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Structural and Functional Characteristics of Rhenium Clusters Derived from Redox Chemistry of the Triangular $[\mathrm{Re^{III}}_3(\mu\text{-Cl})_3]$ Core Unit

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The present study investigates structural and functional aspects of the redox chemistry of rhenium(III) chloride $[\mathrm{Re_3Cl_9}]$ (**1**) in aqueous and organic solvents, with emphasis on the dioxygen-activating capabilities of reduced rhenium clusters bearing the $\mathrm{Re_3}^{8+}$ core. Dissolution of **1** in HCl (6 M) generates $[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_9}]^{3-}$ (**2a**), which can be isolated as the tetraphenylphosphonium salt (**2b**). Anaerobic one-electron reduction of **1** by Hg in HCl (6−12 M) produces $[(\mathrm{C_6H_5})_4\mathrm{P}]_2[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_7}(\mathrm{H_2O})_2]\cdot\mathrm{H_2O}$ (**3**), the structure of which features a planar $[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_3}]$ framework ($\mathrm{Re_3}^{8+}$ core), involving two water ligands that occupy out-of-plane positions in a trans arrangement. Compound **3** dissociates in the presence of CO, yielding $[(\mathrm{C_6H_5})_4\mathrm{P}]_2[\mathrm{Re^{III}}_2\mathrm{Cl_8}]$ (**4**) and an unidentified red carbonyl species. In situ oxidation ($\mathrm{O_2}$) of the reduced $\mathrm{Re_3}^{8+}$-containing cluster in HCl (6 M) produces quantitatively **2a**, whereas oxidation of **3** in organic media results in the formation of $[(\mathrm{C_6H_5})_4\mathrm{P}]_4[\{\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_7}(\mu\text{-OH})\}_2]\cdot2\mathrm{CH_2Cl_2}$ (**5**). The structure of **5** reveals that two oxygen ligands (hydroxo units) bridge asymmetrically two $\mathrm{Re_3}^{9+}$ triangular clusters. The origin of these hydroxo units derives from the aquo ligands, rather than $\mathrm{O_2}$, as shown by $^{18}\mathrm{O_2}$ labeling studies. The hydroxo bridges of **5** can be replaced by chlorides upon treatment with $\mathrm{Me_3SiCl}$ to afford the analogous $[(\mathrm{C_6H_5})_4\mathrm{P}]_4[\{\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_7}(\mu\text{-Cl})\}_2]\cdot10\mathrm{CH_2Cl_2}$ (**6**). The reaction of **5** with Hg in HCl (6 M)/tetrahydrofuran regenerates compound **3**. Complexes **1**−**3** exhibit nitrile hydratase type activity, inducing hydrolysis of $\mathrm{CH_3CN}$ to acetamide. The reaction of **3** with $\mathrm{CH_3CN}$ yields $[(\mathrm{C_6H_5})_4\mathrm{P}]_2[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_{6.5}}(\mathrm{CH_3CN})_{1.5}(\mathrm{CH_3C(O)NH})_{0.5}]$ (**7**), the structure of which is composed of $[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_7}(\mathrm{CH_3CN})_2]^{2-}$ (**7a**) and $[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_6}(\mathrm{CH_3CN})(\mathrm{CH_3C(O)NH})]^{2-}$ (**7b**) ($\mathrm{Re_3}^{8+}$ cores) as a disordered mixture (1:1). Oxidation of **7** with $\mathrm{O_2}$ in $\mathrm{CH_3CN}$ affords $[(\mathrm{C_6H_5})_4\mathrm{P}]_2[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_7}(\mathrm{CH_3C(O)NH})]\cdot\mathrm{CH_3CN}$ (**8**) and small amounts of $[(\mathrm{C_6H_5})_4\mathrm{P}][\mathrm{ReO_4}]$ (**9**). Compound **8** is also independently isolated from the reaction of **2b** with wet $\mathrm{CH_3CN}$, or by dissolving **5** in $\mathrm{CH_3CN}$. In MeOH, **5** dissociates to afford $[(\mathrm{C_6H_5})_4\mathrm{P}]_2[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_8}(\mathrm{MeOH})]\cdot\mathrm{MeOH}$ (**10**).

Introduction

The polymeric rhenium chloride $[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_6}]$ (**1**)[1] and dissociated anion $[\mathrm{Re_3}(\mu\text{-Cl})_3\mathrm{Cl_9}]^{3-}$ (**2a**)[2] in HCl solutions feature a diamagnetic $\mathrm{Re_3}^{9+}$ core (D_{3h}, $(a')^2(a'')^2(e')^4(e'')^4$) composed of three Re═Re double bonds[3] arranged in triangular fashion, having remarkable stability attributed to a pattern of σ- and π-metalloaromaticity.[4] Compounds **1** and **2a** occupy a prominent position in the history of the development of multiply bonded metal cluster chemistry.[5]

Complex **1** and its Re(III) halide congeners have extensive chemistry, systematized in a major contemporary publication[5] under the headings of (i) adduct formation with Lewis bases; (ii) halide exchange and Re−X solvolysis reactions;[6] and (iii) redox chemistry in various media, frequently coupled with disruption of the trirhenium cluster. Whereas the redox chemistry, spectro-electrochemistry, and interconversion of quadruply bonded $[\mathrm{Re^{III}}_2\mathrm{Cl_8}]^{2-}$ and $[\mathrm{Re_2Cl_9}]^{n-}$ ($n = 1−3$) systems is well established,[7] that of the triangular **1** and **2** is ill-defined, for although reduction of **1** is facile, there is often uncertainty surrounding the extent of the reduction and the precise composition of the species formed. Thus, better definition of their redox chemistry is highly desirable[8] for any meaningful employment of these clusters in redox catalysis.

In organic media, aromatic amines of different basicities induce one-, two-, or three-electron reductions, producing

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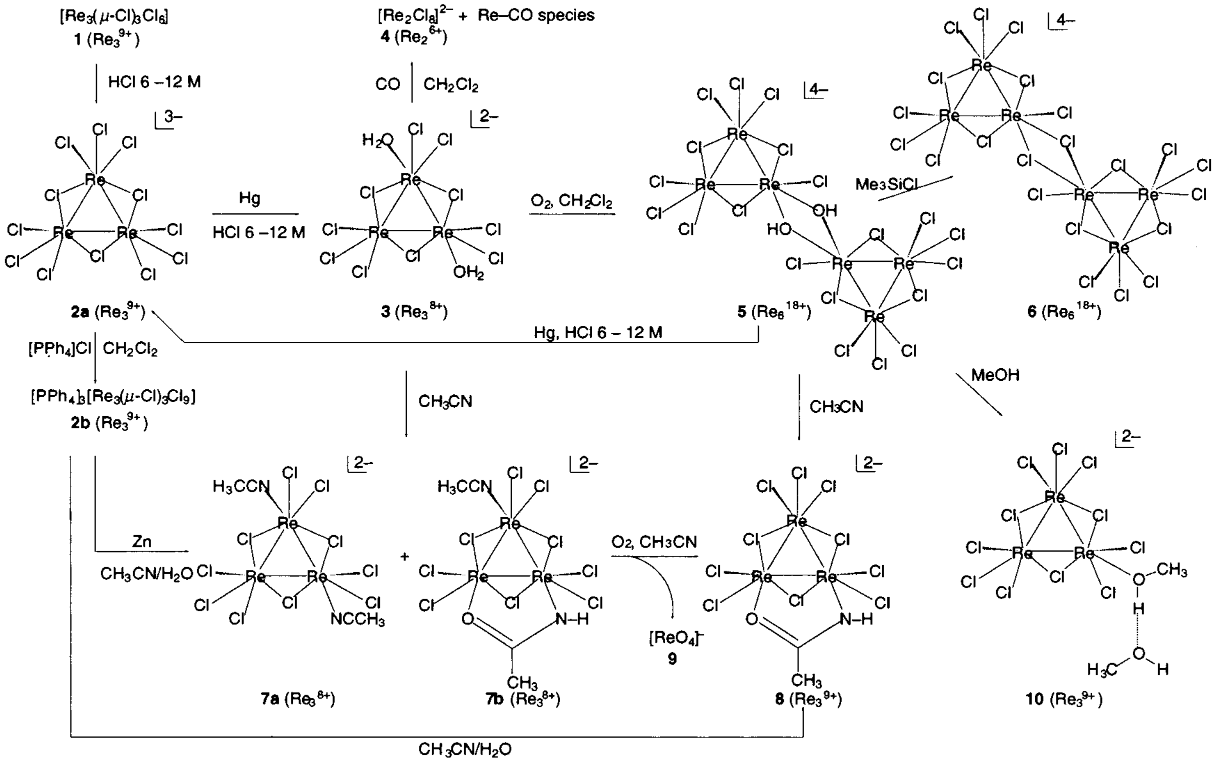
Scheme 1



