

Articles

Multiple Bonds between Transition Metals and Main-Group Elements. 145.¹ Coordination Chemistry of Dirhenium Heptaoxide: Covalent Adducts and "Ionic Perrhenyl-Perrhenates"

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Dirhenium heptaoxide dissolves in donor solvents such as 1,2-dimethoxyethane, thf, and CH₃CN to form adducts of the general formula O₃ReOReO₃·2L (L = monodentate ligand site). A strong reactivity enhancement of Re₂O₇ for alkylation, arylation, and similar reactions follows from this unsymmetric Lewis-base coordination. The terminal and bridging oxygens equilibrate in solution (¹⁷O NMR). These adducts exhibit unsymmetrical bent oxygen bridges in their solid state structures, e.g. O₃ReOReO₃·dme (X-ray diffraction study; crystal data: space group P2₁/c, *a* = 12.162(2) Å, *b* = 10.830(1) Å, *c* = 8.195(1) Å, β = 90.80(1)°, *Z* = 4). With stronger, chelating *N*-donors L₂ such as 2,2'-bipyridine, *N,N'*-dicyclohexyl-1,4-diazabuta-1,3-dien, and 2,2'-bis(pyrazolyl)propane the Re₂O₇·2L complexes have rigid asymmetric bridges even in solution (¹⁷O NMR). Thermal decomposition liberates Re₂O₇ (EI-MS) and the respective ligand (EI-MS, TG-MS). With tridentate ligands L₃ like tris(pyrazolyl)methane, 1,4,7-triazacyclononane (tacn), *N,N',N''*-trimethyl-1,4,7-triazacyclononane (tacn*), 1,4,7-trithiacyclononane (ttcn), the Re—O—Re bridge breaks with formation of the ionic perrhenates [ReO₃L₃]⁺[ReO₄]⁻. An example is the ionic [ReO₃(tacn*)]⁺[ReO₄]⁻, the structure of which compound has been determined by X-ray diffraction (crystal data: space group P1̄, *a* = 7.389(2) Å, *b* = 9.143(2) Å, *c* = 1.2294(3) Å, α = 83.68(2)°, β = 77.99(2)°, γ = 89.29(2)°, *Z* = 2). Intermolecular hydrogen bridging plays a major role in the crystal packing of the ionic perrhenates.

Introduction

Dirhenium heptaoxide is a readily-available rhenium chemical of growing use in research and industry. It belongs to a small group of binary metal oxides that are soluble in some organic solvents, with the other examples being limited to Mn₂O₇, Tc₂O₇, RuO₄, and OsO₄. The crystal lattices of these latter oxides are built of discrete molecules.² In contrast, Re₂O₇ (1) has long been known to exhibit an infinite "polymeric" solid-state structure similar to the features of insoluble metal oxides

such as WO₃ and MoO₃. Recently, Re₂O₇ has proven an appropriate starting material in the synthesis of organorhenium oxides, e.g. RReO₃, R₄Re₂O₄, or R₆Re₂O₃ (R = alkyl, aryl).³⁻⁸

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(2) For a comprehensive collection of data, see for example: (a) Connor, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 4, p 197 f. (b) Chiswell, B.; McKenzie, E. D.; Lindoy, L. F. *Ibid.*, p 110. (c) Griffith, W. P. *Ibid.*, p 588 ff. (d) Rouschias, G. *Chem. Rev.* **1974**, *74*, 531-566. (e) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed., Clarendon Press: Oxford, U.K., 1984; pp 509 and 549 (Re₂O₇ and Re₂O₇(H₂O)₂), 531 and 543 (OsO₄), 553 (Mn₂O₇), 549 (Tc₂O₇). (f) Peacock, R. D. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Jr., et al., Eds.; Pergamon Press: Oxford, U.K., 1973; Vol. 3, p 940 ff.

Among these are catalysts for olefin oxidation, olefin metathesis, the oxidation of metal carbonyls, and aldehyde olefination.⁷

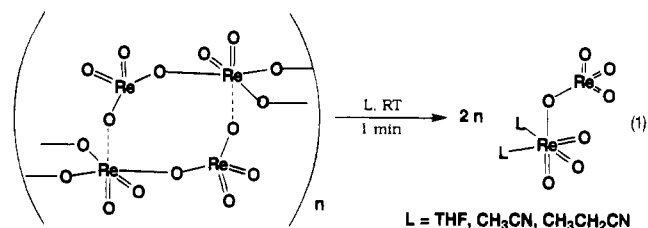
Recent developments in this area originate from structural peculiarities of Re_2O_7 in σ -donor solvents⁹ and from the heterolytic cleavage of this compound by virtue of strong N -bases such as 1,4,7-triazacyclononane.¹⁰ The present report concentrates on the interaction of Re_2O_7 with donor solvents and Lewis-base ligands.

In the gas phase, discrete dirhenium heptaoxide (**1**) molecules with a symmetrical oxo bridge are observed.^{9b} By way of contrast, a "polymeric" structure is seen in the solid state, forming four-membered rings consisting of $[\text{ReO}_4]$ tetrahedra and $[\text{ReO}_6]$ octahedra.¹¹ These features—unique for Re_2O_7 —must be born in mind upon consideration of the results to follow.

Results and Discussion

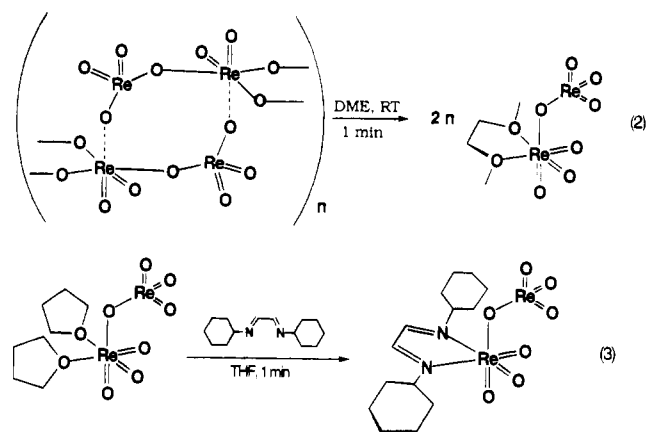
(A) Synthesis and Spectroscopy. Covalent Adducts.

