

A Basis Set of Re_6Se_8 Cluster Building Blocks and Demonstration of Their Linking Capability: Directed Synthesis of an $\text{Re}_{12}\text{Se}_{16}$ Dicluster

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Abstract: A previously developed solid-state route (dimensional reduction) has led to the first molecular clusters containing the face-capped octahedral $[\text{Re}_6(\mu_3\text{-Q})_8]^{2+}$ core (Q = S, Se). Among these is the protonated cluster $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$, whose substitution reactions have been examined in an effort to create a set of site-differentiated precursors for forming multicenter assemblies. Reaction with Et_3P under reflux with different conditions of reactant mole ratio and time affords the clusters *fac*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_3\text{I}_3]^{1-}$ (**2**), *trans*- (**3**) and *cis*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4\text{I}_2]$ (**4**), $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5\text{I}]^{1+}$ (**5**), and $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_6]^{2+}$ (**6**). The synthesis of fully substituted **6** in quantitative yield required the forcing conditions of 20 equiv of phosphine in refluxing DMF for 3 days. Reaction of **4** with AgBF_4 in dichloromethane/acetonitrile gave *cis*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{MeCN})_2]^{2+}$ (**7**); a similar reaction of **5** yielded $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{MeCN})]^{2+}$ (**8**) and that of $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$ led to fully substituted $[\text{Re}_6\text{Se}_8(\text{MeCN})_6]^{2+}$ (**9**). The structures of clusters **2–9** as Bu_4N^+ (**2**), iodide (**5**), SbF_6^- (**7**), or BF_4^- (**6**, **8**, **9**) salts were proven by X-ray crystallography. No significant variance was observed in the face-capped geometry of the core when bound by iodine, phosphine, and nitrile ligands alone or in combination. Terminal Re–P/I/N bond lengths were similarly independent of co-ligands. The combination of ligands of different lability in clusters **2–9** should make them of considerable utility in producing linked cluster assemblies/materials wherein labile ligands are displaced by bridging ligands. The simplest of these reactions, the direct coupling of two $[\text{Re}_6\text{Se}_8]^{2+}$ cluster cores, is demonstrated here. When thermolyzed at 180 °C for 24 h under dynamic vacuum, the compounds $[\mathbf{8}]_2\text{X}_2$ (X = BF_4^- , SbF_6^-) lose acetonitrile and condense to form two new compounds containing the dicluster $[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^{4+}$ (**10**), whose structure has been established by X-ray methods. This cluster is composed of two $[\text{Re}_6\text{Se}_8]^{2+}$ portions which are centrosymmetrically connected by two Re–(μ_4 -Se) bonds to form a rhomboidal Re_2Se_2 unit. The bridge bonds are *ca.* 0.1 Å longer than the Re–(μ_3 -Se) bonds of the remainder of the core; they have the same value as in the bridging rhombs present in the two-dimensional phase $\text{Re}_6\text{Se}_8\text{Cl}_2$, which is a precursor solid to molecular $[\text{Re}_6\text{Se}_8]^{2+}$ clusters by dimensional reduction. The synthesis of **10** is directed by the structure of **8**, which can give only one logical product upon deligation of acetonitrile. The synthesis concept is potentially extendable to other types of oligomerized clusters.

Introduction

Extensive research on metal–chalcogenide clusters with the face-capped octahedral core $\text{M}_6(\mu_3\text{-Q})_8^{1,2}$ has, in significant part, centered on the obtainment of molecular versions of the fundamental cluster unit present in Chevrel phases.³ This initiative has resulted in the synthesis and characterization of M_6Q_8 clusters (Q = S, Se) with M = Cr,⁴ Mo,^{5,6} and W,^{7,8} which themselves or in suitably altered forms might be precursors to these or related phases in low-temperature reactions. We note also the use of this cluster type in the preparation of binary phases by mild thermolysis in “molecule-to-solid” transformations.⁹ Any success that may be achieved in constructing larger molecular clusters or solids based on the M_6Q_8 motif requires forms of these clusters that are sufficiently reactive to engage in intercluster bridging interactions. These would take the forms $\text{M–X}^{a-a}\text{–M}$, where X is a halide or

chalcogenide atom external to both cores, and/or $\text{M–Q}^{a-i}\text{–M}$, involving a chalcogenide atom internal to one core. In Chevrel phases, the latter interactions conjoin $[\text{Mo}_{3n}\text{Q}_{3n+2}]^{2-}$ ($n = 2–6, 8, 10$; Q = S, Se) cores into three-dimensional solid frameworks.