complexes of the type $[Re_3(\mu\text{-}Cl)_3Cl_{6-n}(\text{amine})_n]_x$ ($n = 1, 2, 3$) containing the $Re_3^{(9-n)+}$ core.[9] With pyridine (py), a compound with stoichiometry $[ReCl_2(py)]_x$ has been isolated, which has been proposed to be either the triangulo $[Re_3(\mu\text{-}Cl)_3Cl_3(py)_3]_x$ (Re_3^{6+}) complex possessing a stacked polymeric structure via Re−Cl−Re bridges[10] or the hexanuclear $[Re_6(\mu\text{-}Cl)_6Cl_6(py)_6]$ (Re_6^{12+}) trigonal prismatic cluster containing three Re≡Re and six Re−Re bonds,[11] analogous to the well-documented $[Re_6Br_{14}]^{2-}$ and $[Tc_6Cl_{12}]^{2-}$ clusters.[12,13]

Bulk controlled potential electrolysis (−0.55 V vs Al/Al^{3+}) of dark-red $[Re_3Cl_{12}]^{3-}$ in the basic molten salt $AlCl_3$ (44.4%)/1-Me,3-Et-imidazolium chloride (55.6%) has been reported[8a] to yield a dark purple solution (λ_{max} 540 nm (ϵ_M 1.0 × 10^3)), whose pCl-dependent $E_{1/2}$ values in cyclic voltammetric experiments indicate loss of Cl^- from the coordination sphere of the cluster during the one-electron reduction of $[Re_3Cl_{12}]^{3-}$ in the basic molten salt (eq 1, in which x is most likely 1).

$$[Re_3Cl_{12}]^{3-} + e^- \rightleftarrows [Re_3Cl_{12-x}]^{(4-x)-} + xCl^- \qquad (1)$$

The sites of abstractable chlorides (in or out of plane) have not been defined in the one-electron reduction, but the process has been related to earlier reductions of aqueous HCl solutions (0.5 M) of $[Re_3Cl_{12}]^{3-}$ at a dropping mercury electrode.[8c] Those have also been known to feature a pCl sensitive, albeit six-electron reduction wave, presumed to involve chloride abstraction from the labile in-plane coordination positions.

More recently,[14] purple solutions have been obtained by chemical ($VCl_2 \cdot 4H_2O$, Sn/$SnCl_2$, Hg) or electrochemical ($E_{1/2}$ = −0.400 V versus SCE) reduction of $[Re_3Cl_{12}]^{3-}$ in HCl (6 M) solutions, and derivatized by CsCl/H_2SO_4 to afford $Cs_3[Re_3Cl_9(\mu_3\text{-}O_3SO)]$, in which the one-electron-reduced Re_3^{8+} triangular core is capped on one side by the tripodal sulfate at three out-of-plane sites.[15]

With respect to oxidation processes, hydrochloric acid solutions of **1** are resistant to aerial oxidation, whereas CH_2Cl_2 solutions of the isocyanide complexes $[Re_3(\mu\text{-}Cl)_3Cl_6(NCR)_3]$ exhibit a quasi-reversible one-electron oxidation ($E_{1/2}$ = +1.5−1.7 V versus SCE).[16] In contrast, the purple HCl solutions containing the reduced Re_3^{8+} cluster noted above undergo facile oxidation by molecular oxygen and other oxidants (H_2O_2, NaOCl, *t*-BuOOH) to yield quantitatively the parent cluster **2a**.[14] Dioxygen activation and reduction to water is efficiently catalyzed by a system composed of **1**/Hg/O_2 (P_{O_2} = 1 atm) in HCl (6 M) at 298 K,[14] with the cluster cycling between the Re_3^{9+} and the Re_3^{8+} states.

In the present article, we report the isolation, structural characterization, and reactivity (as summarized in Scheme 1) of Re_3^{8+}-containing rhenium chloride clusters, derived from reduction of **1** in HCl (6 M) or organic media. The catalytic properties of these clusters, particularly toward the oxidation of alcohols to aldehydes/ketones, will be presented in a subsequent publication.

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Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen or argon atmosphere, using Schlenk techniques on an inert gas/vacuum manifold or in a drybox (O_2, H_2O <2 ppm). Hexane, petroleum ether, and toluene were distilled over Na, and THF and diethyl ether over Na/Ph_2CO. Acetonitrile and methylene chloride were distilled over CaH_2. Ethanol and methanol were distilled over the corresponding magnesium alkoxide, and acetone over Drierite. Anhydrous pyridine, dimethyl sulfoxide, dimethylformamide (water <0.005%), and nitromethane were purchased from Sigma-Aldrich, and 1,2-dichlorobenzene was purchased from Fluka. Deuterated solvents for NMR experiments were purchased from Cambridge Isotope Laboratory, with the exception of deuterated nitromethane, which was purchased from Aldrich. All solvents with the exception of methanol and water were degassed by three freeze−pump−thaw cycles. Methanol and water were degassed by bubbling nitrogen or argon for 0.5 h. Starting materials were purchased from Sigma-Aldrich and are of the highest available purities. Rhenium(III) chloride, $[Re_3Cl_9]$ (**1**), was prepared according to a literature procedure[17] or purchased from Alfa Aesar. $[(n\text{-}Bu)_4N]Cl$ was purified by recrystallization from acetone.[18]

$[(C_6H_5)_4P]_3[Re_3Cl_{12}]$ (2b). $[Re_3Cl_9]$ (**1**) powder (99.9+%, 318 mg, 0.36 mmol) was dissolved in HCl (6 M, 40.0 mL) to afford a deep red solution. A solution of 3.1 equiv of tetraphenylphosphonium chloride (433 mg, 1.16 mmol) dissolved in distilled water (10.0 mL) was added to the deep red solution. The reaction mixture was stirred vigorously for 20 min followed by filtration and extraction of the precipitate with 3 × 50 mL of methylene chloride. The combined organic layers were dried over $CaCl_2$. Reduction of the solvent to a minimal volume and refrigeration at −10 °C yielded pink-red crystals of **2b** (620 mg, 85%), suitable for X-ray analysis. IR (KBr): 307, 284, 280 (s, $Re-Cl_{o,t}$), 260, 257 (s, $Re-Cl_{i,t}$) cm^{-1}. UV−vis (HCl, 12 M): λ_{max} (ϵ_M) 520 (1676), 772 (459) nm. ESI-MS: *m/z* 620.2 ($[Re_2Cl_7]^-$), 858.6 ($[Re_3Cl_8O]^-$, low intensity), 877.7 ($[Re_3Cl_9]^-$), 912.5 ($[Re_3Cl_{10}]^-$). Anal. Calcd for $C_{72}H_{60}Cl_{12}P_3Re_3$: C, 43.19; H, 3.02; Cl, 21.25; P, 4.64. Found: C, 43.28; H, 2.99; Cl, 21.52; P, 4.72.

