and without phosphine ligands have been prepared and are stable indefinitely. Some steric and/or electronic property of teflate gives rise to an unusually acute O-Pt-O angle in $\text{Pt}(\text{OTeF}_5)_2(\text{NBD})$. The unique properties of teflate suggest that it may be a useful ligand for catalytic complexes, for which subtle changes in ligand properties can have dramatic effects on catalytic activity.

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Supplementary Material Available: Figure S-1, giving a stereoview of the unit cell packing diagram, and Tables S-I and S-II, listing thermal parameters and hydrogen atom positions and thermal parameters (3 pages); Table S-III, a listing of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

(28) Bondi, A. J. *J. Phys. Chem.* **1964**, *68*, 441.

(29) Boeré, R. T.; Payne, N. C.; Willis, C. J. *Can. J. Chem.* **1986**, *64*, 1474.

- (20) Solid-state (Nujol mull) IR spectra of $\text{Pd}(\text{OTeF}_5)_2(\text{C}_6\text{H}_5\text{CN})_2$ deserve further comment. Noncrystalline (powdered) samples produced by flash evaporation of solvent from benzene or dichloromethane solutions exhibited one band, at 800 cm^{-1} , in the $\nu(\text{TeO})$ region. Assuming a trans geometry for this complex, this band is assigned to the asymmetric Te-O stretching vibration of the two trans Te-O oscillators. Crystalline samples from either solvent exhibited two bands in this region, at 819 and 788 cm^{-1} . Since either type of sample exhibited only one $\nu(\text{CN})$ band at 2293 cm^{-1} , consistent with a trans geometry, we suggest that the splitting of the $\nu(\text{TeO})$ band in the crystals is a solid-state effect.
- (21) (a) Miller, P. K.; Pawlik, M. J.; Taylor, L. F.; Thompson, R. G.; Levstik, M. A.; Anderson, O. P.; Strauss, S. H., manuscript in preparation. (b) TPP = 5,10,15,20-tetraphenylporphyrinate dianion.
- (22) Birchall, T.; Myers, R. D.; DeWaard, H.; Schrobilgen, G. J. *Inorg. Chem.* **1982**, *21*, 1068.
- (23) Schumacher, G. A.; Schrobilgen, G. J. *Inorg. Chem.* **1984**, *23*, 2923.
- (24) Collins, M. J.; Schrobilgen, G. J. *Inorg. Chem.* **1985**, *24*, 2608.
- (25) Baenziger, N. C.; Doyle, J. R.; Carpenter, C. *Acta Crystallogr.* **1960**, *14*, 303.
- (26) Baenziger, N. C.; Valley Goebel, C.; Berg, T.; Doyle, J. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 1340.
- (27) Syed, A.; Stevens, E. D.; Cruz, S. G. *Inorg. Chem.* **1984**, *23*, 3673, and references therein.

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**Synthesis and X-ray Structure of a Dimeric Rhenium(V)
Compound: $\text{Re}_2\text{O}_3\text{Cl}_4(\text{3,5-Me}_2\text{pzH})_4\text{Me}_2\text{CO}$ (pzH =
Pyrazole)**

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Polypyrazolylborate ligands form stable complexes with many transition metals in a wide range of oxidation states.¹ Recently, we demonstrated that an extensive series of mononuclear oxomolybdenum(V) complexes can be stabilized by the hydrotris-(3,5-dimethyl-1-pyrazolyl)borate ligand, abbreviated HB-

(1) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 15-210.