When **1** is dissolved in polar solvents such as acetonitrile,^{9a} thf,^{9b} or propionitrile, solvent adducts are formed (eq 1). For monodentate ligands (L) these adducts are of the general formula $\text{Re}_2\text{O}_7 \cdot 2L$ (**2**), e.g. $\text{Re}_2\text{O}_7 \cdot 2\text{thf}$ (**2a**) and $\text{Re}_2\text{O}_7 \cdot 2\text{CH}_3\text{CN}$ (**2b**). The ^{17}O NMR spectra of **2a** show at room temperature the magnetic equivalence of all seven terminal and bridging oxygen ligands. At -30°C , however, two signals are observed: $\delta = 745$ and 395 ppm. The latter is very low in intensity and is thus assigned to the bridging oxygen atom. In comparison to



terminal ReO groups, bridging $\text{Re}-\text{O}-\text{Re}$ moieties resonate at higher field.¹² The IR spectra of **2a** (thf solution) reveal both a tetrahedral anion (*perrhenate*-type) and an octahedral *cis*- ReO_4L_2 unit.^{9c} The same structural pattern is observed for solid **2a** and **2b**. Both ligands L are located at the *same* Re atom.⁹ This type of structure seems to be preferred for adducts of **1** with weak donor ligands. Stronger donors like pyridine, however, form triple adducts with one pyridine residing at one Re center and two pyridines at the other.^{13,14}

If **1** is dissolved in 1,2-dimethoxyethane (dme) or if bidentate bases [$L_2 = 2,2'$ -bipyridine (bpy), 4,4'-di-*tert*-butyl-2,2'-bipyridine (*tbu*-bpy), 2,2'-bis(pyrazolyl)propane ($(\text{pz})_2\text{C}(\text{CH}_3)_2$), *N,N'*-dicyclohexyl-1,4-diazabuta-1,3-dien (cydab)] are added to a solution of **1** in thf, the adducts $\text{Re}_2\text{O}_7 \cdot \text{dme}$ (**2c**), $\text{Re}_2\text{O}_7 \cdot \text{bpy}$ (**2d**), $\text{Re}_2\text{O}_7 \cdot \text{tbu-bpy}$ (**2e**), $\text{Re}_2\text{O}_7 \cdot (\text{pz})_2\text{C}(\text{CH}_3)_2$ (**2f**), and $\text{Re}_2\text{O}_7 \cdot \text{cydab}$ (**2g**), respectively, are formed (eqs 2 and 3). Similar to



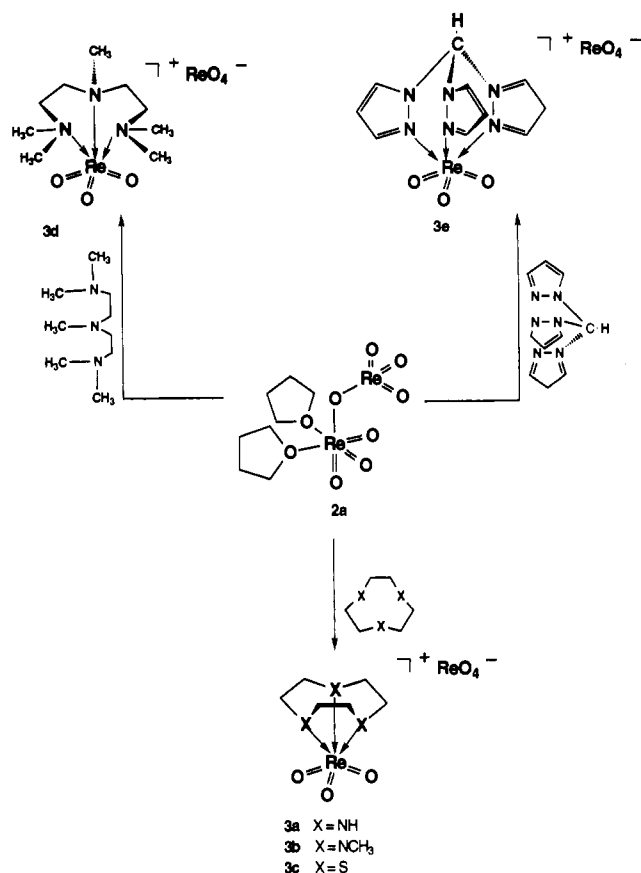
2a,b one tetrahedral and one octahedral rhenium center is observed (IR and ^{17}O NMR spectroscopy). The ^{17}O NMR spectra of **2g** show three peaks at $\delta(^{17}\text{O}) = 794$, 744 , and 660 ppm (solvent: CDCl_3). A comparison with the NMR spectra of other known $\text{Re}^{\text{VII}}\text{O}_3$ derivatives^{12a} shows one Re atom to bear the bidentate ligand *trans* to two of the oxygen atoms which resonate at $\delta(^{17}\text{O}) = 794$. The signal at $\delta(^{17}\text{O}) = 744$ ppm is therefore assigned to the oxygen *trans* to the bridging oxygen atom, and the signal at $\delta(^{17}\text{O}) = 660$ ppm to the ReO_4 group. No signal attributable to a bridging oxygen atom is observed (expected below $\delta(^{17}\text{O}) = 400$ ppm).¹² The IR spectra of compounds **2b-f** show all the same features in terms of the $\text{Re}-\text{O}$ vibrations (Table 1): the $\text{Re}-\text{O}-\text{Re}$ bridge is observed at $\nu = 850$ cm^{-1} , and one tetrahedral and one octahedral Re center is found in all cases. The complexes **2c-g** are structurally analogous to **2a,b**.

If Re_2O_7 is dissolved in pure pyridine and 2,2'-bipyridine is then added, an immediate, quantitative precipitation of a mixed

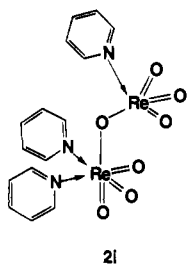
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Scheme 1



pyridine–bipyridine adduct $\text{Re}_2\text{O}_7\cdot\text{bpy}\cdot\text{py}$ (**2h**) occurs by replacement of two single pyridine molecules in the coordination sphere. One metal atom becomes pentacoordinated by addition of one pyridine ligand, while the other one becomes octahedral by coordination of bipyridine. The IR spectra once again show a bridging oxygen atom, which very much resembles those of the known $\text{Re}_2\text{O}_7(\text{py})_3$ (**2i**)^{13,14} [**2h**, 932 vs, 920 vs, 870 m, 845 w; **2i**, 947m, 924 vs, 810 w].