$[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(H_2O)_2]\cdot H_2O$ (3). $[Re_3Cl_9]$ (**1**) powder (99.9+%, 1060 mg, 1.211 mmol) was dissolved in 6 M HCl (50 mL) to afford a deep red solution. Excess mercury (1 g, 4.985 mmol) was added to the solution, and the mixture was vigorously stirred under nitrogen for 24 h. During this period the color of the solution changed from deep red to dark purple. A solution of 2 equivalents of tetraphenylphosphonium chloride (99%, 928 mg, 2.476 mmol) dissolved in distilled water (10 mL) was carefully layered over the purple solution. The resultant mixture was allowed to stand undisturbed under nitrogen at room temperature for 1 week, during which time dark purple crystals were observed in solution. Filtration of the crystalline material, followed by washings with 3 × 3 mL of cold H_2O, yielded analytical quality, dark purple crystals of **3** (1660 mg, 83%). ^1H NMR (CD_2Cl_2): δ 7.928 (t, 2H, PPh_4), 7.780 (m, 1H, PPh_4), 7.635 (dd, 2H, PPh_4). IR (KBr): 3464, 3421 (s, H_2O), 281 (s, $Re-Cl_{o,t}$), 255 (s, $Re-Cl_{i,t}$) cm^{-1}. UV−vis (HCl, 12 M): λ_{max} (ϵ_M) 524 (1135), 860 (270), 1082 (308) nm. ESI-MS: *m/z* 843.6 ($[Re_3Cl_8]^-$), 858.5 ($[Re_3Cl_8O]^-$), 879.7 ($[Re_3Cl_9]^-$). Anal. Calcd for $C_{48}H_{46}Cl_{10}O_3P_2Re_3$: C, 35.03; H, 2.82; Cl, 21.54; P, 3.76. Found: C, 34.88; H, 2.88; Cl, 21.71; P, 3.86.

A sample of the deuterated $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(D_2O)_2]\cdot D_2O$ was prepared by employing deuterated hydrochloric acid and deuterated water in the procedure noted above. The analogous $[(n\text{-}Bu)_4N]^+$ salt of the protonated cluster (**3a**) was also prepared by a similar procedure, by replacing $[(C_6H_5)_4P]Cl$ with $[(n\text{-}Bu)_4N]Cl$.

Reaction of 3 with CO. Compound **3** (130 mg, 0.079 mmol) was dissolved in methylene chloride (40.0 mL). The resultant dark purple solution was immediately exposed to dry carbon monoxide for 10 min. The color of the solution changed from purple to greenish-brown. The solution was filtered, and the solvent was reduced under vacuum to 5.0 mL. Red microcrystalline solid precipitated after the solution was refrigerated at −10 °C, resulting in a green supernatant. Efforts to obtain X-ray quality crystals of the red material were unsuccessful. Slow diffusion of diethyl ether into the green filtrate yielded dark green crystals of $[(C_6H_5)_4P]_2[Re_2Cl_8]$ (**4**) (25 mg, 19%). These can be recrystallized from CH_3CN/Et_2O to yield $[(C_6H_5)_4P]_2[Re_2Cl_8]\cdot 2CH_3CN$. Anal. Calcd for $C_{52}H_{46}Cl_8N_2P_2Re_2$: C, 44.08; H, 3.27; Cl, 20.02; N, 1.98. Found: C, 44.28; H, 3.32; Cl, 20.19; N, 1.92.

$[(C_6H_5)_4P]_4[\{Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}OH)\}_2]\cdot 2CH_2Cl_2$ (5). Compound **3** (250 mg, 0.152 mmol) was dissolved in methylene chloride (75.0 mL) to afford a dark purple solution. The solution was immediately exposed to dry oxygen for 10 min at room temperature. The color of the solution changed from dark purple to dark red. The solution was filtered, and the solvent was reduced to a minimum volume (10 mL). Precipitation of bulk **5** can be induced by addition of excess diethyl ether. Otherwise, refrigeration at −10 °C afforded X-ray quality, dark red crystals of **5** (175 mg, 72%). Alternatively, compound **3** (20 mg, 0.012 mmol) was dissolved in the minimum amount of nitromethane (5 mL) and exposed to dioxygen. Slow diffusion of diethyl ether into the filtrate of the dark red solution afforded X-ray quality, dark red crystals of **5** (12 mg, 60%). ^1H NMR (CD_3NO_2): δ 7.907 (m, 2H, PPh_4), 7.748 (m, 3H, PPh_4). IR (KBr): 664 (w, Re_2O_2), 560 (sh, Re_2O_2), 280 (s, $Re-Cl_{o,t}$), 256 (s, $Re-Cl_{i,t}$) cm^{-1}. UV−vis (CH_3CN): λ_{max} (ϵ_M) 526 (1483), 772 (268) nm. ESI-MS: *m/z* 620.4 ($[Re_2Cl_7]^-$), 843.5 ($[Re_3Cl_8]^-$), 858.2 ($[Re_3Cl_8O]^-$), 879.4 ($[Re_3Cl_9]^-$), 912.4 ($[Re_3Cl_{10}]^-$). Anal. Calcd for $C_{98}H_{86}Cl_{24}O_2P_4Re_6$: C, 34.74; H, 2.56; Cl, 25.12; P, 3.66. Found: C, 34.65; H, 2.61; Cl, 24.97; P, 3.63.

The analogous $[(n\text{-}Bu)_4N]^+$ salt (**5a**) is prepared in a similar manner starting from a sample of **3a**. IR (KBr): 660 (w, Re_2O_2), 554 (sh, Re_2O_2), 280 (s, $Re-Cl_{o,t}$), 252 (s, $Re-Cl_{i,t}$) cm^{-1}. UV−vis (CH_3CN): λ_{max} (ϵ_M) 528 (1475), 778 (270) nm.

$[(C_6H_5)_4P]_4[\{Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}Cl)\}_2]\cdot 10CH_2Cl_2$ (6). Compound **5** (50 mg, 0.015 mmol) was suspended in CH_2Cl_2 (30.0 mL) to generate a dark red slurry. Excess chlorotrimethylsilane (50 μL, 0.39 mmol) was added to this mixture, and the suspension was stirred vigorously overnight, during which time all solid was dissolved to afford a red-brown solution. The solution was reduced under vacuum to 5.0 mL and filtered. Diethyl ether was slowly diffused into this solution at −10 °C to afford dark red-brown crystals of **6** (40 mg, 65%). IR (KBr): 282 (s, $Re-Cl_{o,t}$), 250 (s, $Re-Cl_{i,t}$) cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (ϵ_M) 495 (831), 783 (404) nm. Anal. Calcd for $C_{106}H_{100}Cl_{42}P_4Re_6$: C, 31.02; H, 2.46; Cl, 36.28; P, 3.02. Found: C, 31.24; H, 2.53; Cl, 35.98; P, 3.09.

$[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_{6.5}(CH_3CN)_{1.5}(CH_3C(O)NH)_{0.5}]$ (7). This compound is generated by dissolving **3** (200 mg, 0.12 mmol) in acetonitrile (50 mL) to afford dark blue solutions. Slow diffusion of diethyl ether into these solutions afforded dark blue crystals of **7** (130 mg, 64%) suitable for X-ray analysis. ^1H NMR (CD_2Cl_2): δ 7.930 (t, 32H, PPh_4), 7.774 (m, 16H, PPh_4), 7.625 (dd, 32H, PPh_4), 2.436 (s, 9H, CH_3CN), 2.323 (s, 3H, $CH_3C(O)NH$). IR (KBr): 3050 (s, N−H), 1585 (s, C=O) cm^{-1}. UV−vis (CH_3CN): λ_{max} (ϵ_M) 599 (1364), 980 (305) nm. Anal. Calcd for $C_{52}H_{46.5}Cl_{9.5}N_2O_{0.5}P_2Re_3$: C, 37.52; H, 2.82; Cl, 20.23; N, 1.68. Found: C, 37.50; H, 2.84; Cl, 20.18; N, 1.65.

$[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3C(O)NH)]\cdot CH_3CN$ (8). Compound **7** (100 mg, 0.060 mmol) was dissolved in acetonitrile (30 mL), and the solution was exposed to dry oxygen for 12 h. The color of the solution changed slowly from dark blue to deep red. Filtration and slow diffusion of tetrahydrofuran into the filtrate afforded dark red crystals of **8** (55 mg, 0.033 mmol, 55%), suitable for X-ray analysis. Trace amounts of colorless crystals, identified by X-ray analysis as $[(C_6H_5)_4P][ReO_4]$ (**9**), were detected along with the dark red crystals.

