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Ligand Substitution Reactions of $[Re_6S_8Br_6]^{4-}$: A Basis Set of Re_6S_8 Clusters for Building Multicluster Assemblies

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Access to the molecular solution chemistry of face-capped octahedral cluster cores of the type $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ (Q = S, Se) has recently been realized in this laboratory by the protocol of dimensional reduction of solid frameworks containing bridged cores. A new series of triethylphosphine-ligated hexanuclear rhenium clusters has been prepared from the starting cluster $[Re_6S_8Br_6]^{4-}$ by ligand substitution of terminal bromide ligands using excess Et_3P in DMF at elevated temperatures. These clusters are of the general formula $[Re_6S_8(PEt_3)_nBr_{6-n}]^{(n-4)+}$ ($n = 2-6$). The following compounds were synthesized: $(Bu_4N)_2$[*cis*-$Re_6S_8(PEt_3)_2Br_4$] (in limited quantity), $(Bu_4N)_2$[*trans*-$Re_6S_8(PEt_3)_2Br_4$], (Bu_4N)[*mer*-$Re_6S_8(PEt_3)_3Br_3$], (Bu_4N)[*fac*-$Re_6S_8(PEt_3)_3Br_3$], *cis*-$[Re_6S_8(PEt_3)_4Br_2]$, *trans*-$[Re_6S_8(PEt_3)_4Br_2]$, $[Re_6S_8(PEt_3)_5Br]Br$, and $[Re_6S_8(PEt_3)_6]Br_2$. All clusters exhibit characteristic ^{31}P NMR spectra, and all except (Bu_4N)[*fac*-$Re_6S_8(PEt_3)_3Br_3$] have been characterized by X-ray crystallography. The $[Re_6S_8]^{2+}$ core is analogous to the $[Re_6Se_8]^{2+}$ core also under investigation in this laboratory, but it has the advantage of increased thermal control over the substitution process. Both disubstituted isomers, *cis*- and *trans*-$[Re_6S_8(PEt_3)_2Br_4]^{2-}$, are accessible with the $[Re_6S_8]^{2+}$ core but not with $[Re_6Se_8]^{2+}$. This set of clusters, together with $[Re_6Se_8(PEt_3)_nI_{6-n}]^{(n-4)+}$ ($n = 3-6$) prepared earlier, constitute an array of building blocks for the potential synthesis of multicluster assemblies by halide ligand substitution with bridging ligands or with ligands subject to removal by thermolysis.

Introduction

Much experimentation has accompanied the recent emergence of "supramolecular" inorganic chemistry, wherein metal ions and organic ligands are combined to spontaneously self-assemble into some *preprogrammed* architecture.[1] Employing metal ions with a well-defined stereochemistry along with rigid multicoordinating ligands, this approach has succeeded in producing both molecular[2] and nonmolecular[3] metal−ligand arrays with the expected topologies. We envision an analogous chemistry in which multinuclear cluster cores are utilized in place of single metal centers. While some initial success has been achieved in forming extended ligand−cluster arrays,[4] to our knowledge, no molecular transition metal cluster assemblies have yet been realized with this approach. Herein, we report the preparation and characterization of a set of clusters, $[Re_6S_8(PEt_3)_nBr_{6-n}]^{(n-4)+}$ ($n = 2-6$), intended for use as precursors in the directed synthesis of bridged and nonbridged multicluster assemblies.

Face-capped octahedral cluster cores of the type $[Re_6(\mu_3\text{-}Q_8)]^{2+}$ (Q = S, Se) have long been known to exist in ternary phases—$K_4Re_6Q_{12}$[5] and $Re_6Q_8X_2$ (X = Cl, Br),[6] *inter alia*[7] —prepared by means of high-temperature solid-state reactions. However, owing to the tightly-bound environment of the clusters within these extended framework solids, access to their molecular solution chemistry was not immediately forthcoming. With our recent implementation of dimensional reduction, a general formalism for dismantling solid frameworks, such access has now been made available.[8] As demonstrated, the intractable two- and three-dimensional cluster frameworks of $Re_6Q_8X_2$ can be broken up by introducing M^IX as an additional reactant. Each extra equivalent of halide serves to terminate a bridging interaction between clusters, thereby reducing the connectedness of the resulting framework. For example, when 5 equiv of CsBr is incorporated in the preparation of three-dimensional $Re_6S_8Br_2$ ($[Re_6S^{i}_{6}S^{i-a}_{2/2}]S^{a-i}_{2/2}Br^{a-a}_{4/2}$),[9] a new yellow-orange phase,

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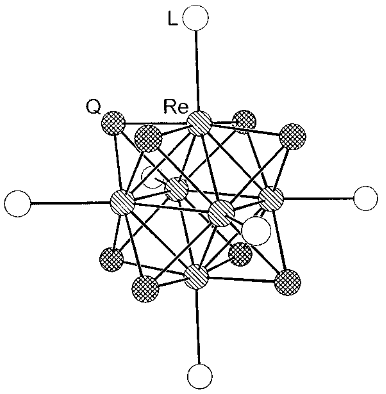

Figure 1. Generic structure of the generalized cluster $[Re_6Q_8L_6]^z$ (Q = S, Se), showing the face-capped octahedral core.