Ionic Adducts. Treatment of a thf solution of **1** with tridentate ligands L_3 like 1,4,7-triazacyclononane, results in immediate, quantitative formation of white precipitates (Scheme 1). Although they analyze for “ $\text{Re}_2\text{O}_7\cdot L_3$ ”, they are not simple adducts in structural terms. The tridentate ligands rather induce cleavage of the $\text{Re}-\text{O}-\text{Re}$ bridge of (solvated) Re_2O_7 ,¹⁰ resulting in a heterolysis of this oxide into $[\text{ReO}_4]^-$ and $[\text{ReO}_3]^+$, with the latter species being stabilized as $[\text{ReO}_3L_3]^+$ by coordination of L_3 : $[\text{ReO}_3L_3]^+[\text{ReO}_4]^-$ (**3**) with $L_3 = 1,4,7$ -triazacyclononane (tacn) (**3a**), N,N,N' -trimethyl-1,4,7-triazacyclononane (tacn*) (**3b**), 1,4,7-trithiacyclononane (ttcn) (**3c**), N,N,N',N'',N''' -pentamethyldiethyltriamine (pmdt) (**3d**), tris-(pyrazolyl)methane ($\text{HC}(\text{pz})_3$) (**3e**). This redox-neutral cleavage of **1** results from the structure of its solvent adducts **2a–c**, where the $\text{Re}-\text{O}-\text{Re}$ bridge has a pronounced asymmetry (see above). **3a–e** show in the IR spectrum no peak at $\nu = 850 \text{ cm}^{-1}$ (Table

Table 1. Selected IR Data [$\nu(\text{ReO})$, cm^{-1}] for Complexes **2a–i** and **3a–e** (in KBr)^a and ^{17}O NMR Data (ppm)

complex	$\nu(\text{ReO})$	$\delta(^{17}\text{O})$ (solvent)
2a		740, 395 (THF- d_6) ^b
2b	937 vs, 910 vs, 849 s	747, 320 (CH_3CN)
2c	967 w, 943 vs, 919 vs, 844 w ^d	740, 365 (DME)
2d	942 vs, 917 vs, 866 m, 850 m	c
2e	937 vs, 918 vs, 859 vs, 835 vs	c
2f	941 w, 923 vs, 864 vs	c
2g	943 vs, 924 vs, 915 vs, 881 m, 839 st	794, 745, 660 (CDCl_3)
2h	932 vs, 920 vs, 870 m, 845 w	
2i	948 w, 924 s, 810 w (pyridine)	766, 312 (pyridine)
3a	935 vs, 912 vs	731, 563 (D_2O)
3b	921 vs, 912 vs	752, 562 (D_2O)
3c	927 vs, 910 vs	782, 570 ($\text{DMSO}-d_6$)
3d	933 vs, 912 vs	c
3e	929 vs, 920 vs	c

^a vs = very strong, st = strong, m = medium, w = weak. ^b Recorded at -30°C . ^c Insoluble. ^d Recorded in acetonitrile.

1) expected for and typical of a $\text{Re}-\text{O}-\text{Re}$ bridging moiety. Only two ^{17}O NMR signals are observed, one for the perrhenate ion ($\delta(^{17}\text{O}) = 570$ ppm) and one for the $[\text{ReO}_3L_3]^+$ cation; the latter species gives rise to only one signal due to its *fac*-octahedral geometry (Table 1). Solvents with a better donor strength induce shifts to higher fields thereby revealing an interaction between the solvent and the strongly Lewis-acidic metal center (Re^{VII}). Further proof of this heterolytic cleavage is given by the crystal structures of **3a**¹⁰ and **3b**. The conductivity data of Table 6 are in accord with 1/1 electrolytes.

Complex **3a** was previously prepared by Wieghardt et al. by nitric acid or H_2O_2 oxidation of $[\text{tacnRe}(\text{CO})_3]\text{Cl}$.¹⁵ The new route, however, enables the ligand to be varied: the derivatives containing *N*-methylated ligands (**3b**), *S*-donor ligands (**3c**), and even air-sensitive complexes like **3d–e** can now be synthesized directly by simple treatment of Re_2O_7 with the ligands (Experimental Section).

The ionic complexes **3a,b** are water-stable. Complex **3c**, however, decomposes slowly in water with formation of perrhenate, which is the usual decomposition product of the majority of known water-sensitive $\text{Re}^{\text{VII}}\text{O}_3$ complexes.^{3–8} Derivatives **3d,e** are even less stable; they hydrolyze within 1 h with quantitative formation of perrhenate. In comparison **2a–h** are all more or less water-sensitive: **2a–c** decompose in water within seconds, and **2d–h** within ca. 1 h. Due to formation of perrhenic acid, the solution become strongly acidic. Evaporation of water from such solutions yields perrhenate and the protonated ligand ($[\text{LH}]^+[\text{ReO}_4]^-$).

As mentioned above, the heterolytic cleavage is in accord with the structure of $\text{Re}_2\text{O}_7\cdot 2L$ adducts. The octahedrally coordinated Re center shows a longer $\text{Re}-\text{O}$ distance within the bridging unit than the four-coordinate Re (see section B), thus resembling the situation of chlorine(VI) oxide, Cl_2O_6 , which forms ion-pairs $[\text{ClO}_2]^+[\text{ClO}_4]^-$ (“chloryl perchlorate”) in the solid state.¹⁶ The driving force of the heterolysis is seen in the formation of the octahedral $[\text{ReO}_3L_3]^+$ complex where the metal attains its preferred octahedral coordination and valence saturation as, for example, in the isoelectronic 18-electron species $(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3$ and $[\text{HB}(\text{pz})_3]\text{ReO}_3$. This reasoning receives support by the similarity of the ^{17}O NMR chemical shifts of $[\text{ReO}_3L_3]^+$ and $(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3$.^{4,12} A recombination of

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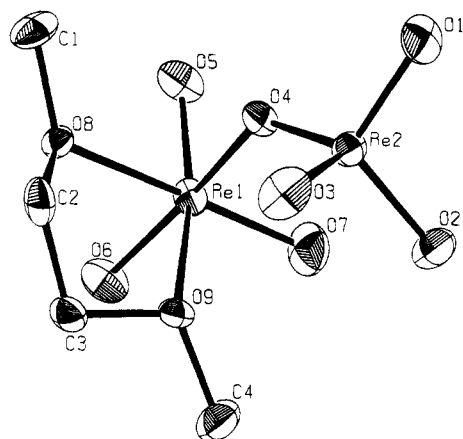


Figure 1. PLATON²⁰ drawing of the crystal and molecular structure of Re₂O₇-dme (**2c**). Thermal ellipsoids are drawn at a 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Re₂O₇-dme (**2c**)

Distances			
Re1—O4	2.113(5)	Re1—O9	2.255(5)
Re1—O5	1.703(5)	Re2—O1	1.710(6)
Re1—O6	1.693(5)	Re2—O2	1.711(5)
Re1—O7	1.693(6)	Re2—O3	1.713(6)
Re1—O8	2.217(5)	Re2—O4	1.783(5)
Angles			
O5—Re1—O4	92.2(2)	O9—Re1—O5	159.8(2)
O6—Re1—O4	155.3(2)	O9—Re1—O6	83.5(2)
O6—Re1—O5	104.4(3)	O9—Re1—O7	90.3(3)
O7—Re1—O4	89.5(3)	O9—Re1—O8	72.9(2)
O7—Re1—O5	105.5(3)	O2—Re2—O1	108.3(3)
O7—Re1—O6	103.1(3)	O3—Re2—O1	109.8(3)
O8—Re1—O4	74.7(2)	O3—Re2—O2	107.0(3)
O8—Re1—O5	88.7(2)	O4—Re2—O1	109.8(3)
O8—Re1—O6	87.4(2)	O4—Re2—O2	110.7(3)
O8—Re1—O7	159.3(3)	O4—Re2—O3	111.2(3)
O9—Re1—O4	75.2(2)	Re2—O4—Re1	138.1(3)

“[ReO₃]⁺[ReO₄]⁻” is excluded due to the cation stabilization provided by the tridentate ligand.