Compound **8** can also be prepared pure in the following manner. Compound **2b** (0.50 g, 0.250 mmol) was added to a mixture of 10.0 mL of CH_3CN and 0.3 mL of H_2O. The dark red-purple solution was stirred for 24 h. The solvent was removed under vacuum, and the residue was crystallized by dissolving in the minimum volume of CH_3CN, followed by diffusion of diethyl ether, to afford dark red-purple crystals of **8** (0.391 g, 0.231 mmol, 92%). ^1H NMR (CD_3CN, 20 °C): δ 2.641 (s, 3H, CH_3), 9.390 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 26.840 (CH_3), 190.153 (*C*O). IR (KBr): 3054 (s, N−H), 1590 (s, C=O), 280 (s, $Re-Cl_{o,t}$), 260 (s, $Re-Cl_{i,t}$). UV−vis (CH_3CN): λ_{max} (ϵ_M) 524 (1743), 792 (361) nm. ESI-MS: *m/z* 858.2 ($[Re_3Cl_8O]^-$), 879.4

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Table 1. Crystallographic Data[a] for $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(H_2O)_2]\cdot H_2O$ (**3**), $[(C_6H_5)_4P]_4[\{Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}OH)\}_2]\cdot 2CH_2Cl_2$ (**5**), $[(C_6H_5)_4P]_4[\{Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}Cl)\}_2]\cdot 10CH_2Cl_2$ (**6**), $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_{6.5}(CH_3CN)_{1.5}(CH_3C(O)NH)_{0.5}]$ (**7**), $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3C(O)NH)]\cdot CH_3CN$ (**8**), and $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_8(MeOH)]\cdot MeOH$ (**10**)

	3	**5**	**6**	**7**	**8**	**10**
formula	$C_{48}H_{46}Cl_{10}$-$O_3P_2Re_3$	$C_{98}H_{84}Cl_{24}$-$O_2P_4Re_6$	$C_{106}H_{100}Cl_{42}$-P_4Re_6	$C_{52}H_{46.5}Cl_{9.5}$-$N_2O_{0.5}P_2Re_3$	$C_{52}H_{47}Cl_{10}$-$N_2OP_2Re_3$	$C_{50}H_{48}Cl_{11}$-$O_2P_2Re_3$
fw	1645.99	3387.77	4104.12	1664.82	1691.05	1691.48
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Z	2	4	1	4	4	2
a, Å	10.3204(2)	16.100(2)	14.481(1)	10.1085(1)	22.5845(3)	10.214(1)
b, Å	13.4754(2)	19.139(4)	15.623(1)	23.3929(7)	9.24980(10)	12.944(1)
c, Å	21.1067(5)	18.307(5)	18.033(1)	23.5415(5)	27.0072(2)	22.069(2)
α, deg	99.774(1)	90	100.282(2)	90	90	92.289(2)
β, deg	94.195(1)	92.03(1)	108.082(2)	90.7040(1)	103.790(1)	93.086(2)
γ, deg	112.321(1)	90	108.964(2)	90	90	107.646(2)
V, Å^3	2645.31(9)	5637(2)	3486.2(4)	5566.4(2)	5479.2(1)	2771.6(4)
T, K	213(2)	213(2)	213(2)	213(2)	213(2)	213(2)
color	dark purple	dark red	dark red	dark blue	dark red-purple	dark red
$d_{calc,}$ g/cm^3	2.066	1.996	1.955	1.986	2.050	2.027
μ, mm^{-1}	7.453	7.087	6.081	7.060	7.198	7.162
R1[b] (wR2[c]), %	3.06 (5.89)	4.01 (6.72)	4.11 (10.39)	3.75 (6.65)	3.62 (4.82)	6.10 (17.37)

[a] Obtained with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

($[Re_3Cl_9]^-$), 935.6 ($[Re_3Cl_9(CH_3C(O)NH]^-$). Anal. Calcd for $C_{52}H_{47}Cl_{10}N_2OP_2Re_3$: C, 36.93; H, 2.80; Cl, 20.97; N, 1.66. Found: C, 37.12; H, 2.84; Cl, 21.03; N, 1.69.

$[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_8(CH_3OH)]\cdot CH_3OH$ (10). Compound **5** (100 mg, 0.030 mmol) was dissolved in MeOH (20 mL) and stirred for 24 h to yield a dark red solution. Diethyl ether was diffused into the filtrate to afford dark red crystals of **10** (70 mg, 0.041 mmol, 68%) over a period of 1−2 days. ^1H NMR (CD_2Cl_2): δ 7.930 (t, 16H, PPh_4), 7.770 (m, 8H, PPh_4), 7.640 (dd, 16H, PPh_4), 3.410 (s, 6H, CH_3OH), 3.245 (br, 2H, CH_3OH). IR (KBr): 3422, 3400 (s, O−H), 2955 (s, OCH_3 (C−H)), 280 (s, $Re-Cl_{o,t}$), 256 (s, $Re-Cl_{i,t}$) cm^{-1}. UV−vis (CH_3OH): λ_{max} (ϵ_M) 512 (2262), 753 (919) nm. Anal. Calcd for $C_{50}H_{48}Cl_{11}O_2P_2Re_3$: C, 35.50; H, 2.86; Cl, 23.06; P, 3.66. Found: C, 35.61; H, 2.89; Cl, 23.14; P, 3.71.

X-ray Structure Determinations. Crystallographic data for compounds **2**−**10** for which structures were determined are listed in Table 1 and also as Supporting Information (crystallographic data for **2b**, **4**, and **9** appear only as Supporting Information). Single crystals were picked from the crystallization vessel (coated with Paratone-N oil if necessary due to air-sensitivity or desolvation), mounted on a glass fiber using grease, and transferred to a Siemens (Bruker) SMART CCD (charge-coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. Data were measured using ω scans of 0.3° per frame for 30 s, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were re-collected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software[19] and refined using the SAINT software[20] which corrected for Lp and decay. Absorption corrections were applied using SADABS[21] supplied by George Sheldrick. The structures were solved by the direct method using the SHELXS-97[22] program and refined by a least-squares method on F^2, SHELXL-97,[23] incorporated in SHELXTL-PC V 5.10.[24]

The structures were solved in the space groups specified in Table 1 and in the Supporting Information, by analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystals used for the diffraction studies showed no decomposition during data collection. All drawings (Figures 1−6) were done at 50% probability ellipsoids.

Other Physical Measurements. ^1H and ^{13}C NMR spectra were recorded on JEOL GSX-270, Varian XL-400, and Varian 300 Unity Plus NMR spectrometers. FT-IR spectra were obtained on a Perkin-Elmer 1800 and Spectra 2000 spectrometers. Raman spectra were recorded on a Jobin Yvon HG2S Air Laser model 165 spectrometer. UV−vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrometer, and on a Hitachi U-2000 or a Varian Cary 3E spectrophotometer. GC−MS experiments were performed on a Varian 3400 CX GC coupled to a Varian Saturn 2000 MS. Electrospray ionization (ESI) mass spectra were recorded using a Platform II MS (Micromass Instruments, Danvers, MA) or a TSQ 7000 Finnigan-MAT. Samples were introduced from solutions specified in the text at a flow rate of 5 μL/min from a syringe pump (Harvard Apparatus). The electrospray probe capillary was maintained at a potential of 3.0 kV, and the orifice to skimmer potential (“cone voltage”) was varied from 15 to 30 V. Spectra were collected in the multichannel acquisition mode. EPR spectra were recorded on a Bruker ER 200D-SRC EPR or on a Varian E9 spectrometer, employing an Oxford ESR-10 liquid-helium cryostat. Magnetic susceptibility measurements were made on a Mettler magnetic balance with a Newport electromagnet, and on a Quantum Design AC MRMS-5S SQUID magnetosusceptometer. Microanalyses were done by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany, and by Quantitative Technologies Inc., Whitehouse, NJ.

Results and Discussion

Synthesis and Characterization of Compounds. When dissolved in HCl (12 M), the dark red powder of polymeric $[Re_3Cl_9]$ (**1**) has been known[2] to dissociate into discrete triangular clusters of $[Re_3Cl_{12}]^{3-}$ (**2a**). To ensure that the integrity of the complex (especially with respect to hydrolysis of terminal chlorides) is retained in the entire region of HCl concentrations (6−12 M) employed in this study, a dark red solution of **1** in HCl (6 M) was extracted by CH_2Cl_2 with the assistance of the phase-transfer agent $[(C_6H_5)_4P]Cl$. Indeed, the complex obtained from the organic layer upon diffusion of diethyl ether is $[(C_6H_5)_4P]_3[Re_3Cl_{12}]$ (**2b**). The structure of **2b** (see Supporting Information for crystallographic data) confirms the familiar features of $[Re_3Cl_{12}]^{3-}$ (average Re−Re 2.471(6)

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(19) *SMART V 5.050 (NT) Software for the CCD Detector System*; Bruker Analytical X-ray Systems: Madison, WI, 1998.