$Cs_5Re_6S_8Br_7$ ($Cs_4[Re_6S_8Br_6]\cdot CsBr$), containing the discrete molecular cluster $[Re_6S_8Br_6]^{4-}$ is produced.[10] This material readily dissolves in water to give a bright yellow solution of the cluster, which, upon workup, may be isolated as $(Bu_4N)_4[Re_6S_8Br_6]\cdot H_2O$ or $(Bu_4N)_3[Re_6S_7(SH)Br_6]$ (two forms conveniently soluble in polar organic solvents). The structure of the unprotonated cluster is depicted in Figure 1 and, as expected, consists of a central Re_6 octahedron embedded within a cube of eight μ_3-S atoms and an outer octahedron of six apically-radiating terminal bromide ligands.

The anticipated substitutional lability of these outer bromide ligands makes the $[Re_6S_8Br_6]^{4-}$ cluster a reasonable point of departure for constructing multicluster aggregates in which the electron-precise $[Re_6S_8]^{2+}$ core is viewed as the fundamental building block. However, in order to gain some control over the degree and direction of aggregation, it is helpful to differentiate one or more of its possible bridge-forming sites. As established in our prior investigation of the $[Re_6Se_7(SeH)I_6]^{3-}$ cluster, such control may be garnered by the substitutionally inert triethylphosphine ligand.[11] By careful regulation of the amount of phosphine delivered, as well as the temperature and duration of the reaction, five new clusters were generated and isolated in varying yields: *fac*-$[Re_6Se_8(PEt_3)_3I_3]^{1-}$, *cis*-$[Re_6Se_8(PEt_3)_4I_2]$, *trans*-$[Re_6Se_8(PEt_3)_4I_2]$, $[Re_6Se_8(PEt_3)_5I]^+$, and $[Re_6Se_8(PEt_3)_6]^{2+}$. The first four members of this series retain one or more of their reactive iodide ligands and are therefore capable of participating in further, geometrically-restricted reactions. For example, reaction of the monoiodo cluster with $AgBF_4$ in acetonitrile produces $[Re_6Se_8(PEt_3)_5(MeCN)](BF_4)_2$, a compound ideally suited for synthesizing bridged molecular

Chart 1

***cis*-$[Re_6S_8(PEt_3)_2Br_4]^{2-}$**	**1**
***trans*-$[Re_6S_8(PEt_3)_2Br_4]^{2-}$**	**2**
***mer*-$[Re_6S_8(PEt_3)_3Br_3]^{1-}$**	**3**
***fac*-$[Re_6S_8(PEt_3)_3Br_3]^{1-}$**	**4**
***cis*-$[Re_6S_8(PEt_3)_4Br_2]$**	**5**
***trans*-$[Re_6S_8(PEt_3)_4Br_2]$**	**6**
$[Re_6S_8(PEt_3)_5Br]^{1+}$	**7**
$[(Re_6S_8)(PEt_3)_6]^{2+}$	**8**

Table 1. Crystallographic Data[a] and Structure Refinement for $(Bu_4N)_2$[**1**], $(Bu_4N)_2$[**2**], (Bu_4N)[**3**]$\cdot$MeCN, and [**5**]$\cdot 4CHCl_3$

	$(Bu_4N)_2$[**1**]	$(Bu_4N)_2$[**2**]	(Bu_4N)[**3**]$\cdot$MeCN	[**5**]$\cdot 4CHCl_3$
formula	$C_{44}H_{102}Br_4N_2P_2Re_6S_8$	$C_{44}H_{102}Br_4N_2P_2Re_6S_8$	$C_{36}H_{84}Br_3N_2P_3Re_6S_8$	$C_{28}H_{63}Br_2Cl_{12}P_4Re_6S_8$
fw	2414.54	2414.54	2251.37	2482.56
T, K	223	213	223	223
space group	$P\bar{1}$	$P\bar{1}$	$P2/c$	$P2_1/c$
Z	4	2	4	4
a, Å	17.576(5)	14.4347(2)	10.464(2)	20.409(4)
b, Å	18.100(6)	14.7079(2)	40.813(7)	16.067(3)
c, Å	24.806(7)	16.8583(1)	14.339(2)	21.424(4)
α, deg	83.54(2)	77.389(1)		
β, deg	70.34(2)	83.379(1)	98.16(1)	115.26(3)
γ, deg	88.57(2)	86.104(1)		
V, $Å^3$	7384(4)	3466.07(7)	6062(2)	6353(2)
d_{calc}, g/cm^3	2.172	2.314	2.467	2.595
μ, cm^{-1}	122.59	130.57	142.93	135.36
R_f,[b] wR_2,[c] %	7.25, 15.15	4.02, 8.18	8.09, 19.02	7.65, 16.61

[a] Obtained with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. [b] $R_1 = \sum||F_o| - F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Crystallographic Data[a] and Structure Refinement for [**6**], [**7**](BPh_4), and [**8**]$Br_2\cdot 2CH_2Cl_2$

	[**6**]	[**7**](BPh_4)	[**8**]$Br_2\cdot 2CH_2Cl_2$
formula	$C_{24}H_{60}Br_2P_4Re_6S_8$	$C_{54}H_{95}BBrP_5Re_6S_8$	$C_{38}H_{94}Br_2Cl_4P_6Re_6S_8$
fw	2006.10	2363.55	2412.25
T, K	213	213	213
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Z	4	4	1
a, Å	15.7021(7)	21.297(4)	11.5142(1)
b, Å	15.3330(7)	13.328(3)	12.8059(1)
c, Å	19.8585(9)	26.360(5)	12.8253(1)
α, deg			67.185(1)
β, deg	103.522(1)	111.44(3)	79.384(1)
γ, deg			76.320(1)
V, $Å^3$	4648.6(4)	6964(2)	31684.62(2)
d_{calc}, g/cm^3	2.866	2.254	2.378
μ, cm^{-1}	177.95	113.49	124.97
R_f,[b] wR_2,[b] %	7.42, 15.63	4.11, 8.58	3.73, 9.56

[a] Obtained with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. [b] For definitions, *cf.* Table 1.