(B) Crystallography. One representative example of each class of adducts was structurally established by means of single X-ray diffraction.

Covalent Adduct Re₂O₇-dme. To the best of our knowledge, complex **2c** is the first structurally characterized adduct of Re₂O₇ coordinated by a bidentate ligand (Figure 1). However, there is a strong relationship with other solvent adducts such as **2a,b** and the hydrate Re₂O₇·2H₂O (**2k**).¹⁷ Important bond distances, angles, and coordinates are given in Tables 2 and 3.

The structure consists of an almost undistorted ReO₄ tetrahedron sharing one oxygen atom with a (distorted) ReO₆ octahedron. Like in the case of **2a,b** and **2k**, the geometry at the oxygen bridge is *strongly asymmetric* (Re1—O4 = 2.113(5) Å; Re2—O4 = 1.783(5) Å). The basic geometrical features of all four compounds are similar except the bridging angle Re—O—Re which is rather variable. The angle in **2c** is the smallest of all four compounds (Re1—O4—Re2 = 138.1(3)°; **2a**, 149.8(3)°; **2b**, 147.0(4)°; **2k**, almost linear). The terminal oxo groups exhibit distances to the metal as expected: 1.693(5)–1.713(6) Å (*facial* configuration within the ReO₆ octahedron).

Complexes Re₂O₇·2L differ in the position of the tetrahedron relative to the octahedron (Figure 2). A view along an axis from the bridging oxygen atom to the hexacoordinate rhenium in **2a,b** shows the ReO₄ tetrahedron above the O—O edge of

Table 3. Final Atomic Coordinates for Re₂O₇-dme (**2c**)

atom	x/a	y/b	z/c
Re1	0.17200(2)	0.86266(3)	0.25109(3)
Re2	0.33769(2)	1.05282(3)	0.52631(3)
O1	0.4379(5)	1.0067(6)	0.6616(7)
O2	0.2229(5)	1.0906(6)	0.6340(7)
O3	0.3789(5)	1.1839(5)	0.4275(8)
O4	0.3085(4)	0.9314(5)	0.3852(6)
O5	0.2234(5)	0.7164(5)	0.2526(7)
O6	0.0771(5)	0.8622(5)	0.0979(7)
O7	0.0944(5)	0.8736(6)	0.4204(7)
O8	0.2955(4)	0.9123(5)	0.0657(5)
O9	0.1640(4)	1.0692(5)	0.2182(6)
C1	0.3976(6)	0.8442(8)	0.052(1)
C2	0.3098(7)	1.0427(7)	0.0344(9)
C3	0.2004(6)	1.1012(7)	0.0548(9)
C4	0.0632(7)	1.1331(9)	0.261(1)

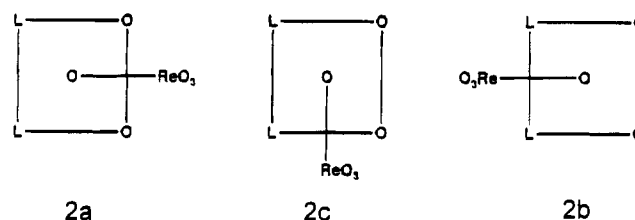


Figure 2. Relative positions of the ReO₄ tetrahedron with respect to the ReO₆ octahedron. L = ligand donor atom, and O = oxygen.

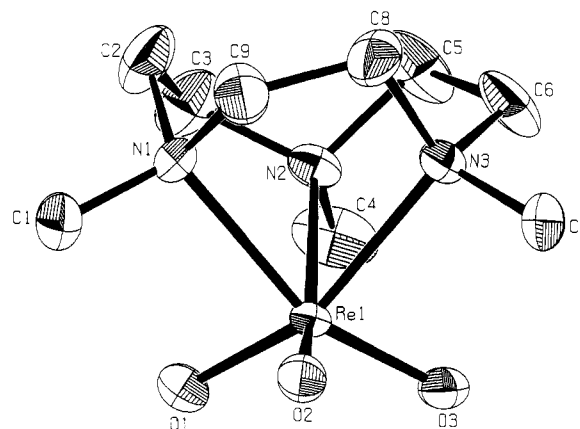


Figure 3. Crystal and molecular structure of **3b** (PLATON²⁰ drawing), showing 50% probability ellipsoids. Hydrogen atoms are omitted for better clarity.

the ReO₆ octahedron, whereas in **2c** the tetrahedron is found above an L—O edge. Only **2k** has a different geometry, with a *linear* oxo bridge. Concerning the structure of **2a**, this result is consistent with the steric demand of the thf groups. (Packing effects may influence the conformational details of **2b,c** in the solid state.)

Ionic Heterolysis Product “[{(tacn*)ReO₃][ReO₄]⁻”. The solid-state structures of the heterolysis products **3a**¹⁰ and **3b** exhibit an ionic assembly of [ReO₃L₃]⁺ and [ReO₄]⁻ ions (L = tacn and tacn*, respectively). The cations differ only slightly in their coordination geometry from what is known for [ReO₃L₃]⁺Cl⁻ (L = tacn) (**3f**).¹⁵ They possess either a crystallographically imposed C_{3v} symmetry (**3f**) or a nearly ideal C_{3v} symmetry (**3a,b**) (Figure 3). The octahedral environment of the N,N,N-coordinated rhenium in all three structures is highly distorted. The average Re—N bond lengths (**3a**, 2.242(2) Å;¹⁰ **3b**, 2.276(2) Å;¹⁰ **3f**, 2.197(5) Å¹⁵) are in the expected range¹⁵ if one considers the *trans* influence of the terminal oxo groups. The average Re=O bond lengths vary in a narrow range (**3a**,

(17) Beyer, H.; Glemser, O.; Krebs, B. *Angew. Chem.* **1968**, *80*, 286–287; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 295–296.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [tacn*ReO₃]⁺[ReO₄]⁻ (**3b**)