Our recent research in this area has resulted in the synthesis of electron-precise molecular $[\text{Re}_6\text{Q}_8]^{2+}$ clusters utilizing the approach of dimensional reduction, whereby cluster-containing extended solids of the type $\text{Re}_6\text{Q}_8\text{X}_2$ (Q = S, Se; X = Cl, Br, I) are dismantled into discrete molecular clusters.^{10,11} These are of the type $[\text{Re}_6\text{Q}_8\text{X}_6]^{4-}$ and the protonated forms

(5) $[\text{Mo}_6\text{Q}_8(\text{PEt}_3)_6]^{0,1-}$ (Q = S, Se): (a) Saito, T.; Yamamoto, N.; Yamagata, T.; Imoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 1646. (b) Saito, T.; Yamamoto, N.; Nagase, T.; Tsuboi, T.; Kobayashi, K.; Yamagata, T.; Imoto, H.; Unoura, K. *Inorg. Chem.* **1990**, *29*, 764.

(6) $[\text{Mo}_6\text{S}_8\text{L}_6]$ (L = py, pyrrolidine, piperidine): Hilsenbeck, S. J.; Young, V. G., Jr.; McCarley, R. E. *Inorg. Chem.* **1994**, *33*, 1822.

(7) $[\text{W}_6\text{S}_8(\text{PEt}_3)_6]$: Saito, T.; Yoshikawa, A.; Yamagata, T.; Imoto, H.; Unoura, K. *Inorg. Chem.* **1989**, *28*, 3588.

(8) $[\text{W}_6\text{S}_8(\text{py})_6]$: (a) Zhang, X.; McCarley, R. E. *Inorg. Chem.* **1995**, *34*, 2678. (b) Ehrlich, G. M.; Warren, C. J.; Vennos, D. A.; Ho, D. M.; Haushalter, R. C.; DiSalvo, F. J. *Inorg. Chem.* **1995**, *34*, 4454.

(9) (a) Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 2257. (b) Hessen, B.; Siegrist, T.; Palstra, T.; Tanzler, S. M.; Steigerwald, M. L. *Inorg. Chem.* **1993**, *32*, 5165.

(10) Long, J. R.; Williamson, A. S.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 226.

(11) Long, J. R.; McCarty, L. S.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4603. This article explains the standard “i,a” notation used in describing intercluster bridges.

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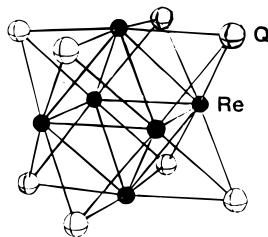
(1) (a) Saito, T. In *Early Transition Metal Clusters with π -Donor Ligands*; Chisholm, M. H., Ed.; VCH Publishers, Inc.: New York, 1995; Chapter 3. (b) Saito, T.; Imoto, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2403.

(2) Goddard, C. A.; Long, J. R.; Holm, R. H. *Inorg. Chem.* **1996**, *35*, 4347 and references therein.

(3) (a) Chevrel, R.; Sergent, M.; Prigent, J. *J. Solid State Chem.* **1971**, *3*, 515. (b) Bars, O.; GuilleVIC, J.; Grandjean, D. *J. Solid State Chem.* **1973**, *6*, 48. (c) Fischer, Ø. *Appl. Phys.* **1978**, *16*, 1 and references therein.

(4) $[\text{Cr}_6\text{Q}_8(\text{PR}_3)_6]$ (Q = S, Se): Tsuge, K.; Imoto, H.; Saito, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 627.

$[\text{Re}_6\text{Q}_7(\text{QH})\text{X}_6]^{3-}$, a number of which have been structurally defined by X-ray diffraction.^{11,12} These clusters place at our disposal for the first time the core units **1** in soluble form, and