(20) *SAINT V 5.01 (NT) Software for the CCD Detector System*; Bruker Analytical X-ray Systems: Madison, WI, 1998.

(21) *SADABS Program for Absorption Corrections Using Siemens CCD Based on the Method of Robert Blessing*; Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38.

(22) Sheldrick, G. M. *SHELXS-97 Program for the Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

(23) Sheldrick, G. M. *SHELXL-97 Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

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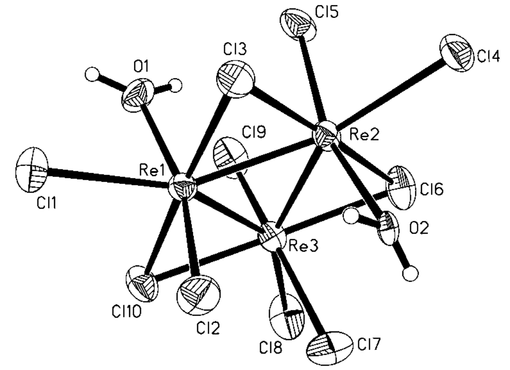

Figure 1. The solid-state structure of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(H_2O)_2]\cdot H_2O$ (**3**), showing 50% probability ellipsoids and the atom-labeling scheme for the anion. Selected interatomic distances (Å) and angles (deg): Re1−Re2 2.4843(3), Re2−Re3 2.4827(3), Re1−Re3 2.4785(3), Re1−Cl3 2.4038(15), Re2−Cl3 2.4055(16), Re2−Cl6 2.3970(17), Re3−Cl6 2.4113(16), Re3−Cl10 2.4008(16), Re1−Cl10 2.3977(15), Re1−Cl2 2.3331(16), Re1−O1 2.118(4), Re1−Cl1 2.4734(16), Re2−Cl5 2.3399(16), Re2−O2 2.209(3), Re2−Cl4 2.5097(15), Re3−Cl7 2.3494(18), Re3−Cl9 2.3650(16), Re3−Cl8 2.5216(17), Re1−Re2−Re3 59.867(10), Re2−Re1−Re3 60.035(10), Re1−Re3−Re2 60.098(10), Cl2−Re1−O1 162.73(10), O1−Re1−Cl1 76.14(12), O1−Re1−Cl3 89.39(12), O1−Re1−Re2 93.92(11), O2−Re2−Re1 95.07(8), O2−Re2−Cl5 163.08(9).

Å, $Re-Cl_{i,b}$ 2.404(8) Å, $Re-Cl_{o,t}$ 2.320(9) Å, and $Re-Cl_{i,t}$ 2.566(5) Å) as first revealed in the structure of the historic $Cs_3[Re_3Cl_{12}]$.[2]

One-Electron Reduction of the Re_3^{9+} Core. In order to investigate the structural features of the compound(s) present in the one-electron-reduced, purple HCl solutions, **1** was dissolved in HCl (6 M) and treated with excess Hg. Over a period of several hours the dark red color is progressively transformed to deep purple with concomitant deposition of Hg_2Cl_2. The insolubility of calomel is a critical factor for driving the reaction to completion. Removal of the insoluble components, followed by careful layering of a solution of 2 equiv of $[(C_6H_5)_4P]Cl$ in the minimum amount of water, affords upon standing dark purple crystals of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(H_2O)_2]\cdot H_2O$ (**3**).

The structure of **3** (Figure 1) reveals a rare Re_3^{8+} core, the distinctive feature of which is the replacement of two *out-of-plane* Cl atoms in adjacent rhenium sites by two trans-oriented water molecules. The average Re−Re bond distance (2.482(3) Å) is slightly longer by comparison to that found in **2b**, as is the average $Re-Cl_{o,t}$ bond length (2.347(18) Å), reflecting the reduced state of the Re_3^{8+} core. In contrast, the average in-plane Re−Cl bond distances in **3** are either the same ($Re-Cl_{i,b}$ 2.403(8) Å) or even shorter ($Re-Cl_{i,t}$ 2.50(3) Å) than those observed in **2b**. This suggests that the extra electron in **3** is placed in an orbital lying perpendicular to the $[Re_3(\mu\text{-}Cl)_3]$ plane, most likely derived from the lowest unoccupied $2a_1''$ π^* orbital of $[Re_3Cl_{12}]^{3-}$ (D_{3h} symmetry) which is dominated by Re (72%) and $Cl_{o,t}$ (20%) contributions. This may also explain the lability of out-of-plane chlorides in $[Re_3Cl_{12}]^{3-}$ once an extra electron enters the electronic manifold, in sharp contrast to the usual substitution of terminal in-plane chlorides encountered in Re_3^{9+} clusters. Indeed, the reported structure of $[NMe_4][Re_3Cl_{10}(H_2O)_2]\cdot 2H_2O$,[25] which contains the Re_3^{9+} core, positions the two water molecules and a chloride in statistical distribution over the three in-plane terminal sites.

The UV−vis spectrum of **3** in HCl (12 M) (λ (ϵ_M) 524 (1135), 860 (270) nm) exhibits band shifts to lower energies by comparison to **2a** (λ (ϵ_M) 520 (1676), 772 (459) nm), which are similar to those previously reported[8a] in molten salts for the purple $[Re_3Cl_{12-x}]^{(4-x)-}$ (λ (ϵ_M) 540 (1×10^3), 890 (5.2×10^2) nm). Shifts to lower-energy optical absorptions have also been reported by Walton for the reduced, or partially reduced, compounds of $[Re_3Cl_9]$ with amines ($[ReCl_2\cdot L]_n$, $[ReCl_{2.5}\cdot py]_n$).[8b] Conceivably, initial chloride abstraction to generate this cluster may also occur at out-of-plane position(s).

At 295 K, the effective magnetic moment of **3** ($\mu_{eff} = 1.20\ \mu_B$ (corrected for diamagnetic contributions[26])) is substantially reduced by comparison to the spin-only value (1.73 μ_B) for $S = {}^1/_2$ systems, most likely due to contributions from the orbital angular moment. The magnetic data as a function of temperature indicate an almost linear increase of the magnetic moment with decreasing temperature (25−295 K), reaching a plateau region at low temperatures (5−25 K; $\mu_{eff} = 1.47\ \mu_B$ at 5 K). Efforts to simulate the temperature-dependent magnetic data will be reported elsewhere.

Compound **3** dissociates upon treatment with CO in CH_2Cl_2 to yield a green-brownish solution, from which green crystals of $[(C_6H_5)_4P]_2[Re^{III}_2Cl_8]$ (**4**) (crystallographic data available as Supporting Information) as well as orange-red crystals of an unidentified rhenium−carbonyl species (ν_{CO} 2013, 1992 (sh), 1976 cm^{-1}) are obtained. Efforts to obtain a structure of the carbonyl compound have not been successful. Notably, several complexes of stoichiometry $[Re^{II}(CO)_2Cl_2(L)_2]$ have been reported in the literature.[27]

Oxidation of the Re_3^{8+} Core. In HCl solutions (6−12 M), compound **3** is oxidized by dioxygen to regenerate the $[Re_3Cl_{12}]^{3-}$ cluster (**2a**), which, as noted above, can be extracted in CH_2Cl_2 upon addition of $[(C_6H_5)_4P]Cl$ and isolated as $[(C_6H_5)_4P]_3[Re_3Cl_{12}]$ (**2b**). The reaction of **3** with dioxygen in organic media (CH_2Cl_2, $MeNO_2$) is much faster, most likely due to the availability of open coordination sites upon facile removal of coordinated H_2O, and leads to a different product. Under anaerobic conditions (N_2), **3** is unstable in CH_2Cl_2, slowly converting to **2b**, probably via reductive dechlorination of CH_2Cl_2. Dissolution of **3** in O_2-saturated CH_2Cl_2 leads to generation of a dark red solution, from which the hexarhenium compound $[(C_6H_5)_4P]_4[\{Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}OH)\}_2]\cdot 2CH_2Cl_2$ (**5**) is isolated in good yields. Treatment of compound **5** with excess Hg in HCl (6 M)/THF regenerates the reduced core of **3**.