Distances			
Re1-O1	1.725(2)	N1-C2	1.505(5)
Re1-O2	1.721(2)	N2-C3	1.478(5)
Re1-O3	1.703(2)	N2-C4	1.487(5)
Re1-N1	2.273(2)	N2-C5	1.492(5)
Re1-N2	2.289(3)	N3-C6	1.494(4)
Re1-N3	2.267(2)	N3-C7	1.488(4)
Re2-O4	1.731(2)	N3-C8	1.499(4)
N1-C1	1.470(5)		
Angles			
O2-Re1-O1	105.8(1)	N3-Re1-O2	87.9(1)
O3-Re1-O1	105.3(1)	N3-Re1-O3	86.3(1)
O3-Re1-O2	106.2(1)	N2-Re1-N1	75.4(1)
N1-Re1-O1	87.9(1)	N3-Re1-N1	76.13(9)
N1-Re1-O2	85.8(1)	N3-Re1-N2	75.19(9)
N1-Re1-O3	158.5(1)	O5-Re2-O4	110.2(1)
N2-Re1-O1	86.7(1)	C1-N1-Re1	108.8(2)
N2-Re1-O2	157.1(1)	C2-N1-Re1	113.1(2)
N2-Re1-O3	88.3(1)	C9-N1-Re1	106.0(2)
N3-Re1-O1	158.3(1)	C2-N1-C1	112.3(3)

Table 5. Final Atomic Coordinates of [tacn*ReO₃]⁺[ReO₄]⁻ (**3b**)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Re1	0.94270(1)	0.71687(1)	0.147111(8)
Re2	1.19905(2)	0.19301(1)	0.28575(1)
O1	1.0655(3)	0.5572(3)	0.1640(2)
O2	1.0849(3)	0.8574(3)	0.1624(2)
O3	0.9259(3)	0.7368(3)	0.0102(2)
O4	0.9703(3)	0.2027(3)	0.2727(2)
O5	1.2538(4)	0.3394(3)	0.3509(2)
O6	1.3447(4)	0.1965(4)	0.1570(2)
O7	1.2279(4)	0.0328(3)	0.3669(3)
O8	1.3223(4)	0.8052(3)	0.5243(3)
N1	0.8489(4)	0.6986(3)	0.3363(2)
N2	0.6830(4)	0.5706(3)	0.1854(2)
N3	0.7033(4)	0.8754(3)	0.1751(2)
C1	1.0112(6)	0.6705(5)	0.3870(3)
C2	0.6977(6)	0.5856(5)	0.3811(3)
C3	0.6760(6)	0.4897(4)	0.2971(3)
C4	0.7085(7)	0.4650(5)	0.0998(4)
C5	0.5113(5)	0.6577(4)	0.1839(5)
C6	0.5471(5)	0.8117(5)	0.1350(4)
C7	0.7564(6)	1.0165(4)	0.1033(3)
C8	0.6451(7)	0.9066(5)	0.2945(3)
C9	0.7760(6)	0.8477(5)	0.3634(3)

1.724(3) Å;¹⁰ **3b**, 1.716(2) Å;¹⁰ **3f**, 1.756(5) Å¹⁵), quite typical for terminal oxo groups in rhenium(VII) oxo complexes (Tables 4 and 5).¹⁸

The three structures vary merely in the packing of cations and anions. Compound **3a** forms three-dimensional chains of cations and anions, connected by linear hydrogen bridges NH••O-ReO₃.¹⁰ In contrast, hexagonal close-packed layers of [ReO₃L₃]⁺ cations and Cl⁻ anions are present in **3f**,¹⁵ with N-H••Cl bridges interconnecting the cations and anions. The cation of complex **3b** does not show hydrogen bridges. Instead two water molecules provide linear hydrogen bridges between two perrhenate ions to form four-membered rings consisting of two perrhenate ions and two water molecules.

(C) **Electric Conductivity.** Conductivity measurements support the structural assignments made by NMR and IR spectroscopy. Two classes can be discriminated: (i) adducts of Re₂O₇ that show virtually no conductivity and (ii) "perrhenyl-perrhenates" that resemble 1/1 electrolytes in solution. Conductivities of 1/1 electrolytes in CH₃NO₂ (ca. 10⁻³ M) are

Table 6. Conductivity Λ (Recorded in CH₃NO₂) of Selected Complexes of Types Re₂O₇•2L and [LReO₃]⁺[ReO₄]⁻

compd	MW	concn (mol/L)	Λ (Ω ⁻¹ cm ² mol ⁻¹)
2d	640.58	4.13•10 ⁻³	8.8
2e	752.79	2.19•10 ⁻³	14.3
3b	655.68	2.60•10 ⁻³	76.0
3c	664.75	1.32•10 ⁻³	83.3
3d	657.69	8.80•10 ⁻³	72.3
3e	698.62	2.50•10 ⁻³	62.9

usually in the range Λ = 60–115 Ω⁻¹ cm² mol⁻¹ (Table 6).¹⁹ Covalent adducts such as **2d,e** show only little conductivity. The Lewis-base adducts with three donor atoms in one molecule (*e.g.*, HC(pz)₃, tacn, tacn*, and pmtd) are all fairly typical 1/1 electrolytes in nitromethane and must therefore exist also in solution as [ReO₃L₃]⁺[ReO₄]⁻. Small variations of the conductivity are obviously caused by different solubilities and by different mobilities of the cations.

(D) **Thermogravimetry and Thermal Decomposition.** The covalent complexes **2e,g,h** are similar in terms of their thermogravimetric behavior (TG-MS). Upon heating they first loose solvent molecules in two or three steps. For example, **2h** shows a three-step decomposition with a total loss of mass amounting to 49.2%. In the first step—75 to 244 °C—the compound mainly loses pyridine (MS: *m/z* = 79) and small amounts of bipyridine (MS: *m/z* = 156). For the second step—244 to 453 °C—mainly bipyridine together with residual pyridine is liberated (34%) (MS: *m/z* = 79 and 156). In the third step—453 to 686 °C—only bipyridine is lost. Unsolvated **1** sublimes partially together with volatile decomposition products but could not be detected by TG-MS.

The ionic complexes **3a,c,e** decompose in a different way. For example, **3e** shows a multistep decomposition with liberation of mainly H₂O and CO₂ in the first step (MS: *m/z* = 28, 44). In the second step, only oxidized fragments (*e.g.* ligand) occur. This suggests a redox reaction between the ligand HC(pz)₃ and [ReO₃]⁺. A small amount of the free ligand HC(pz)₃ was detected during extrusion of oxidized fragments. This same behavior is also observed for **3a,c**.

The observed differences are explained in terms of the coordination chemistry: the HC(pz)₃ ligand is more tightly bound to the cationic rhenium center of [ReO₃]⁺ than other *N*-ligands that are attached to the neutral [ReO₃] sites. The ligands of **2h** can thus be extruded as they are, while the ligand of **3e** gets oxidized upon thermal decomposition.

The EI-mass spectra agree with these observations. For compounds **2a–h**, peaks for **1** at *m/z* = 484 and for the respective ligands are recorded (Lewis acid–base adducts). In contrast, no peaks for **1** are seen in the decomposition of **3a–e** of type [ReO₃L₃]⁺[ReO₄]⁻. EI/MS thus clearly discriminates the two observed classes of *N*-ligand complexes of Re₂O₇.