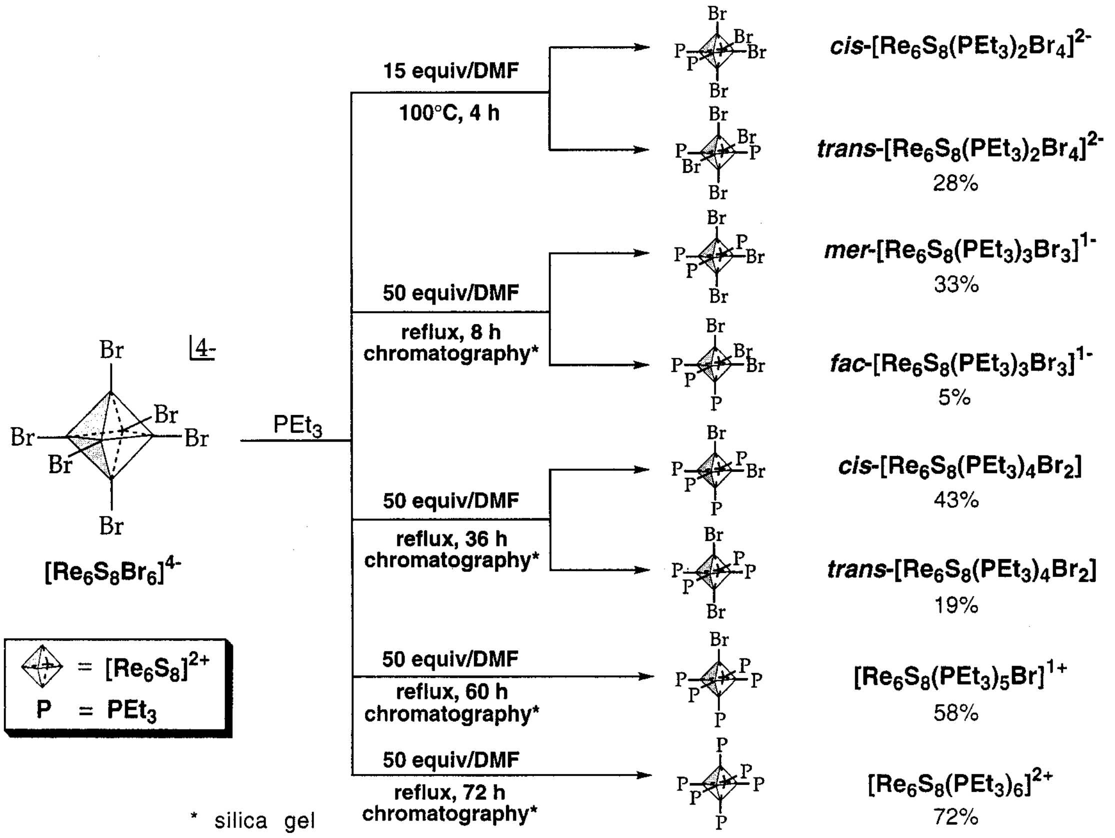

Figure 2. Terminal ligand substitution reactions of $[Re_6S_8Br_6]^{4-}$, allowing access to the set of clusters $[Re_6S_8(PEt_3)_nBr_{6-n}]^{(n-4)+}$ ($n = 2-6$). Bulk quantities of *trans*-$[Re_6S_8(PEt_3)_2Br_4]^{2-}$ could not be obtained.

diclusters. Indeed, under appropriate conditions, its acetonitrile ligand is displaced by 4,4′-bipyridine which can then linearly span two cores, as in the structurally verified dicluster $[(PEt_3)_5Re_6Se_8(4,4'\text{-bipy})Re_6Se_8(PEt_3)_5]^{4+}$.[12] Additionally, solid $[Re_6Se_8(PEt_3)_5(MeCN)](BF_4)_2$ can be thermolyzed under dynamic vacuum, liberating acetonitrile to form the nonbridged dicluster $[Re_{12}Se_{16}(PEt_3)_{10}]^{4+}$, wherein two $[Re_6Se_8]^{2+}$ cores are directly coupled via a rhombic $Re_2(\mu_4\text{-Se})_2$ linkage.[11] Similarly, *cis*-$[Re_6Se_8(PEt_3)_4(MeCN)_2](SbF_6)_2$ affords the dicluster *trans*-$[Re_{12}Se_{16}(PEt_3)_8(MeCN)_2]^{4+}$.[13] Studies involving the bis(iodo) and tris(iodo) clusters and their potential for generating larger, more complex multicluster assemblies are currently ongoing. It is hoped that a parallel, and perhaps more extensive, chemistry will be developed for $[Re_6S_8]^{2+}$ on the basis of the even broader range of phosphine-derivatized clusters detailed below.