The structure of **5** (Figure 2) reveals two symmetry-related (by inversion) triangular rhenium clusters of stoichiometry $[Re_3(\mu\text{-}Cl)_3Cl_7]$, connected via two hydroxo groups, bridging asymmetrically between those rhenium sites (one per triangular cluster) which carry only one terminal chloride. Obviously, the asymmetry of the $Re_2(OH)_2$ core (Re1−O1A 1.995(5) Å, Re1−O1 2.219(5) Å, Re1−Re1A 3.470(6) Å), viewed from the perspective of each contributing triangular unit, derives from the positioning of the two hydroxo groups in out-of-plane and in-plane coordination sites (O1−Re1−O1A 69.3°), respectively. The average Re−Re bond length (2.454(21) Å) within each triangle is slightly shorter than that observed in compound **2b**, and the difference is more pronounced for those Re−Re bond distances in **5** associated with the Re atom involved in the intercluster bridge (average Re1−Re = 2.443(2) Å). The average $Re-Cl_{o,t}$ bond length (2.32(3) Å) in **5** is not unlike

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(27) (a) Hillary, K. M.; Hughes, A. K.; Peat, K. L.; Wade, K. *Polyhedron* **1998**, *17*, 2803−2815. (b) Hertzer, C. A.; Myers, R. E.; Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2383−2389.

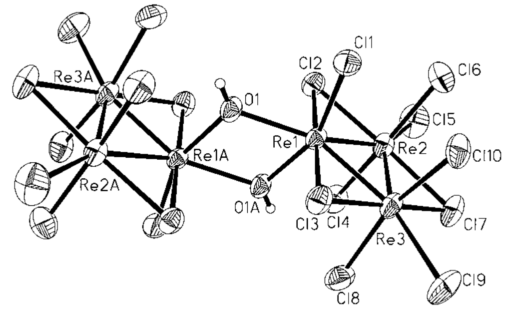

Figure 2. The solid-state structure of $[(C_6H_5)_4P]_4[\{Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}OH)\}_2]\cdot 2CH_2Cl_2$ (**5**), showing 50% probability ellipsoids and the atom-labeling scheme for the anion. Selected interatomic distances (Å) and angles (deg): Re1−Re2 2.4449(7), Re2−Re3 2.4756(8), Re1−Re3 2.4409(6), Re1−Cl2 2.403(2), Re2−Cl2 2.407(2), Re2−Cl7 2.405(2), Re3−Cl7 2.406(2), Re3−Cl3 2.410(2), Re1−Cl3 2.400(2), Re1−Cl1 2.285(2), Re1−O1A 1.995(5), Re1−O1 2.219(5), Re2−Cl4 2.339(2), Re2−Cl6 2.307(2), Re2−Cl5 2.507(3), Re3−Cl8 2.346(2), Re3−Cl10 2.318(2), Re3−Cl9 2.504(2), Re1−Re2−Re3 59.48(2), Re2−Re1−Re3 60.888(19), Re1−Re3−Re2 59.636(16), Cl1−Re1−O1A 154.24(16), Cl1−Re1−O1 85.01(14), O1−Re1−O1A 69.3(2), Re1−O1−Re1A 110.7(2), O1A-Re1−Cl3 90.01(16), O1−Re1−Cl2 89.24(15), O1−Re1−Re2 147.43(14), O1A−Re1−Re2 99.34(16).

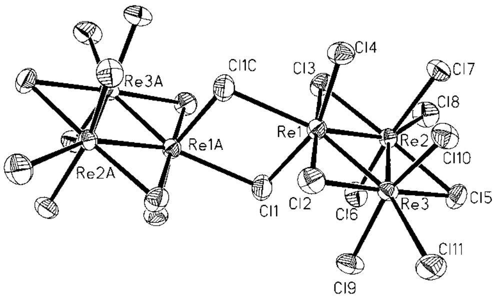

Figure 3. The solid-state structure of $[(C_6H_5)_4P]_4[\{Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}Cl)\}_2]\cdot 10CH_2Cl_2$ (**6**), showing 50% probability ellipsoids and the atom-labeling scheme for the anion. Selected interatomic distances (Å) and angles (deg): Re1−Re2 2.4394(4), Re2−Re3 2.4841(4), Re1−Re3 2.4460(4), Re1−Cl3 2.3977(18), Re2−Cl3 2.4043(18), Re2−Cl5 2.4027(19), Re3−Cl5 2.4057(19), Re3−Cl2 2.4054(19), Re1−Cl4 2.2904(19), Re1−Cl1 2.371(2), Re1−Cl1C 2.6329(19), Re2−Cl6 2.3126(19), Re2−Cl7 2.3133(18), Re2−Cl8 2.5176(19), Re3−Cl9 2.3119(19), Re3−Cl10 2.3026(18), Re3−Cl11 2.520(2), Re1−Re2−Re3 59.568(12), Re2−Re1−Re3 61.124(12), Re1−Re3−Re2 59.308(11), Cl1−Re1−Cl2 90.25(7), Cl1C−Re1−Cl2 90.70(7), Cl1−Re1−Cl1C 77.31(7), Re1−Cl1−Re1A 102.69(7), Cl1−Re1−Cl4 156.78(7), Cl4−Re1−Cl1C 79.49(7), Cl1−Re1−Re2 99.22(5).

that observed for **2b**, although the unique Re1−Cl1 bond distance (2.285(2) Å) is significantly shorter by comparison to all others. Average interatomic distances for $Re-Cl_{i,b}$ (2.405(5) Å) and $Re-Cl_{i,t}$ (2.506(2) Å) are analogous to those observed in **2b** or **3**.

The nature of the intercluster bridging groups (either oxo or hydroxo) presented a particularly difficult problem, as IR and Raman spectra of both **5** and its deuterated congener, prepared by bubbling O_2 through a solution of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(D_2O)_2]\cdot D_2O$ (**3**-d_6) in CH_2Cl_2, provided no evidence for $\nu_{O-H(D)}$ stretching modes. Furthermore, these compounds, which are diamagnetic, show no detectable O−*H*(*D*) groups by means of ^1H or ^2H NMR spectroscopy. Importantly, admittance of $^{18}O_2$ through a solution of **3** or **3**-d_6 in CH_2Cl_2 indicates that the so-generated **5** incorporates oxygen atoms *not* from dioxygen, but rather from water present in **3**, as evidenced by negative-ion electrospray MS analysis of the oxo-containing fragment $[Re_3Cl_8{}^{16}O]^-$ (*m*/*z* 858.2). This significant finding, however, does not permit facile labeling of the bridging oxo groups to assist identification of the vibrational features associated with the $Re_2(O(H))_2$ core. However, a prominent IR-active band at 560 cm^{-1} and a weak broad band at 664 cm^{-1} (not present in the IR spectrum of **2b**) are probably due to A_u-symmetric core vibrations.

The assignment of the bridging groups as hydroxo units is thus deduced indirectly. To start with, the metrical parameters for **5** noted above are consistent with the presence of two $Re_3{}^{9+}$ cores, expected on the assumption that the bridging oxygen atoms are counted as hydroxo moieties. In addition, the shorter Re−O(H) bond length (1.995(5) Å) in **5** is longer than the median Re−O distance (1.929 Å) reported for bridging Re−O−Re units in 128 compounds retrieved from the Cambridge Structural Database, although it also falls short of the median Re−O(H) bond length (2.152 Å) in the few known Re−O(H)−Re-containing structures. Notably, the UV−vis spectrum of **5** (λ_{max} (ϵ_M) 526 (1483), 772 (268) nm) features optical absorptions typical of $Re_3{}^{9+}$ clusters. These data, although indicative, cannot unequivocally distinguish between the proposed $[Re_3{}^{9+}(\mu\text{-}OH)_2Re_3{}^{9+}]$ core and the two-electron-oxidized $[Re_3{}^{10+}(\mu\text{-}O)_2Re_3{}^{10+}] \Leftrightarrow [Re_3{}^{9+}(\mu\text{-}O^\bullet)_2Re_3{}^{9+}]$ unit. The latter, if present, should be electronically coupled, since **5** has been measured to be diamagnetic in the temperature region 5−295 K. As alluded to at the outset, and confirmed for **2b**, the $Re_3{}^{9+}$ core effects complete electronic coupling, predominantly via the metal−metal double bonds.