Table I. Crystallographic Data for $\text{Re}_2\text{O}_3\text{Cl}_4(\text{Me}_2\text{pzH})_4\text{Me}_2\text{CO}$

| | |
|--|--|
| formula | $\text{Re}_2\text{Cl}_4\text{N}_8\text{O}_3\text{C}_{20}\text{H}_{28}(\text{CH}_3)_2\text{CO}$ |
| fw | 1004.79 |
| crystal color | green |
| cryst shape | prismatic |
| cryst size, mm | $0.42 \times 0.43 \times 0.53$ |
| cryst system | orthorhombic |
| space group | <i>Pbca</i> |
| <i>a</i> , Å | 15.802 (3) |
| <i>b</i> , Å | 16.125 (3) |
| <i>c</i> , Å | 27.331 (6) |
| vol, Å ³ | 6964.1 |
| <i>Z</i> | 8 |
| d_{calcd} , g cm ⁻³ | 1.91 |
| d_{obsd} , g cm ⁻³ | 1.92 |
| abs coeff, cm ⁻¹ | 79.3 |
| radiation (Mo K α) λ , Å | 0.71073 ^a |
| diffractometer | Nicolet P2 ₁ |
| data collcn scan method | $2\theta/\omega$ |
| no. of unique data | 4583 |
| final residuals: <i>R</i> , <i>R_w</i> | 0.036, 0.040 |

^a *International Tables for Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 1.1A.

$(\text{Me}_2\text{pz})_3$.² We sought to extend this chemistry to oxorhenium(V) because such species would be potentially useful diamagnetic host lattices for detailed single-crystal EPR studies of the oxomolybdenum(V) species. One common way of preparing oxorhenium(V) compounds is to react perhenate with an appropriate ligand in strongly acidic solution.³ Monomeric monooxo complexes of rhenium(V) are formed preferentially by this procedure,^{4,5} and this technique had previously been used to prepare $[\text{HB}(\text{pz})_3]\text{ReOCl}_2$.⁶ However, a quite different type of product is observed when ammonium perhenate in ethanolic hydrochloric acid is reacted with a 5-fold excess of the tridentate ligand $[\text{HB}(\text{Me}_2\text{pz})_3]^-$. Under these conditions is formed a green compound that can be recrystallized from acetone to give green prismatic crystals shown to contain the dimeric oxo-bridged compound $\text{Re}_2\text{O}_3\text{Cl}_4(\text{Me}_2\text{pzH})_4$, in which the $\text{HB}(\text{Me}_2\text{pz})_3^-$ ligand has been cleaved to give pyrazole ligands.

Experimental Section

Rhenium as NH_4ReO_4 was obtained as a gift from the Duval Mine in Southern Arizona. Infrared spectra (KBr pellet) were recorded on a Perkin-Elmer PE983 instrument. Electronic spectra were taken on a UV-vis IBM 9420 spectrophotometer. ¹H NMR measurements were obtained with a Bruker WM 250 spectrometer using CDCl_3 as solvent and TMS as internal calibrant.

Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate was prepared by a literature method,⁷ and all other chemicals were used without further purification. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Cyclic voltammetric measurements were performed in acetonitrile solutions, with a 0.1 M solution of tetra-*n*-butylammonium tetrafluoroborate in acetonitrile in all cases. The electrochemical cell used employed a platinum electrode as working electrode, a platinum-wire counter electrode, and a Hg/Hg₂Cl₂ reference electrode. Data were taken on an IBM EC 225 voltammetric analyzer equipped with an IBM 742 MT X-Y-T recorder.

Preparation. To a slurry of 0.5 g of NH_4ReO_4 in 100 mL of 95% EtOH and 2 mL concentrated HCl was added 1.5 g (74 mmol) of $[\text{KB}(\text{Me}_2\text{pz})_3]$. After refluxing for 90 min, the deep green reaction mixture was allowed to cool to room temperature for about 20 min. The green solid was collected by filtration, washed with water, and quickly washed with ice-cold ethanol and allowed to dry in air. It is stable in air and at room temperature; yield 74%. Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{N}_8\text{Cl}_4\text{O}_3\text{Re}_2$ (*M_r* 946.7): C, 25.35; H, 3.38; N, 11.84; Cl, 14.98. Found: C,