Experimental Section

Preparation of Compounds. Standard Schlenk and vacuum line techniques were employed for all manipulations of dioxygen- and/or moisture-sensitive compounds. Solvents and reagents were of commercial origin and were used as received. $(Bu_4N)_3[Re_6S_7(SH)Br_6]$ was prepared as described.[8b] NMR spectra of compounds **1** and **8** (*vide infra*) were determined in CD_3CN solutions; all other NMR spectra were determined in $CDCl_3$ solutions.

$(Bu_4N)_2[Re_6S_8(PEt_3)_2Br_4]$. To a mixture of 0.200 g (0.0700 mmol) of $(Bu_4N)_3[Re_6S_7(SH)Br_6]$ in 40 mL of DMF was added excess PEt_3 (0.150 mL, 1.02 mmol). The mixture was heated to 100 °C under dinitrogen for 4 h. The solvent was removed *in vacuo*, leaving an orange-red oily residue which was triturated with ether to give an orange-red powder. To this material, which is a mixture of products, was added dichloromethane, dissolving all but *trans*-$(Bu_4N)_2[Re_6S_8(PEt_3)_2Br_4]$, which is less soluble in this solvent.

(a) $(Bu_4N)_2[$*cis*-$Re_6S_8(PEt_3)_2Br_4]$. Despite multiple attempts, a pure bulk fraction of this compound could not be isolated in pure form from the dichloromethane solution, owing to a small difference in R_f values between it and the *trans* compound. (For example, both elute at $R_f \sim 0.40$ in 1:10 acetonitrile/dichloromethane (v/v)). On occasion, however, very small amounts of crystalline product were obtained, from which a suitable single crystal was withdrawn for an X-ray structure determination.

(b) $(Bu_4N)_2[$*trans*-$Re_6S_8(PEt_3)_2Br_4]$. The orange solid remaining from the dichloromethane treatment was washed with dichloromethane to give 0.042 g (28%) of product. ^1H NMR (anion): δ 1.13 (q, 3), 2.11 (q, 2). ^{31}P NMR: δ −10.50. FAB-MS: *m/z* 2172 ($M^- - Bu_4N$).

$(Bu_4N)[Re_6S_8(PEt_3)_3Br_3]$. A solution of 0.719 g (0.252 mmol) of $(Bu_4N)_3[Re_6S_7(SH)Br_6]$ and PEt_3 (1.90 mL, 12.9 mmol) in 90 mL of DMF was stirred and heated to reflux under dinitrogen for 8 h. The solvent was removed *in vacuo*, and the oily residue was triturated with ether to give an orange-red powder. This material was dissolved in dichloromethane and the solution chromatographed on a silica gel column.

(a) $(Bu_4N)[$*mer*-$Re_6S_8(PEt_3)_3Br_3]$. This compound was eluted with 1:20 acetonitrile/dichloromethane ($R_f = 0.38$) to afford 0.182 g (33%) of product. ^1H NMR: δ 1.16 (q, 3), 1.23 (q, 6), 1.99 (q, 2), 2.09 (q, 4). ^{31}P NMR: δ −20.60 (2), −22.19 (1). FAB-MS: *m/z* 1968 ($M^- - Bu_4N$). Anal. Calcd for $C_{34}H_{81}Br_3NP_3Re_6S_8$: C, 18.48; H, 3.69;

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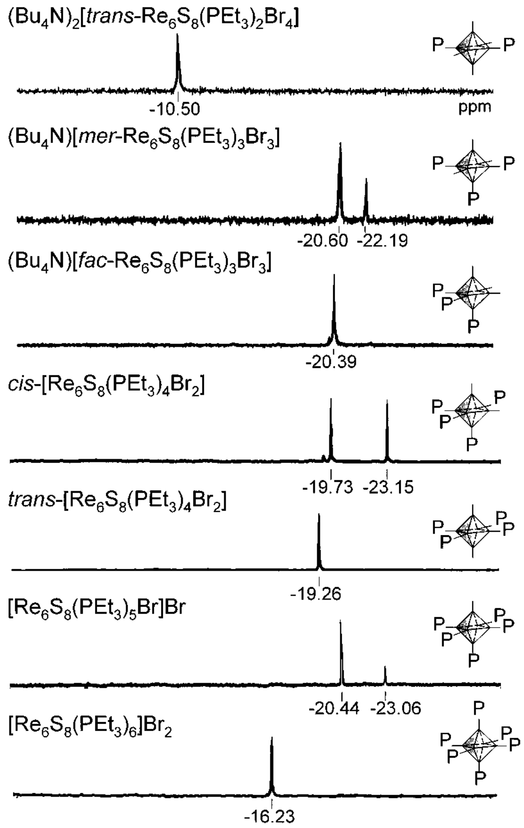


Figure 3. ^{31}P NMR spectra of clusters **2**−**8** referenced externally to 85% H_3PO_4. Spectra of $(Bu_4N)_2[trans\text{-}Re_6S_8(PEt_3)_4Br_2]$ (**2**) and $[Re_6S_8(PEt_3)_6]Br_2$ (**8**) were obtained in acetonitrile solution; all others were determined in chloroform solution.

Br, 10.84; N, 0.63; P, 4.20; Re, 50.55; S, 11.60. Found: C, 18.44, H, 3.65; Br, 10.69; N, 0.72; P, 4.16; Re, 50.67; S, 11.48.