Further interrogation of the oxidation state of the $[Re_3(\mu\text{-}O(H))_2Re_3]$ core in **5** has been attempted through derivatization. The most compelling illustration of the retention of the $Re_3{}^{9+}$ core is derived from the reaction of **5** with excess Me_3SiCl in CH_2Cl_2 to afford the related cluster $[(C_6H_5)_4P]_4[\{Re_3(\mu\text{-}Cl)_3Cl_7(\mu\text{-}Cl)\}_2]\cdot 10CH_2Cl_2$ (**6**). The structure of **6** (Figure 3) closely resembles that observed for **5**, featuring two inversion-related triangular clusters connected by two asymmetrical bridging chlorides. The distances associated with the intercluster bridges (Re1−Cl1 2.371(2) Å, Re1−Cl1C 2.6329(19) Å, Re1−Re1A 3.911(2) Å) are analogous to those reported for $[Re_3Cl_9]$ (**1**). Other metrical parameters for **6**, as for instance the average Re−Re (2.46(3) Å) and $Re-Cl_{o,t}$ (2.31(2) Å) bond lengths, are very similar to those observed for **5**, as are the bond distances and angles associated with the Re sites involved in intercluster bridging (average Re1−Re 2.443(4) Å, Re1−Cl4 2.2904(19) Å, Cl1−Re1−Cl1C 77.31(7)°). Provided that no reduction has taken place in the course of the conversion of **5** to **6**, this transformation is most consistent with replacement of hydroxo bridges of **5** by chlorides. Two more cases in which $Re_3{}^{9+}$ cores are obtained by derivatizing **5** are discussed in a following section.

Compound **6** appears to be a rare fragment of **1** containing only two $Re_3{}^{9+}$ building blocks. Apparently, direct transformation of **5** to $[Re_3(\mu\text{-}Cl)_3Cl_9]^{3-}$ (**2b**) by means of Me_3SiCl is not achieved probably due to lack of additional chlorides. However, in the presence of excess $[(C_6H_5)_4P]Cl$, compound **6** (or **5** and Me_3SiCl) readily transforms to **2b** in CH_2Cl_2, as evidenced by UV−vis data.

Other $Re_3{}^{8+}$/$Re_3{}^{9+}$ Interconversions. Compound **3** dissolves in acetonitrile to afford a dark blue solution, from which crystals of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_{6.5}(CH_3CN)_{1.5}(CH_3C(O)NH)_{0.5}]$ (**7**) are obtained upon diffusion of diethyl ether. The structure of **7** (Figure 4) reveals a disordered mixture of species (50:50 occupancy) composed of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3CN)_2]$ (**7a**) and $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_6(CH_3CN)(CH_3C(O)NH)]$ (**7b**). Compound **7** retains the reduced $Re_3{}^{8+}$ core of the starting material, as required by charge balancing, and further supported

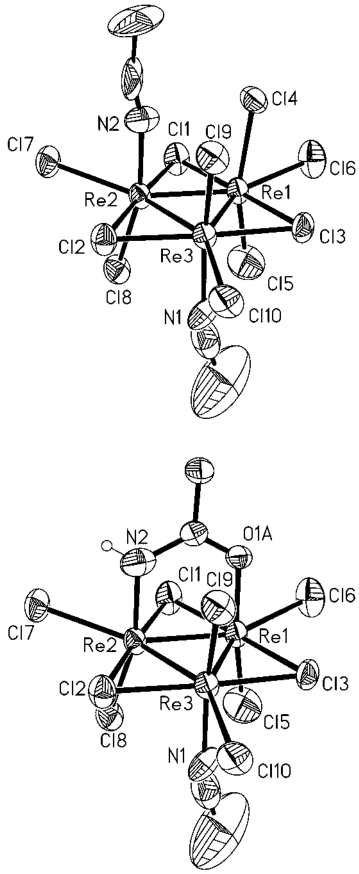

Figure 4. The solid-state structure of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_{6.5}(CH_3CN)_{1.5}(CH_3C(O)NH)_{0.5}]$ (**7**), showing 50% probability ellipsoids and the atom-labeling scheme for the anion. Top: Structure of anionic component (50%) $[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3CN)_2]^{2-}$ (**7a**). Bottom: Structure of anionic component (50%) $[Re_3(\mu\text{-}Cl)_3Cl_6(CH_3CN)(CH_3C(O)NH)]^{2-}$ (**7b**). Selected interatomic distances (Å) and angles (deg): Re1−Re2 2.4742(5), Re2−Re3 2.4798(5), Re1−Re3 2.4727(5), Re1−Cl1 2.400(2), Re2−Cl1 2.423(2), Re2−Cl2 2.396(2), Re3−Cl2 2.384(2), Re3−Cl3 2.402(2), Re1−Cl3 2.399(2), Re1−Cl4 2.425(9), Re1−O1A 1.96(2), Re1−Cl5 2.324(4), Re1−Cl6 2.507(3), Re2−N2 2.028(9), Re2−Cl8 2.337(3), Re2−Cl7 2.501(3), Re3−N1 2.089(11), Re3−Cl9 2.344(3), Re3−Cl10 2.486(2), Re1−Re2−Re3 59.887(14), Re2−Re1−Re3 60.168(14), Re1−Re3−Re2 59.945(14), Cl5−Re1−O1A 162.9(8), O1A−Re1−Cl1 85.2(7), O1A−Re1−Cl6 82.4(8), O1A−Re1−Re2 89.8(8), N2−Re2−Re1 89.3(3), N2−Re2−Cl8 164.1(3), N2−Re2−Cl7 77.6(3), N1−Re3−Cl9 163.5(4), N1−Re3−Re1 93.3(4), N1−Re3−Cl10 79.1(4).

by the relatively long Re−Re (2.476(4) Å) and $Re-Cl_{o,t}$ (2.335(11) Å, excluding half-occupancy Cl4) average bond distances. The reduced Re_3^{8+} core state is also consistent with the observed shift of diagnostic optical absorptions to lower energies (λ (ϵ_M) 599 (1364), 980 (305) nm) by comparison to those of Re_3^{9+}-containing species. Component **7a** is a close analogue of the aquo congener **3**, featuring two trans-oriented acetonitrile moieties (average Re−NCMe 2.074(8) Å) attached to out-of-plane coordination sites of adjacent Re atoms. The structure of the other half-occupancy component **7b** is a perturbation of that observed in **7a**, inasmuch as one of the acetonitrile moieties in **7a** has been transformed to a chelating acetamidato group in **7b**. The acetamidato carbonyl unit in **7b** replaces the Cl4 atom (50:50 O/Cl occupancy in **7**) in the coordination sphere of Re1. The presence of a singly protonated N−H unit (ν_{N-H} 3050 cm^{-1}) and a carbonyl group ($\nu_{C=O}$ 1585 cm^{-1}) is consistent with IR data. Apparently, the source of the acetamidato ligand is not the presence of acetamide (CH_3CONH_2) as an impurity in the CH_3CN employed, but is rather due to hydrolysis of metal-bound acetonitrile. This important transformation, which is certainly facilitated by the increased electrophilicity of the coordinated nitrile, has been previously documented[28] and has also been reported by Eglin and coworkers[29] in conjunction with $[Re_2Cl_8]^{2-}$-mediated conversion of nitriles (CH_3CN, PhCN) in the presence of water to afford the corresponding amidates.