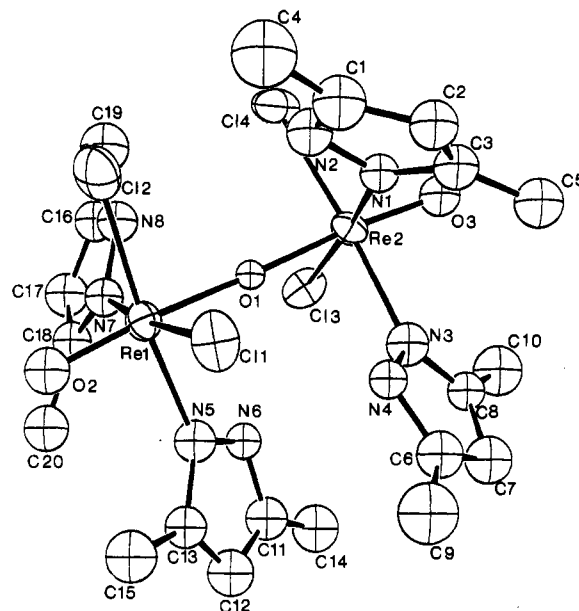


Figure 1. Perspective view of the structure of the $\text{Re}_2\text{O}_3\text{Cl}_4(\text{Me}_2\text{pzH})_4$ molecule showing the atom-labeling scheme.

25.88; H, 3.39; N, 12.17; Cl, 15.30. IR (KBr; cm⁻¹): $\nu(\text{NH})$ 3223 (vs), 3146 (sh), $\nu(\text{Re}=\text{O})$ 972 (s), $\nu(\text{Re}-\text{O}-\text{Re})$ 704 (s, b). Electronic spectrum (in acetone): λ_{max} = 681 nm ($\epsilon = 3.6 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$), $\lambda_{\text{max}2}$ = 329 nm ($\epsilon = 2.9 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). ¹H NMR (CDCl_3): δ 2.27 (singlet) and 2.32 (singlet) (total intensity 12, CH₃ of $\text{C}_3\text{HMe}_2\text{N}_2\text{H}$), 5.86 (singlet, intensity 2, 4-H of $\text{C}_3\text{HMe}_2\text{N}_2\text{H}$), 6.13 (singlet, intensity 2, 4-H of $\text{C}_3\text{HMe}_2\text{N}_2\text{H}$), 10.9 (broad weak signal, probably NH).

X-ray Crystallography. Evaporation of an acetone solution at 0 °C gave green prismatic crystals of $\text{Re}_2\text{O}_3\text{Cl}_4(\text{Me}_2\text{pzH})_4\text{Me}_2\text{CO}$ suitable for X-ray structure determination. Table I contains the crystallographic data for the crystal and the cell dimensions from automatic centering, indexing, and least-squares routines. Several ω scans showed widths at half-height of 0.22°, indicating good crystal quality. The axial photographs showed the lattice to be orthorhombic. The space group *Pbca* was determined from systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$. A total of 5219 reflections, of which 4583 were unique, were collected on a Nicolet-Syntex P₂ autodiffractometer to a maximum 2θ of 45°. Lorentz and polarization corrections were applied to the data. An absorption correction was made by the empirical method of Walker and Stuart.⁸ Scattering factors were taken from Cromer and Waber.⁹

The structure was solved by direct methods. The rhenium and chlorine atoms were located from the resulting *E* map, and the remaining atoms were located in succeeding difference Fourier syntheses. Only 3034 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The final cycle of refinement included 370 variable parameters and converged with $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.036$ and $R_w = \{\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2} = 0.046$ when $w = 4F_o^2/(\sigma^2(I) + p^2(F_o^2)^2)$ and p , the uncertainty factor, was set equal to 0.03. The standard deviation of an observation of unit weight was 1.5. The highest peak in the final difference Fourier map had a height of 0.775 e Å⁻³. Plots of $w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed no unusual trends.