Conclusion

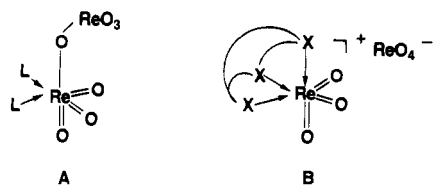
Dirhenium heptaoxide is a pronouncedly Lewis-acidic metal oxide that forms adducts of general formula Re₂O₇•*n*L with a variety of *O*, *N*, and *S* donor ligands L. It appears that ether-type ligands coordinate preferably to one metal center, thus forming *unsymmetrical* adducts of type **A** (*fac*-configuration) exhibiting covalent Re–O–Re bonds. This accounts also for the water adduct Re₂O₇•2H₂O which, however, exhibits a nearly linear Re–O–Re bridge situation.

Chelating *tripod* ligands of the nitrogen and sulfur types effect heterolytic Re–O–Re cleavage to yield ionic perrhenyl–

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(19) Geray, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.

(20) Spek, A. L. PLATON-93. *Acta Crystallogr., Sect. A.* **1990**, C34.



perrhenates of general formula **B**. The unsymmetrical coordination mode of **A** implies a reactivity enhancement of Re_2O_7 which has been repeatedly exploited in alkylation and arylation reactions.^{3–6}

Experimental Section

All reactions were performed with standard Schlenk techniques in oxygen-free and water-free nitrogen atmosphere. Solvents were dried with standard methods and distilled under N_2 . Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer and ^{17}O NMR spectra at 54.14 MHz on a FT-JEOL GX 400 instrument. All NMR solvents were "freeze-pump-thaw" degassed and (except water) stored over molecular sieves before use. Elemental analyses were performed in the Analytical Laboratory of our institute. Mass spectra were obtained with Finnigan MAT-311A and MAT-90 spectrometers. Re_2O_7 (Degussa), 2,2'-bipyridine (Aldrich), and pyridine (Aldrich) were used as received. **2a**,^{9b} **2b**,^{9a} and **2d**^{9d} were prepared according to literature procedures or modified methods.

The conductivity of degassed ca. 10^{-3} M solutions of the complexes prepared in dry nitromethane was measured under a nitrogen atmosphere, against the conductivity of the pure solvent (taken as zero) using a Schott-Geräte digital conductometer CG 855 with a Schott-Geräte LF 1100 calibrated conductivity cell with $K = 0.97 \text{ cm}^{-1}$. The values were interpreted according to the discussion in ref 19.

The TG-MS study was performed using a Perkin-Elmer TGA 7 thermobalance coupled with a Balzers QMG 420 mass spectrometer. The thermolysis experiments were carried out in a dynamic helium atmosphere (purity 5.0, 45 sccm) using a 50 to 400 °C temperature program at a rate of 10 °C/min. The temperature of the capillary interface was 280 °C.

(1) (1,2-Dimethoxyethane)dirhenium Heptaoxide (2c). A 0.50 g (1.03 mmol) amount of Re_2O_7 is dissolved in 25 mL of 1,2-dimethoxyethane. The solution is slowly cooled to -35 °C and kept at this temperature for 1 day. The mother liquor is decanted from the resulting crystals that are dried subsequently under vacuum for several hours at -10 °C. Colorless crystals are isolated with decomposition at 137 °C (under argon). Yield: 563 mg (98%). Anal. Found (calcd for $\text{C}_4\text{H}_{10}\text{O}_9\text{Re}_2$ (574.52)): C, 8.42 (8.36); H, 1.75 (1.75); Re, 65.45 (64.82).

Spectroscopic Data: IR (acetonitrile) ν (cm^{-1}) = 2955 vs, 2924 vs, 2877 st, 2830 st, 2796 m, 1474 m, 1446 m, 1284 m, 1250 st, 1198 st, 1140 st, 1078 st, 1038 st, 982 st, 967 m, 943 vs, ($\nu(\text{Re}=\text{O})$ of octahedral Re), 919 vs, ($\nu(\text{Re}=\text{O})$ of tetrahedral Re), 862 st, $\nu(\text{Re}-\text{O})$, 854 m, $\nu(\text{Re}-\text{O})$, 844 st, 459 m, 423 m; IR (nujol) ν (cm^{-1}) = 980 m, 973 m, 939 vs, ($\nu(\text{Re}=\text{O})$ of octahedral Re), 929 vs, ($\nu(\text{Re}=\text{O})$ of tetrahedral Re), 899 m, 874 s, 861 s, $\nu(\text{Re}-\text{O})$; ^1H NMR (400 MHz, thf, RT): δ (ppm) = 2.30 (6H, s, CH_3), 3.46 (4H, s, CH_2); EI-MS (70 eV) m/z = 486 ($[\text{Re}_2\text{O}_7]^+$, rel. int. 25%), 251 ($[\text{ReO}_4]^+$, 27%), 235 ($[\text{ReO}_3]^+$, 34%), 90 ($[\text{dme}]^+$, 56%), 60 ($[\text{O}-\text{CH}_2-\text{CH}_2-\text{O}]^+$, 100%).

(2) Adducts of General Formula $\text{Re}_2\text{O}_7 \cdot 2\text{L}$ (2e–h). A 0.50 g (1.03 mmol) amount of Re_2O_7 is dissolved in 10 mL of thf, and 2.06 mmol of the base is then added. A white or pale-yellow precipitate occurs immediately. The reaction mixture is stirred for 20 min. The mother liquor is then filtered away, and the remaining precipitate is washed three times with 10 mL of thf and twice with 10 mL of Et_2O . Then the residue is dried in an oil pump vacuum.

(A) (4,4'-Di-*tert*-butyl-2,2'-bipyridine)dirhenium Heptaoxide (2e). Yield: 715 mg (95%). Anal. Found (calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_7\text{Re}_2$ (752.81)): C, 29.33 (28.72); H, 1.96 (1.82); N, 5.76 (5.84); Re, 52.01 (51.74).

Spectroscopic Data: IR (KBr) ν (cm^{-1}) = 3099 w, 3065 w, 2969 st, 2871 m, 1617 m, 1546 m, 1485 w, 1458 w, 1418 m, 1364 w, 1301 w, 1253 m, 1204 w, 1161 m, 1133 m, 1079 m, 1040 w, 1027 w, 978 w, 961 m, 941 w, 937 vs ($\nu(\text{Re}=\text{O})$ of octahedral Re), 918 vs ($\nu(\text{Re}=\text{O})$ of tetrahedral Re), 859 vs, $\nu(\text{Re}-\text{O})$, 835 st, 740 m, 720 m, 668 m, 605 st, 562 m, 556 m, 424 w.