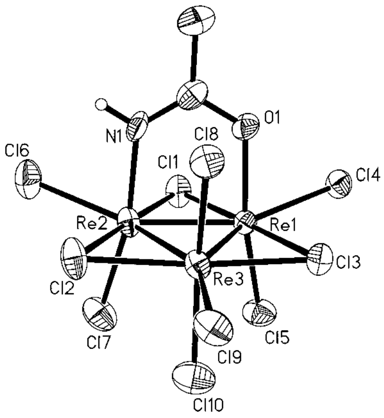

Figure 5. The solid-state structure of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3C(O)NH)]\cdot CH_3CN$ (**8**), showing 50% probability ellipsoids and the atom-labeling scheme for the anion. Selected interatomic distances (Å) and angles (deg): Re1−Re2 2.4460(3), Re2−Re3 2.4695(3), Re1−Re3 2.4525(3), Re1−Cl1 2.4056(15), Re2−Cl1 2.4033(16), Re2−Cl2 2.3973(16), Re3−Cl2 2.4015(15), Re3−Cl3 2.4056(15), Re1−Cl3 2.3908(14), Re1−Cl5 2.2950(15), Re1−O1 2.046(3), Re1−Cl4 2.4906(15), Re2−N1 2.030(4), Re2−Cl7 2.2946(16), Re2−Cl6 2.4812(16), Re3−Cl8 2.3452(15), Re3−Cl10 2.3266(16), Re3−Cl9 2.5232(15), Re1−Re2−Re3 59.856(10), Re2−Re1−Re3 60.549(10), Re1−Re3−Re2 59.595(10), Cl5−Re1−O1 163.12(12), O1−Re1−Cl1 85.28(11), O1−Re1−Cl4 78.38(12), O1−Re1−Re2 87.83(11), N1−Re2−Re1 86.27(13), N1−Re2−Cl7 164.22(13), N1−Re2−Cl1 84.32(14), N1−Re2−Cl6 78.65(13).

Compound **7** can also be isolated at the early stages (first 5 min) of the reaction of “aged” $[Re_3Cl_9]$ with activated Zn in CH_3CN. The reaction is arrested by quick filtration of Zn, followed by crystallization of the compound from the resulting dark purple-blue filtrate. In the presence of Zn, this initial solution turns rapidly into dark blue-green from which crystals of the familiar $[(C_6H_5)_4P]_2[Re_2Cl_8]\cdot 2CH_3CN$ (**4**) are isolated, indicating dissociation of the triangular cluster. Further reduction leads to uncharacterized green-brown solutions.

Compound **7** is slowly (12 h) oxidized by O_2 in CH_3CN to afford dark red-purple solutions, from which crystals of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3C(O)NH)]\cdot CH_3CN$ (**8**) are obtained in good yields. The structure of **8** (Figure 5), which now features the oxidized Re_3^{9+} core, reveals retention of one chelating acetamidato group as in **7b**, but all remaining coordination sites are occupied by chlorides. As expected for the one-electron-oxidized core, the average Re−Re (2.456(13) Å) and $Re-Cl_{o,t}$ (2.315(30) Å) bond lengths are shorter than those found in **7**, as are the slightly shorter acetamidato-associated Re1−O1 (2.046(3) Å) and Re2−N1 (2.030(4) Å) bond distances. ^1H NMR (CD_3CN) and/or IR spectra of **8** confirm that the acetamidato moiety is singly protonated at the

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N atom (δ 9.39 (N*H*); ν_{N-H} 3054, $\nu_{C=O}$ 1590 cm^{-1}). UV−vis spectra of **8** in CH_3CN (λ (ϵ_M) 524 (1743), 792 (361) nm) are also consistent with the usual higher-energy shift of the oxidized Re_3^{9+} core versus the reduced Re_3^{8+} core in **7**. The oxidation of **7** to **8** affords also trace amounts of colorless crystals, which have been identified crystallographically to be the perrhenate $[(C_6H_5)_4P][ReO_4]$ (**9**) (crystallographic data deposited as Supporting Information).

Compound **8** can also be prepared by dissolving $[Re_3Cl_9]$ (**1**) in a mixture of H_2O (3%) and CH_3CN. Importantly, compound **5** dissolves in dry CH_3CN to afford **8** (60%) and recovered **5** (40%) upon diffusion of diethyl ether over a period of several days. It is presently unclear whether residual water or the bridging hydroxo groups in **5** are responsible for the hydrolysis of acetonitrile. It is also not known why the reaction does not run to completion.

The partial transformation of **5** in CH_3CN prompted us to explore other media. Apparently, **5** is stable both in $MeNO_2$ and in DMF, but it dissolves in methanol to afford dark red solutions upon overnight stirring, from which crystals of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_8(MeOH)]\cdot MeOH$ (**10**) are obtained upon slow diffusion of diethyl ether. The reaction was attempted in anticipation[30] of protonating and replacing the hydroxo bridges of **5** by the slightly more acidic MeOH, in order to install readily detectable methoxo bridges. As suggested by the presence of an additional chloride in **10** and the conversion yield (68%), the stoichiometry of the reaction is much more complex and most likely involves generation of other, currently unidentified, rhenium clusters in MeOH solutions which are expected to be chloride deficient.

The structure of **10** (Figure 6) reveals the usual triangular rhenium chloride framework, featuring a bound MeOH moiety at a terminal in-plane position, hydrogen-bonded to a second solvated MeOH. That the bound methoxide is protonated is suggested by the long Re1−O1 bond length (2.289(12) Å) and Re1−O1−C1 angle (133.4(16)°). It is further indicated by the C1−O1−O1S angle (125.4(6)°) versus the alternative C1S−O1S−O1 angle (95.6(8)°), which suggests that hydrogen-bonding occurs via a hydrogen of the bound rather than solvated MeOH. The average Re−Re (2.454(12) Å) and Re−$Cl_{o,t}$ (2.305(15) Å) bond lengths are consistent with the presence of the Re_3^{9+} oxidation state, although at the shorter end of values anticipated for these interatomic distances. Interestingly, the Re1−Re2(3) bond distances associated with the Re1 atom bearing the MeOH moiety are shorter (average 2.4473(6) Å) than the unique Re2−Re3 bond length (2.4662(10) Å). Analogous differences are observed in the crystal structure of the closely related $[AsPh_4]_2[Re_3Cl_{11}(H_2O)_2]\cdot H_2O$, reported by B. Jung and G. Meyer.[31] The transformations of **5** in CH_3CN and MeOH document two more instances in which Re_3^{9+} cores are obtained via derivatization of **5**.

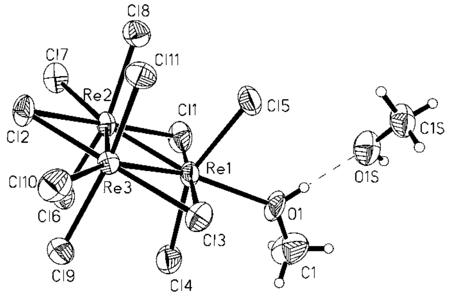

Figure 6. The solid-state structure of $[(C_6H_5)_4P]_2[Re_3(\mu\text{-}Cl)_3Cl_8(MeOH)]\cdot MeOH$ (**10**), showing 50% probability ellipsoids and the atom-labeling scheme for the anion. Selected interatomic distances (Å) and angles (deg): Re1−Re2 2.4467(10), Re2−Re3 2.4662(10), Re1−Re3 2.4478(10), Re1−Cl1 2.427(6), Re2−Cl1 2.397(5), Re2−Cl2 2.404(4), Re3−Cl2 2.403(5), Re3−Cl3 2.416(5), Re1−Cl3 2.407(6), Re1−Cl5 2.304(5), Re1−Cl4 2.290(5), Re1−O1 2.289(12), Re2−Cl6 2.310(5), Re2−Cl8 2.318(5), Re2−Cl7 2.563(5), Re3−Cl9 2.314(5), Re3−Cl11 2.295(4), Re1−Re2−Re3 59.77(3), Re2−Re1−Re3 60.51(3), Re1−Re3−Re2 59.72(3), Cl5−Re1−O1 77.1(4), O1−Re1−Cl1 89.4(5), O1−Re1−Cl4 78.3(4), O1−Re1−Re2 148.3(4).

Future research work will address aspects of the catalytic oxidation of organic substrates (alcohols, alkenes) mediated by rhenium clusters isolated in the present study.

While the present article was under review, a paper by Treichel[32] and co-workers was published describing several dinuclear and trinuclear Re(III) acetamidato clusters, including $[(C_4H_9)_4N]_2[Re_3(\mu\text{-}Cl)_3Cl_7(CH_3C(O)NH)]$, as well the interesting hydroxo-bridged hexanuclear species $[(C_4H_9)_4N]_2[\{Re_3Cl_8(CH_3C(O)NH)(OH)\}_2]$, which is structurally related to **5**.

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Supporting Information Available: Nine X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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