Results and Discussion

Treatment of NH_4ReO_4 in ethanolic HCl with $[\text{KB}(\text{Me}_2\text{pz})_3]$ affords a dimeric, μ -oxo-bridged rhenium(V) compound of the formula $\text{Re}_2\text{O}_3\text{Cl}_4(\text{Me}_2\text{pzH})_4$. Obviously, these conditions result in a breakup of the pyrazolylborate group to form pyrazole ligands, which coordinate to the Re(V) center. Cleavage of the $\text{HB}(\text{Me}_2\text{pz})_3^-$ ligand and formation of the dimeric oxo-bridged complex also occur when the reaction is carried out in slightly acidic solution in the presence of hypophosphorous acid. The use of

(2) Cleland, W. E., Jr.; Barnhart, K. M.; Yamanouchi, K.; Collison, D.; Mabbs, F. E.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 1017.

(3) Rouschias, G. *Chem. Rev.* **1974**, *74*, 531.

(4) Davis, R.; Fergusson, J. E. *Inorg. Chim. Acta* **1970**, *4*, 16.

(5) (a) Chatt, J.; Rowe, G. A. *J. Chem. Soc.* **1962**, 4019. (b) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054.

(6) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125.

(7) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288.

(8) (a) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 159. (b) Frenz, B. A. In *Computing in Crystallography*; Olthoff-Hazelkamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64-71.

(9) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

Table II. Selected Bond Distances (Å) and Angles (deg)

| | | | |
|-------------|-----------|------------|------------|
| Re1-Cl1 | 2.394 (3) | Re2-O1 | 1.937 (6) |
| Re1-Cl2 | 2.380 (3) | Re2-O3 | 1.685 (7) |
| Re1-O1 | 1.921 (6) | Re2-N1 | 2.115 (12) |
| Re1-O2 | 1.694 (7) | Re2-N3 | 2.110 (9) |
| Re1-N5 | 2.105 (8) | Re2-Cl3 | 2.409 (3) |
| Re1-N7 | 2.105 (9) | Re2-Cl4 | 2.394 (3) |
| Re1-O1-Re2 | 177.7 (4) | Cl3-Re2-O1 | 96.5 (3) |
| Cl1-Re1-Cl2 | 90.7 (1) | Cl3-Re2-N1 | 171.0 (3) |
| Cl3-Re2-Cl4 | 89.6 (1) | O1-Re1-O2 | 172.5 (3) |
| Cl1-Re1-O2 | 96.7 (3) | O1-Re2-O3 | 173.5 (3) |
| Cl2-Re1-O1 | 89.7 (2) | | |

H₃PO₂ as reducing agent is a very common method to prepare monomeric oxorhenium(V) species.¹⁰

McCleverty and co-workers have previously reported¹¹ that the reaction of K[HB(Me₂pz)₃] with {Re(CO)₄Cl}₂ yields the bis-(pyrazole) complex Re(3,5-Me₂pzH)₂(CO)₃Cl, as well as the desired tricarbonyl pyrazolylborate complex [HB(Me₂pz)₃]Re(CO)₃. Thus, it appears that some rhenium species are effective at promoting the decomposition of the tridentate HB(Me₂pz)₃⁻ ligand into pyrazole fragments.

The structure of Re₂O₃Cl₄(Me₂pzH)₄ is shown in Figure 1. The oxo-bridged structure is similar to that found in the [Re₂OCl₁₀]⁴⁻ ion,¹² in the dithiocarbamate Re(V) dimer Re₂O₃(S₂CNEt₂)₄,¹³ and in Re₂O₃Cl₄(C₅H₅N)₄.¹⁴ Selected bond angles and distances are listed in Table II; Table III gives the final positional parameters for the non-hydrogen atoms. Each rhenium(V) center is in a pseudooctahedral environment of the two chloride, two pyrazole N, and two oxygen atoms, with the chlorine atoms in cis position relative to each other. The complex shows a strong infrared band at 972 cm⁻¹, which is assigned to the Re=O stretching mode. The band at 704 cm⁻¹ can be assigned to ν_{as}(Re-O-Re).