(B) **[2,2'-(*N,N'*-Bispyrazolyl)propane]dirhenium Heptaoxide (2f).** Yield: 396 mg (60%). Anal. Found (calcd for $\text{C}_9\text{H}_{12}\text{N}_4\text{O}_7\text{Re}_2$ (660.61)): C, 15.52 (16.36); H, 2.23 (1.83); N, 8.56 (8.48).

Spectroscopic Data: IR (KBr) ν (cm^{-1}) = 3146 m, 3122 m, 2963 w, 1632 w, 1537 w, 1514 m, 1454 m, 1406 m, 1312 m, 1262 st, 1240 m, 1167 m, 1109 m, 1094 m, 1082 m, 1036 m, 990 m, 941 m ($\nu(\text{Re}=\text{O})$ of octahedral Re), 923 vs ($\nu(\text{Re}=\text{O})$ of tetrahedral Re), 864 vs, $\nu(\text{Re}-\text{O})$, 785 st, 710 m, 687 m, 613 m, 602 m.

(C) ***N,N'*-Dicyclohexyl-1,4-diazabuta-1,3-dien (2g).** Yield: 549 mg (78%). Anal. Found (calcd for $\text{C}_{14}\text{H}_{24}\text{N}_2\text{O}_7\text{Re}_2$ (704.77)): C, 24.03 (23.86), H, 3.48 (3.43), N, 3.96 (3.97), Re, 52.04 (52.04).

Spectroscopic Data: IR (KBr) ν (cm^{-1}) = 3070 w, 3046 w, 2934 st, 2854 st, 1615 w, 1449 m, 1416 m, 1389 w, 1354 w, 1316 w, 1268 w, 1248 w, 1152 w, 1078 m, 1025 m, 982 w, 943 vs ($\nu(\text{Re}=\text{O})$ of octahedral Re), 924 vs, 915 vs ($\nu(\text{Re}=\text{O})$ of tetrahedral Re), 881 m, 839 st, $\nu(\text{Re}-\text{O})$, 812 st, 765 w, 647 m, 502 m, 489 m, 485 w, 418 m; ^1H NMR (400 MHz, CD_2Cl_2 , 20 °C): δ (ppm) = 2.5–1.1 (20H, m, $\text{NCH}(\text{CH}_2)_4\text{CH}_2$); 4.16 (2H, m, $\text{NCH}(\text{CH}_2)_4\text{CH}_2$); 8.85 (2H, s, $\text{HCN}=\text{C}_6\text{H}_{11}$).

(3) (2,2'-Bipyridine)(pyridine)dirhenium Heptaoxide (2h). A 0.5 g (1.03 mmol) amount of Re_2O_7 is dissolved in 10 mL of dry pyridine. A 321 mg (2.06 mmol) amount of 2,2'-bipyridine is then added. After a few seconds a white precipitate forms. After being stirred for 10 min, the solution is filtered and the residue is handled as described under (2). Yield: 677 mg (94%). Anal. Found (calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_7\text{Re}_2$ (719.70)): C, 25.06 (25.03), H, 1.96 (1.82), N, 5.76 (5.84), Re, 52.01 (51.75).

Spectroscopic Data: IR (KBr) ν (cm^{-1}) = 3086 m, 3063 m, 1617 m, 1586 m, 1531 m, 1487 w, 1473 w, 1458 w, 1434 w, 1222 w, 1178 w, 1092 w, 994 w, 932 vs ($\nu(\text{Re}=\text{O})$ of octahedral Re), 920 vs ($\nu(\text{Re}=\text{O})$ of tetrahedral Re), 870 m, 845 w, 725 w, 681 m, 611 m; EI-MS (70 eV) m/z : = 486 ($[\text{Re}_2\text{O}_7]^+$, rel. int. 18%), 251 ($[\text{ReO}_4]^+$, 6%), 235 ($[\text{ReO}_3]^+$, 14%), 156 ($[\text{bpy}]^+$, 100%), 79 ($[\text{C}_5\text{H}_5\text{N}]^+$, 12%).

(4) Ionic Complexes of General Formula $[\text{ReO}_3\text{L}][\text{ReO}_4]$ (3a–3f). To a stirred solution of **1** (245 mg, 0.5 mmol) in 10 mL of thf was added 0.5 mmol of the base at room temperature. A white microcrystalline precipitates occurs within 10–60 s. After 15 min the solvent was decanted and the solid washed with thf and dried in vacuum.

(A) [(*N,N',N''*-1,4,7-Triazacyclononane)perrhenyl] Perrhenate (3a). Yield: 300 mg (98%). Anal. Found (calcd for $\text{C}_9\text{H}_{15}\text{N}_3\text{O}_7\text{Re}_2$ (610.59)): C, 11.31 (11.74); H, 2.45 (2.46); N, 6.43 (6.85); Re, 60.07 (60.69).

Spectroscopic Data: IR (KBr) ν (cm^{-1}) = 3038 s, 2844 m, 935 vs ($\nu(\text{Re}=\text{O})$ of $[\text{ReO}_3]^+$), 912 vs ($\nu(\text{Re}=\text{O})$ of $[\text{ReO}_4]^-$); ^1H NMR (400 MHz, D_2O , 20 °C) δ (ppm) = 3.07 (12H, s, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.53 MHz, D_2O , 20 °C) δ (ppm) = 42.04 (CH_2); $^{17}\text{O}\{^1\text{H}\}$ NMR (54.21 MHz, D_2O , 20 °C) δ (ppm) = 563 (ReO_4^-), 731 (ReO_3^+); EI-MS (70 eV) m/z = 111 ($[\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}]^+$, rel. int. 38%), 70 ($[\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2]^+$, 26%); 56 ($[\text{N}-\text{CH}_2-\text{CH}_2-\text{N}]^+$, 100%).

(B) [(1,4,7-Trimethyl-*N,N',N''*-triazacyclononane)perrhenyl] Perrhenate (3b). Yield: 325 mg (99%). Anal. Found (calcd for $\text{C}_9\text{H}_{21}\text{N}_3\text{O}_7\text{Re}_2$ (655.70)): C, 16.39 (16.49); H, 3.27 (3.23); N, 6.20 (6.41); Re, 56.51 (56.80).

Spectroscopic Data: IR (KBr) ν (cm^{-1}) = 3345 m, 3400 m, 1471 m, 921 vs ($\nu(\text{Re}=\text{O})$ of $[\text{ReO}_3]^+$), 912 vs ($\nu(\text{Re}=\text{O})$ of $[\text{ReO}_4]^-$), 800 m; ^1H NMR (400 MHz, D_2O , 20 °C) δ (ppm) = 2.70 (9H, s, CH_3), 3.15–3.50 (12H, m, CH_2); $^{17}\text{O}\{^1\text{H}\}$ NMR (54.21 MHz, D_2O , 20 °C) δ (ppm) = 562 (ReO_4^-), 752 (ReO_3^+); EI-MS (70 eV) m/z = 72 ($[\text{HN}-\text{CH}_2-\text{CH}_2-\text{HN}-\text{CH}_2]^+$, rel. int. 100%).