(b) $(Bu_4N)[$*fac*$\text{-}Re_6S_8(PEt_3)_3Br_3]$. This compound was eluted with 1:20 acetonitrile/dichloromethane (v/v) ($R_f = 0.26$) to afford 0.025 g (5%) of product. ^1H NMR (anion): δ 1.08 (q, 3), 2.04 (q, 2). ^{31}P NMR: δ −20.39. FAB-MS: *m/z* 1968 ($M^- - Bu_4N$).

$[Re_6S_8(PEt_3)_4Br_2]$. A mixture of 0.204 g (0.071 mmol) of $(Bu_4N)_3[Re_6S_7(SH)Br_6]$ and PEt_3 (0.310 mL, 2.10 mmol) in 20 mL of DMF was refluxed under dinitrogen for 36 h. The solvent was removed *in vacuo*, and the oily residue was triturated with ether to give an orange-red powder. This material was then dissolved in dichloromethane and the solution chromatographed on a silica gel column.

(a) *trans*-$[Re_6S_8(PEt_3)_4Br_2]$. This compound was eluted with dichloromethane ($R_f = 0.39$) to afford 0.028 g (19%) of product. ^1H NMR: δ 1.12 (q, 3), 2.09 (q, 2). ^{31}P NMR: δ −19.26. FAB-MS: *m/z* 2006 (M^+).

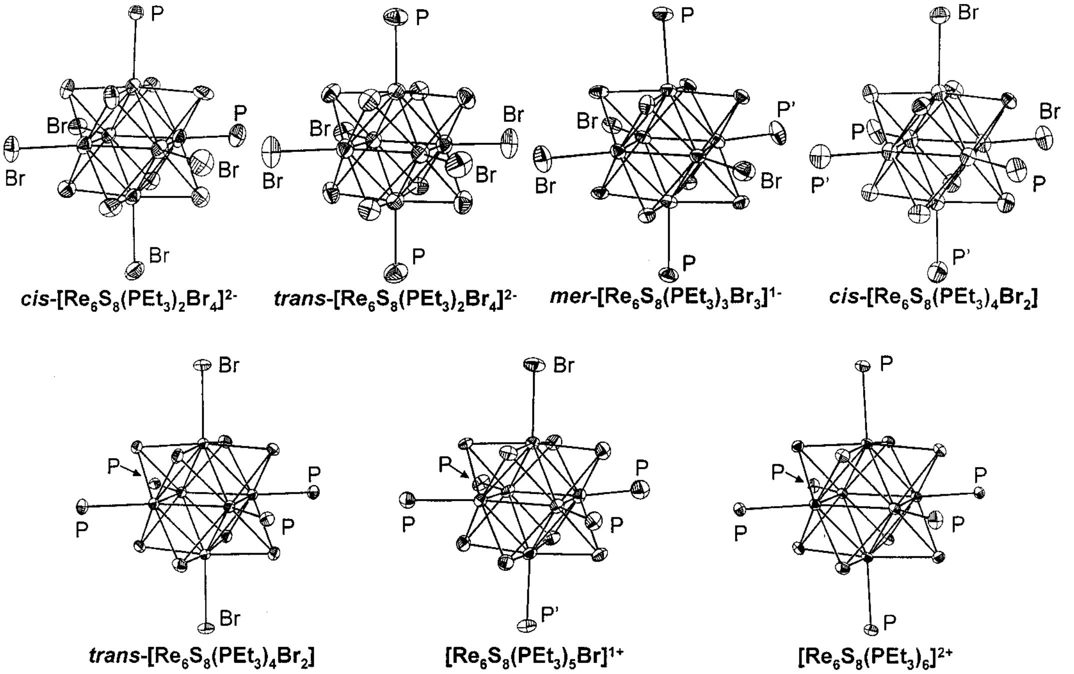
(b) *cis*-$[Re_6S_8(PEt_3)_4Br_2]$. This compound was eluted with 1:15 acetonitrile/dichloromethane ($R_f = 0.53$) to afford 0.614 g (43%) of product. ^1H NMR: δ 1.10 (m, 6), 2.02 (q, 2), 2.10 (q, 2). ^{31}P NMR: δ −23.15 (1), −19.73 (1). FAB-MS: *m/z* 2006 (M^+). Anal. Calcd for $C_{24}H_{60}Br_2P_4Re_6S_8$: C, 14.37; H, 3.01; Br, 7.97; P, 6.18; Re, 55.69; S, 12.87. Found: C, 14.35; H, 3.00; Br, 7.99; P, 6.16; Re, 55.48; S, 12.85.

$[Re_6S_8(PEt_3)_5Br]Br$. A mixture of 0.500 g (0.175 mmol) of $(Bu_4N)_3[Re_6S_7(SH)Br_6]$ and PEt (1.03 mL, 8.80 mmol) in 20 mL of DMF was refluxed under dinitrogen for 60 h. The solvent was removed *in vacuo*, and the oily residue was triturated with ether to give an orange-red powder. This material was dissolved in a minimal volume (≤5 mL) of dichloromethane, and the solution was chromatographed on a silica gel column. Elution with acetonitrile ($R_f = 0.11$) afforded the product as 0.214 g (58%) of an orange solid. ^1H NMR: δ 1.14 (m, 3), 2.10 (m, 2). ^{31}P NMR: δ −23.06 (1), −20.44 (4). FAB-MS: *m/z* 2044 ($M^+ - Br$).