The Re-O-Re unit is nearly linear (177.7°), and the terminal oxygen atom of each rhenium is trans to the bridging oxygen atom. The Re=O_t bond distances are 1.694 and 1.685 Å for the terminal oxygens; the mean rhenium-oxygen bond length for the Re-O_b-Re unit is 1.93 Å. These values are in good agreement with those found for oxygen-bridged complexes of Re(V) containing the Re₂O₃ unit, 1.67–1.72 Å for Re=O_t and 1.90–1.92 Å for Re-O_b.¹⁴

The overall rotational stereochemistry of the Re₂O₃Cl₄(Me₂pzH)₄ molecule about the nearly linear Re-O-Re fragment is very similar to that found previously for Re₂O₃Cl₄(C₅H₅N)₄.¹⁴ The latter molecule also has cis Cl ligands and cis N atoms (from the pyridine ligands) about each Re atom, and the two ReCl₂N₂ planes are twisted about the Re-Re vector with a twist angle of about 23°. For Re₂O₃Cl₄(Me₂pzH)₄ the Cl and N ligands have the same orientation relative to the Re-Re vector, and the twist angle is 32°. The twist about the Re-Re vector is ascribed to interactions between the bulky heterocycle rings on the two Re centers.¹⁴ Such interactions among the Me₂pzH rings have not been analyzed in detail for Re₂O₃Cl₄(Me₂pzH)₄ but are consistent with the observed stereochemistry.

The cyclic voltammogram of Re₂O₃Cl₄(Me₂pzH)₄·Me₂CO in acetonitrile exhibits one two-electron reduction peak at -1.31 V vs Fc⁺/Fc⁰ at a scan rate of 50 mV s⁻¹. The same behavior is found in DMF.

Summary

Our attempts to prepare the mononuclear oxorhenium(V) compound [HB(Me₂pz)₃]ReOCl₂, from perhenate and K[HB-