(C) [(1,4,7-Trithiacyclononane)perrhenyl] Perrhenate (3c). Yield: 258 mg (86%). Anal. Found (calcd for $\text{C}_6\text{H}_{12}\text{O}_7\text{Re}_2\text{S}_3$ (664.75)): C, 10.55 (10.84), H, 1.96 (1.82), S, 14.47 (14.47), Re, 57.04 (56.04).

Spectroscopic Data: IR (KBr) ν (cm^{-1}) = 2980 m, 2920 m, 1620 m, 1449 m, 1413 m, 927 vs ($\nu(\text{Re}=\text{O})$ of $[\text{ReO}_3]^+$), 910 vs ($\nu(\text{Re}=\text{O})$ of $[\text{ReO}_4]^-$), 583 (m, br, $\nu(\text{CS})$). ^1H NMR (400 MHz, $\text{dms}-d_6$, 20 °C) δ (ppm) = 3.51 (12 H, s, CH_2); $^{17}\text{O}\{^1\text{H}\}$ NMR (54.21 MHz, $\text{dms}-d_6$, 20 °C) δ (ppm) = 570 (ReO_4^-), 782 (ReO_3^+).

(D) (*N,N,N',N''*-Pentamethyldiethylenetriamine)perrhenyl Perrhenate (**3d**). Yield: 322 mg (98%). Anal. Found (calcd for $C_{19}H_{23}N_2O_7Re_2$ (657.71)): C, 16.41 (16.44); H, 3.63 (3.52); N, 6.50 (6.39); Re, 56.16 (56.62).

Spectroscopic Data: IR (KBr) ν (cm^{-1}) = 2988 w, 2833 w, 1472 m, 1261 w, 1097 m, 1023 m, 933 vs ($\nu(Re=O)$ of $[ReO_3^+]$), 912 vs ($\nu(Re=O)$ of $[ReO_4^-]$), 867 m, 802 m; EI-MS (70 eV) m/z = 218 ($[ReO_2]^+$, rel. int. 0.2%), 115 ($[(CH_3)_2N-CH_2-CH_2-N(CH_3)]^+$, 6%), 72 ($[(CH_3)_2N-CH_2-CH_2-]^+$, 36%), 58 ($[(CH_3)_2N-CH_2-]^+$, 100%).

(E) [Tris(pyrazolyl)methane]perrhenyl Perrhenate (**3e**). Yield: 317 mg (91%). Anal. Found (calcd for $C_{10}H_9N_6O_7Re_2$ (697.63)): C, 17.27 (17.19); H, 1.50 (1.44); N, 11.89 (12.05); Re, 54.13 (53.30).

Spectroscopic Data: IR (KBr) ν (cm^{-1}) = 3416 w, 3131 m, 3113 m, 2978 w, 2951 w, 1510 w, 1447 m, 1410 st, 1273 st, 1226 w, 1099 w, 1067 m, 957 w, 929 vs ($\nu(Re=O)$ of $[ReO_3^+]$), 910 vs ($\nu(Re=O)$ of $[ReO_4^-]$), 772 st, 650 w, 606 w.

(5) **X-ray Structure Determination of 2c.** **2c** of formula $C_4H_{10}O_9Re_2$ crystallized from a solution of 1,2-dimethoxyethane at $-30^\circ C$. Final lattice parameters were obtained by least-squares refinement of 25 reflections ($40.3 < 2\theta < 48.3$; $\lambda = 0.7093 \text{ \AA}$, Mo $K\alpha_1$). The space group was identified from the systematic absences: monoclinic, $P2_1/c$, $a = 12.162(2) \text{ \AA}$, $b = 10.830(1) \text{ \AA}$, $c = 8.195(1) \text{ \AA}$, $\beta = 90.80(1)^\circ$, $V = 1079.3 \text{ \AA}^3$, $Z = 4$, $D_{calc} = 3.54 \text{ g/cm}^3$. A colorless crystal fragment was mounted in a glass capillary. Data were collected at $-50^\circ C$ on an Enraf-Nonius CAD4 diffractometer ($2^\circ < 2\theta < 50^\circ$) with graphite-monochromatized Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation using the ω -scan mode.²¹ All 6129 data were corrected for Lorentz and polarization terms and for absorption (ψ -scans, $\mu = 227.5 \text{ cm}^{-1}$) using the SDP System.²² The structure was solved by the Patterson method (SHELXS-86)²³ and refined by full-matrix least squares methods using the program CRYSTALS.²⁴ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms positions were calculated in ideal geometry ($d_{C-H} = 0.96 \text{ \AA}$, $U_{iso} = 1.3U_C$) and were not refined. Final refinement using 1597 unique observed ($I > 3\sigma(I)$) reflections converged at $R = 0.025$

and $R_w = 0.029$. A final difference-Fourier synthesis map was featureless, the largest peak being 1.6 e/\AA^3 , 0.88 \AA from Re1.

(6) **X-ray Structure Determination of 3b.** **3b** of formula $C_9H_{15}O_7Re_2$ crystallized from water at $25^\circ C$ in the triclinic space group $P\bar{1}$ with $a = 7.389(2) \text{ \AA}$, $b = 9.143(2) \text{ \AA}$, $c = 12.294(3) \text{ \AA}$, $\alpha = 83.68(2)^\circ$, $\beta = 77.99(2)^\circ$, $\gamma = 89.29(2)^\circ$, $Z = 2$, $V = 807 \text{ \AA}^3$, $\rho_{calcd} = 2.785 \text{ g/cm}^3$, $F(000) = 624$; Mo $K\alpha$ radiation, CAD4 Enraf Nonius, ω -scan, maximum, 50 s, 6045 measured reflections ($1^\circ < \theta < 25^\circ$), $h(-8/8)$, $k(-10/10)$, $l(-14/14)$, 2785 independent reflections, of which 2506 with $I > 3.0\sigma(I)$ used for the refinement. Structure solutions were obtained by virtue of Patterson methods. All hydrogen atoms were located from the difference Fourier map and were freely refined. No intensity correction was performed, and the empirical absorption correction is based on ψ -scan data ($\mu = 153 \text{ cm}^{-1}$). Larson's extinction parameter was $23.15 R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.018$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.019$, and residual electron density = $+0.92/-0.85 \text{ e \AA}^{-3}$. For further details of the crystal structure determination, the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, may be contacted, quoting the reference to this paper, the names of the authors, and the registration number CSD-57636.

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Supporting Information Available: Tables of final coordinates and equivalent isotropic thermal parameters, hydrogen atom positions and thermal parameters, anisotropic thermal parameters, and bond distances and angles (3 pages). Ordering information is given on any current masthead page.

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