$[Re_6S_8(PEt_3)_6]Br_2$. A mixture of 0.547 g (0.191 mmol) of $(Bu_4N)_3[Re_6S_7(SH)Br_6]$ and PEt_3 (1.40 mL, 9.48 mmol) in 20 mL of DMF was refluxed under dinitrogen for 72 h. The solvent was removed *in vacuo*, and the oily residue was triturated with ether to give an orange-red powder. This material was then dissolved in a minimal volume (≤5 mL) of dichloromethane, and the solution was chromatographed on a silica gel column. Elution with 1:5 methanol in dichloromethane (v/v) ($R_f = 0.74$) afforded the product as 0.306 g (72%) of an orange solid. ^1H NMR: δ 1.14 (q, 3), 2.11 (q, 2). ^{31}P NMR: δ −16.23. FAB-MS: *m/z* 2160 ($M^+ - Br$).

Designation of Clusters. The clusters of principal interest in this work are designated as shown in Chart 1; none have been previously prepared.

X-ray Structure Determinations. Structures were determined for **1**−**3** and **5**−**8**; crystallographic data are collected in Tables 1 and 2.



$cis\text{-}[Re_6S_8(PEt_3)_2Br_4]^{2-}$ $trans\text{-}[Re_6S_8(PEt_3)_2Br_4]^{2-}$ $mer\text{-}[Re_6S_8(PEt_3)_3Br_3]^{1-}$ $cis\text{-}[Re_6S_8(PEt_3)_4Br_2]$

$trans\text{-}[Re_6S_8(PEt_3)_4Br_2]$ $[Re_6S_8(PEt_3)_5Br]^{1+}$ $[Re_6S_8(PEt_3)_6]^{2+}$

Figure 4. Structures of seven of the eight possible members of the cluster series $[Re_6S_8(PEt_3)_nBr_{6-n}]^{(n-4)+}$ ($n = 2-6$) with 50% probability ellipsoids shown. Carbon and hydrogen atoms have been omitted for clarity.

X-ray-quality crystals were grown at room temperature by layering ether on concentrated dichloromethane (**1**, **2**, **6**, **8**), chloroform (**5**), or acetonitrile (**3**) solutions. The BPh_4^- salt of **7** was prepared via anion exchange by treating an acetonitrile solution of [**7**]Br with $NaBPh_4$ and crystallizing the solid product from acetonitrile. All crystals were orange-red with a block-type morphology. Crystals were coated with Apiezon L grease, attached to glass fibers, transferred to a Nicolet P3 (**1**, **3**, **5**) or a Siemens SMART (all others) diffractometer, and cooled in a dinitrogen stream. Lattice parameters were obtained from least-squares analysis of more than 30 carefully centered reflections. None of the crystals showed significant decay during data collection. The raw intensity data were converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure factor amplitudes and their esd's. An empirical absorption correction was applied to each data set. For cluster **1**, ψ scan data were unavailable and an absorption correction was applied using the XABS2 software package.[14]

Space group assignments were based on systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and refined against all data using the SHELXTL 5.0 software package. For the structures of **1**, **3**, and **5**, thermal parameters for all non-hydrogen and non-carbon atoms were refined anisotropically. For all other structures, thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). In the structure of **1**, one of the four Bu_4N^+ cations in the asymmetric unit was heavily disordered and constrained to an idealized geometry. In the structure of **7**, the ethyl arms of three PEt_3 ligands and a phenyl group of the BPh_4^- anion were disordered over two positions. Further details of the structure determinations are deposited as Supporting Information.[15]

Other Physical Measurements. NMR spectra were recorded on a Bruker AM 500 spectrometer. Chemical shifts of $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 (negative values upfield). FAB mass spectra were determined using a JEOL SX-102 spectrometer with 3-nitrobenzyl alcohol as the matrix material.

Results and Discussion

We are interested in the controlled aggregation of Re_6Q_8 (Q = S, Se) molecular clusters. To that end, we have developed the ligand substitution chemistry of molecular species with a particular emphasis on subsite differentiation to allow directed synthesis of aggregated molecular assemblies. Triethylphosphine is used as the substituting ligand because it has been shown to be substitutionally inert relative to the halide, thereby allowing further reaction selectively at the halide sites. Previously, we demonstrated that the selenide cluster $[Re_6Se_8I_6]^{4-}$ is susceptible to ligand substitution at the terminal iodide position when treated with triethylphosphine under reflux conditions.[11] Furthermore, the extent of substitution can be controlled by varying the amount of phosphine added as well as the duration of the reaction. Thermal control has led to the preparation of five stereochemically distinct cluster compounds of the general formula $[Re_6Se_8(PEt_3)_nI_{6-n}]^{(n-4)+}$ ($n = 3-6$).