1

presage a rich solution chemistry of them. We view **1** as a plausible source of a large number of individual clusters $[\text{Re}_6\text{Q}_8\text{L}_6]^z$ with uniform or mixed terminal ligand sets introduced by substitution reactions of a suitably labile precursor. Further, **1** is a potential building block in the construction of oligomeric clusters. In principle, **1** can support up to six bridging interactions whose $\text{Re}-\text{X}/\text{Q}$ bonds are disposed at 90° or 180° to one another and originate at Re atoms typically separated by 2.60 Å (*cis*) and 3.68 Å (*trans*). Both $\text{Re}-\text{X}^{\text{a-a}}-\text{Re}$ and $\text{Re}-\text{Q}^{\text{a-i}}-\text{Re}$ bridges have been established in solid phases containing **1**. The structures of the parent solids $\text{Re}_6\text{Q}_8\text{X}_6\text{Cl}_2$ ($\text{Q} = \text{S},^{13} \text{Se}^{14}$), from which the clusters $[\text{Re}_6\text{Q}_8\text{X}_6]^{4-}$ ultimately are obtained by dimensional reduction, are especially pertinent. The phase $\text{Re}_6\text{Se}_8\text{Cl}_2$ exhibits a two-dimensional (sheet-like) structure, with each unit **1** involved in four $\text{Re}-\text{Q}^{\text{a-i}}-\text{Re}$ and four $\text{Re}-\text{Q}^{\text{i-a}}-\text{Re}$ bridges, generating four Re_2 -(μ_4 -Se)₂ rhombic interactions per cluster.^{11,14} The two terminal chloride ligands are situated at *trans* Re apices. In $\text{Re}_6\text{S}_8\text{Cl}_2$, each core is linked to six neighboring cores by means of two rhombic Re_2S_2 interactions and four μ_2 -Cl atoms, resulting in a three-dimensional structure. These extremely tight Re_2Q_2 rhombic interactions lead to nearly intractable cluster frameworks. Such interactions need not be confined to extended solid phases, as has been shown for several molecular clusters,¹⁵⁻¹⁸ including $[\text{Co}_{12}\text{S}_{16}(\text{PET}_3)_{10}]^{2+}$ ^{18a} and $[\text{Cr}_{12}\text{S}_{16}(\text{PET}_3)_{10}]^{18b}$ in which two $[\text{M}_6(\mu_3\text{-S})_8]^{1+/0}$ cores are connected by an M_2S_2 rhomboid.¹⁸

We have initiated a detailed investigation of the reaction chemistry of the clusters $[\text{Re}_6\text{Q}_8\text{X}_6]^{4-}$ and $[\text{Re}_6\text{Q}_7(\text{QH})\text{X}_6]^{3-}$ with the intention of generating new monoclusters and multi-cluster arrays. The latter, also describable as “clusters of clusters”, represent access to a class of mesoscale molecules

(12) We also note the preparation of the first molecular solid, $[\text{Re}_6\text{Te}_8(\text{TeBr}_2)_6]\text{Br}_2$, containing the face-capped octahedral Re_6Te_8 core: Mironov, Y. V.; Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 2709.

(13) Fischer, C.; Fiechter, S.; Tributsch, H.; Reck, G.; Schultz, B. *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 1652.

(14) $[\text{Re}_6\text{Se}_8\text{Cl}_2] = [\text{Re}_6\text{Se}_4\text{Se}^{\text{i-a}}\text{Cl}_2] \text{Se}^{\text{a-i}}\text{Cl}_2$: Leduc, P. L.; Perrin, A.; Sergent, M. *Acta Crystallogr.* **1983**, *C39*, 1503.

(15) Cubane-type $\text{M}_2\text{M}'_6\text{S}_8$ clusters ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Pd}$; $\text{M}' = \text{Mo}, \text{W}$): (a) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1988**, *110*, 3313. (b) Shibahara, T.; Akashi, H.; Yamasaki, M.; Hashimoto, K. *Chem. Lett.* **1991**, 689. (c) Murata, T.; Gao, H.; Mizobe, Y.; Nakano, F.; Motomura, S.; Tanase, T.; Yano, S.; Hidai, M. *J. Am. Chem. Soc.* **1992**, *114*, 8287. (d) Murata, T.; Mizobe, Y.; Gao, H.; Ishii, Y.; Wakabayashi, T.; Nakano, F.; Tanase, T.; Yano, S.; Hidai, M.; Echizen, I.; Nanikawa, H.; Motomura, S. *J. Am. Chem. Soc.* **1994**, *116*, 3389. (e) Shibahara, T.; Yamamoto, T.; Sakane, G. *Chem. Lett.* **1994**, 1231.

(16) Cubane-type $[\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PET}_3)_6(\text{O}_2\text{C}_6\text{Cl}_4)_2]$: Demadis, K. D.; Campana, C. F.; Coucouvanis, D. *J. Am. Chem. Soc.* **1995**, *117*, 7832.

(17) Cubane-type $[\text{Fe}_8\text{S}_8(\text{PR}_3)_6]$ and $[\text{Fe}_{16}\text{S}_{16}(\text{PR}_3)_8]$: (a) Cai, L.; Segal, B. M.; Long, J. R.; Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 8863. (b) Goh, C.; Segal, B. M.; Huang, J.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 11844.