Table III. Positional Parameters and Their Estimated Standard Deviations

| atom | x | y | z | B _{eq} , ^a Å ² |
|------|-------------|-------------|-------------|---|
| Re1 | 0.43661 (3) | 0.14107 (3) | 0.18251 (2) | 2.664 (9) |
| Re2 | 0.52271 (3) | 0.24410 (3) | 0.06526 (2) | 2.853 (9) |
| Cl1 | 0.2987 (2) | 0.1855 (2) | 0.1576 (1) | 3.81 (7) |
| Cl2 | 0.4206 (2) | 0.0155 (2) | 0.1377 (1) | 4.18 (8) |
| Cl3 | 0.6524 (2) | 0.2734 (2) | 0.1082 (1) | 4.52 (8) |
| Cl4 | 0.5786 (2) | 0.1122 (2) | 0.0414 (1) | 4.86 (8) |
| O1 | 0.4807 (4) | 0.1940 (4) | 0.1249 (2) | 1.9 (1) |
| O2 | 0.4074 (5) | 0.1015 (4) | 0.2374 (3) | 3.7 (2) |
| O3 | 0.5486 (5) | 0.2934 (5) | 0.0130 (3) | 4.2 (2) |
| O4 | 0.520 (1) | 0.6895 (8) | 0.1109 (5) | 10.5 (4) |
| N1 | 0.4029 (6) | 0.2088 (6) | 0.0377 (3) | 3.1 (2) |
| N2 | 0.3773 (6) | 0.1289 (6) | 0.0426 (4) | 3.7 (2) |
| N3 | 0.4692 (6) | 0.3539 (6) | 0.0937 (4) | 3.5 (2) |
| N4 | 0.3966 (6) | 0.3521 (5) | 0.1204 (3) | 3.2 (2) |
| N5 | 0.4589 (6) | 0.2568 (6) | 0.2157 (4) | 3.4 (2) |
| N6 | 0.5336 (6) | 0.2981 (5) | 0.2041 (4) | 3.0 (2) |
| N7 | 0.5640 (6) | 0.1091 (6) | 0.1947 (3) | 2.9 (2) |
| N8 | 0.6115 (7) | 0.0800 (6) | 0.1577 (4) | 3.9 (2) |
| C1 | 0.3005 (8) | 0.1176 (8) | 0.0251 (5) | 4.1 (3) |
| C2 | 0.2740 (9) | 0.1925 (9) | 0.0063 (5) | 4.9 (4) |
| C3 | 0.3402 (8) | 0.2477 (7) | 0.0145 (4) | 3.4 (3) |
| C4 | 0.258 (1) | 0.0357 (9) | 0.0278 (6) | 6.9 (4) |
| C5 | 0.3455 (9) | 0.3359 (8) | -0.0014 (5) | 5.6 (4) |
| C6 | 0.3721 (8) | 0.4286 (8) | 0.1347 (5) | 4.1 (3) |
| C7 | 0.4330 (9) | 0.4804 (8) | 0.1145 (5) | 4.9 (3) |
| C8 | 0.4897 (8) | 0.4349 (7) | 0.0896 (5) | 3.5 (3) |
| C9 | 0.2957 (9) | 0.4387 (9) | 0.1640 (6) | 5.7 (4) |
| C10 | 0.5637 (9) | 0.4643 (8) | 0.0629 (5) | 5.1 (4) |
| C11 | 0.5436 (9) | 0.3661 (7) | 0.2320 (5) | 4.5 (3) |
| C12 | 0.4758 (9) | 0.3700 (8) | 0.2630 (5) | 4.7 (3) |
| C13 | 0.4254 (8) | 0.3009 (7) | 0.2520 (4) | 3.4 (3) |
| C14 | 0.619 (1) | 0.4205 (9) | 0.2239 (6) | 8.1 (5) |
| C15 | 0.3442 (9) | 0.2740 (9) | 0.2767 (5) | 5.9 (4) |
| C16 | 0.6931 (8) | 0.0701 (9) | 0.1702 (5) | 5.1 (3) |
| C17 | 0.6963 (8) | 0.0879 (8) | 0.2175 (5) | 4.3 (3) |
| C18 | 0.6162 (8) | 0.1115 (8) | 0.2343 (5) | 3.7 (3) |
| C19 | 0.756 (1) | 0.043 (1) | 0.1338 (6) | 8.5 (5) |
| C20 | 0.5881 (9) | 0.1400 (9) | 0.2825 (4) | 4.8 (3) |
| C21 | 0.498 (1) | 0.756 (1) | 0.1036 (6) | 7.6 (5) |
| C22 | 0.555 (1) | 0.828 (1) | 0.0925 (6) | 8.4 (5) |
| C23 | 0.410 (1) | 0.779 (1) | 0.1000 (7) | 10.6 (7) |

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $8PP^2(U(11) + U(22) + U(33))/3$.

(Me₂pz)₃] in acidic ethanol produced instead the binuclear oxorhenium(V) compound Re₂O₃Cl₄(Me₂pzH)₄ and cleavage of the HB(Me₂pz)₃⁻ ligand. This result is surprising because the parent polypyrazolylborate ligand, HB(pz)₃⁻, has been shown⁶ to preferentially form the mononuclear oxorhenium(V) compound [HB(pz)₃]ReOCl₂, under the same reaction conditions. Relatively few rhenium complexes of polypyrazolylborate ligands have been synthesized.^{1,3} However, the results available^{11,16} suggest that rhenium complexes of the HB(Me₂pz)₃⁻ ligand are either difficult to form or especially sensitive to hydrolysis of the B-N bond of the ligand.

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Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom fractional coordinates (2 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.

- Chakravorti, M. C. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1991.
- McCleverty, J. A.; Wolochowicz, I. *J. Organomet. Chem.* **1979**, *169*, 289.
- Morrow, L. *Acta Crystallogr.* **1962**, *15*, 851.
- Tisley, D. G.; Walton, R. A.; Wills, D. L. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 523.
- Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1978**, *56*, 179.
- The redox system ferrocenium/ferrocene (Fc⁺/Fc) was used as internal standard for measurements in organic solvents. The formal redox potentials are given in volts versus Fc⁺/Fc.

- Jones, C. J., personal communication.