Synthesis and Structures of $[Re_6S_8(PEt_3)_nBr_{6-n}]^{(n-4)+}$ ($n = 2-6$). In our current investigation, we show that the cluster $[Re_6S_8Br_6]^{4-}$ exhibits a substitution chemistry similar to, but more extensive than, that of $[Re_6Se_8I_6]^{4-}$. The use of a less labile terminal halide (Br^-) has increased the extent to which phosphine substitution may be controlled, with the result that the amount of phosphine has a lesser effect on the degree of substitution. By simple variation of the duration of the reaction,

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $Cs_4[Re_6S_8Br_6]\cdot CsBr$, $(Bu_4N)_2$[**1**], $(Bu_4N)_2$[**2**], (Bu_4N)[**3**], [**5**], [**6**], [**7**](BPh_4), and [**8**]Br_2

	$Cs_4[Re_6S_8Br_6]\cdot CsBr$[a]	$(Bu_4N)_2$[**1**]	$(Bu_4N)_2$[**2**]	(Bu_4N)[**3**]	[**5**]	[**6**]	[**7**](BPh_4)	[**8**]Br_2
Re−Br	2.579(6)−2.606(6)	2.574(4)−2.602(4)	2.560(5)−2.583(5)	2.551(4)−2.581(4)	2.552(8)−2.564(8)	2.547(2)−2.551(2)	2.557(2)	
mean	2.60(1)	2.589(8)	2.57(1)	2.57(2)	2.566(11)	2.549(3)		
Re−P		2.45(1)−2.51(1)	2.46(2)−2.48(2)	2.45(1)−2.47(1)	2.39(3)−2.49(2)	2.457(5)−2.472(5)	2.465(3)−2.479(4)	2.481(2)−2.488(2)
mean		2.48(3)	2.47(1)	2.46(1)	2.46(3)	2.465(6)	2.472(5)	2.483(4)
Re−Re	2.583(3)−2.608(3)	2.589(2)−2.615(2)	2.590(3)−2.611(2)	2.583(2)−2.608(2)	2.583(5)−2.608(4)	2.594(1)−2.606(1)	2.596(1)−2.6122(9)	2.610(1)−2.615(1)
mean	2.594(7)	2.603(6)	2.598(6)	2.600(6)	2.593(6)	2.600(4)	2.601(5)	2.614(1)
Re−S	2.37(2)−2.42(1)	2.37(1)−2.47(1)	2.38(1)−2.43(2)	2.385(8)−2.420(9)	2.33(3)−2.43(2)	2.393(5)−2.414(5)	2.383(3)−2.415(4)	2.397(2)−2.413(2)
mean	2.40(1)	2.40(2)	2.40(1)	2.403(9)	2.38(2)	2.403(6)	2.400(8)	2.405(4)
Re−Re−Re[b]	59.6(1)−60.4(1)	59.5(1)−60.4(1)	59.7(1)−60.5(1)	59.5(1)−60.4(1)	59.7(1)−60.5(1)	59.8(1)−60.2(1)	59.7(1)−60.3(1)	59.9(1)−60.1(1)
mean	60.0(2)	60.0(2)	60.0(2)	60.0(2)	60.0(2)	60.0(1)	60.0(2)	60.0(1)
Re−Re−Re[c]	89.8(1)−90.2(1)	89.5(1)−90.6(1)	89.7(1)−90.3(1)	89.5(1)−90.3(1)	89.6(1)−90.3(2)	89.6(1)−90.4(1)	89.8(1)−90.3(1)	89.9(1)−90.1(1)
mean	90.0(1)	90.0(3)	90.0(2)	90.0(3)	90.0(2)	90.0(2)	90.0(2)	90.0(1)
Re−Re−S	56.5(4)−58.1(3)	55.9(3)−59.1(3)	56.6(3)−58.0(3)	56.8(2)−57.7(2)	55.5(6)−58.4(5)	56.9(1)−57.5(1)	56.7(1)−57.7(1)	56.9(1)−57.3(1)
mean	57.2(4)	57.2(5)	57.2(4)	57.2(2)	57.0(6)	57.2(2)	57.2(2)	57.1(1)
Re−S−Re	64.9(3)−66.1(4)	64.6(3)−66.6(3)	64.8(3)−66.1(3)	64.9(2)−65.9(2)	64.6(4)−67.6(8)	65.3(1)65.7(1)	65.3(1)−66.0(1)	65.7(1)66.0(1)
mean	65.5(3)	65.5(4)	65.5(3)	65.5(2)	66.0(6)	65.5(1)	65.6(2)	65.8(1)
S−Re−S	88.8(5)−90.6(5)	88.3(4)−91.5(4)	88.6(5)−90.7(5)	88.7(3)−90.7(3)	87.3(8)−91.7(8)	89.3(2)−90.3(2)	89.0(1)−90.5(1)	89.5(1)−90.3(1)
mean	89.8(5)	89.8(8)	89.8(6)	89.8(4)	90(1)	89.8(3)	89.8(4)	89.8(2)

[a] Reference 8b. [b] Within triangular faces. [c] Within equatorial squares.

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(14) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.
(15) See paragraph at the end of this article for Supporting Information available.

eight new cluster compounds of the general formula $[Re_6S_8(PEt_3)_nBr_{6-n}]^{(n-4)+}$ ($n = 2-6$) have been prepared and are reported here.

The synthetic procedures are summarized in Figure 2; all reactions were carried out in DMF under forcing conditions. As in our previous study, the Bu_4N^+ salt of the protonated form of a cluster, $(Bu_4N)_3[Re_6S_7(SH)Br_6]$, was used as the starting material owing to its ease of preparation and purification and its solubility in polar organic solvents. Upon treatment with PEt_3, a red-orange solution of the protonated cluster quickly changes to yellow-orange as the cluster is deprotonated to give the reactant cluster $[Re_6S_8Br_6]^{4-}$. The amount of phosphine added in synthesis is much less important than for $[Re_6Se_8I_6]^{4-}$, as evidenced by the fact that for all but the least substituted clusters **1** and **2** ($n = 2$) the amount of triethylphosphine was held constant at 50 equiv. The duration of reflux is the primary control of the extent of substitution; altering the reaction time from 4 to 72 h afforded the di- (*cis* and *trans*), tri- (*fac* and *mer*), tetra- (*cis* and *trans*), penta-, and hexasubstituted products, **1**−**8**. No evidence for the monosubstituted cluster $[Re_6S_8(PEt_3)Br_5]^{3-}$ was found. Solubility difference was used to isolate the *trans*-disubstituted isomer **2**. The *cis*-disubstituted isomer **1** could not be obtained pure in substantial quantity; for this reason, no yield is entered in Figure 2. All other clusters were purified by silica gel chromatography. The neutral *trans*-tetrasubstituted isomer **6**, the least polar cluster, was eluted with dichloromethane. The *cis*-tetrasubstituted isomer **5** was eluted with 1:15 acetonitrile/dichloromethane (v/v) because of its increased polarity. Increasingly polar eluents were required as polarity increased with isomerism and as charge increased with degree of substitution. The charge of the cluster had a more significant influence on the separation. For example, the dianions **1** and **2** could not be separated because of the small difference in R_f value despite the difference in polarity of the *cis* and *trans* isomers. The hexasubstituted cluster **8**, a dication, could not be eluted even with pure acetonitrile, but 1:5 methanol/dichloromethane proved sufficient.

Identification of Clusters. All clusters were characterized by mass spectrometry, NMR, and X-ray structure determinations (excluding **4**). Two compounds (**3**, **5**) were subjected to total elemental analysis, with entirely satisfactory results. From Figures 2 and 4, the pattern of equivalent and inequivalent phosphines in **1**−**8** is evident. As a result, these clusters are easily distinguished by ^{31}P NMR as shown in Figure 3 for **2**−**8**. The resonances of **3**−**7** occur in the range of −19 to −24 ppm in chloroform solution, downfield by some 12 ppm from those of the analogous selenide clusters.[11] For **3**, **5**, and **7**, the number of resonances (2) and the ratio of intensities (2:1, 1:1, and 4:1, respectively) are those expected, readily identifying these clusters. For the others, a single resonance is found because of symmetry equivalence. These clusters are, however, readily distinguished by differences in chemical shifts. The spectra of **2** and **8** were obtained in acetonitrile solution due to limited solubility in chloroform. ^{31}P NMR spectra have proven extremely useful in monitoring cluster separation and purity.

The foregoing structures of clusters **1**−**3** and **5**−**8** have been further confirmed by X-ray structural determinations. Structures are depicted in Figure 4; the $[Re_6S_8]^{2+}$ cores have the structure in Figure 1 and dimensions that are very similar to those previously found for molecular and bridged solid-state clusters.[8,10] For this reason and because the values show no significant variation within the set of seven clusters determined here, no extensive discussion of the structures is warranted and the metric parameters in Table 3 are confined to ranges and mean values.[15] The mean Re−Br bond lengths (2.60(1)−2.557(2) Å) decrease as the number of bromide ligands decreases. Otherwise, bond distances and angles accord well with those in $Cs_4[Re_6S_8Br_6]\cdot CsBr$,[8b] taken as a reference structure. These results further substantiate a structurally constant $[Re_6S_8]^{2+}$ core, at least with halide and phosphine ligands.

At this stage of our investigation of Re_6Q_8 clusters,[8,11−13] the main advantage of the $[Re_6S_8Br_6]^{4-}/PEt_3$ system over the analogous selenide system is the increased thermal control of the ligand substitution. The $[Re_6S_8Br_6]^{4-}$ cluster is less reactive owing to the decreased lability of the bromide ligands. Longer reaction times are required to obtain substitution comparable to that in the $[Re_6Se_8I_6]^{4-}/PEt_3$ system. As a result, the substitution process may be stopped more readily, and the duration can be tuned to target the desired substitution product. Indeed, the increased control has allowed the isolation in substantial quantity (**2**) and structure determination (**1**, **2**) of the two isomeric disubstituted clusters previously unattainable in the selenide system.[8b]

Clusters **1**−**7** are intended for use as molecular building blocks for multicluster assemblies. As noted earlier and explained elsewhere,[11,13] replacement of halide by a ligand subject to removal by thermolysis or direct substitution of halide by a bridging ligand can lead to bridged multiclusters. The nuclearity and structure of such species will be dependent upon the stereochemistry of substitution of the initial building-block cluster. With the rhenium sites differentiated by substitution with inert phosphines, the clusters potentially may be used in further reactions which displace the remaining bromides and systematically build up multicluster assemblies. We now possess a basis set of Re_6Q_8 clusters for synthesizing multicluster assemblies. It remains to be seen whether clusters based on the Re_6S_8 or Re_6Se_8 core are comparable or preferable in this respect. Further research is directed toward testing such clusters in reactions intended to yield multiclusters, as well as continued delineation of the fundamental substitution chemistry of the $[Re_6Q_8]^{2+}$ cores.

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Supporting Information Available: X-ray structural information for the compounds in Tables 1 and 2, including tables of crystal and intensity collection data, positional and thermal parameters, and interatomic distances and angles (130 pages). Ordering information is given on any current masthead page.

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