(18) (a) Ceconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chim. Acta* **1993**, *214*, 13. (b) Kamiguchi, S.; Imoto, H.; Saito, T. *Chem. Lett.* **1996**, 555.

not yet constructed in a predictable mode. The M_6Q_8 species that have been synthesized as representations of Chevrel phase clusters, while of considerable importance, are isolated clusters and, as such, cannot convey the unknown electronic features of $[\text{Mo}_{3n}\text{Q}_{3n+2}]^{z-}$ clusters whose repeating units are oligomerized as confacial Mo_6 octahedra. While there is as yet no synthetic route to polynuclear molecular clusters of this type, we show here that the Re_2Se_2 rhombic interaction can be deliberately effected, thereby providing the first entry to a potentially extensive series of multiclusters conjugated through one or more interactions of this type.

Experimental Section

Preparation of Compounds. Standard Schlenk and vacuum line techniques were employed for all manipulations of dioxygen- and/or moisture-sensitive compounds. Solvents were distilled from appropriate drying agents and degassed prior to use. Reagents were of commercial origin and were used as received. $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]$ was prepared as described.¹¹ NMR spectra were determined in CDCl_3 solutions unless indicated otherwise.

$(\text{Bu}_4\text{N})(\text{fac}-[\text{Re}_6\text{Se}_8(\text{PET}_3)_3\text{I}_3])$. To a solution of 250 mg (0.077 mmol) of $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]$ in 30 mL of acetonitrile was added excess Et_3P (0.5 mL, 3.7 mmol). The mixture was refluxed under dinitrogen for 1 h. The solvent was removed *in vacuo* to give an orange-red oily residue which was triturated with ether to give an orange-red powder. This material, which is a mixture of products, was dissolved in dichloromethane and chromatographed on a silica gel column. The third band was collected as an orange-red eluate, which was reduced *in vacuo* to afford the product as an orange-red solid in small yield (5–10 mg). ^1H NMR: δ 1.06 (q, 3), 2.07 (q, 2). ^{31}P NMR: δ -34.8. FAB-MS: m/z 2484 ($\text{M}^+ - \text{Bu}_4\text{N}$).

$[\text{Re}_6\text{Se}_8(\text{PET}_3)_4\text{I}_2]$ and $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5\text{I}]$. A mixture of 1.56 g (0.482 mmol) of $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]$ and 0.34 g (2.88 mmol) of Et_3P in 120 mL of DMF was stirred and refluxed for 3 days to give an orange-red solution. Solvent was removed *in vacuo* at 90°C ; the oily residue was triturated with ether to give an orange-red powder. This material was dissolved in dichloromethane and the solution was chromatographed on a flash silica gel column.

(a) *trans*- $[\text{Re}_6\text{Se}_8(\text{PET}_3)_4\text{I}_2]$. This compound was eluted with dichloromethane ($R_f = 0.77$) to afford 0.35 g (30%) of product. ^1H NMR: δ 1.10 (q, 3), 2.14 (q, 2). ^{31}P NMR: δ -33.0. FAB-MS: m/z 2475 (M^+), 2348 ($\text{M}^+ - \text{I}$). Anal. Calcd for $\text{C}_{24}\text{H}_{60}\text{I}_2\text{P}_4\text{Re}_6\text{Se}_8$: C, 11.65; H, 2.44; I, 10.25; P, 5.01; Re, 45.13; Se, 25.52. Found: C, 11.72; H, 2.47; I, 10.28; P, 5.08; Re, 45.04; Se, 25.34.

(b) *cis*- $[\text{Re}_6\text{Se}_8(\text{PET}_3)_4\text{I}_2]$. This compound was eluted with dichloromethane/acetonitrile (20:1 (v/v), $R_f = 0.72$) to give 0.56 g (47%) of product. ^1H NMR: δ 1.02–1.11 (m, 6), 2.06 (q, 2), 2.12 (q, 2). ^{31}P NMR: δ -33.0, -35.7. Anal. Calcd for $\text{C}_{25}\text{H}_{60}\text{I}_2\text{P}_4\text{Re}_6\text{Se}_8$: C, 11.65; H, 2.44; I, 10.25; P, 5.01; Re, 45.13; Se, 25.52. Found: C, 11.68; H, 2.39; I, 10.35; P, 5.20; Re, 44.98; Se, 25.68.

(c) $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5\text{I}]$. This compound was eluted with dichloromethane/acetonitrile (3:1 (v/v), $R_f = 0.55$) to give 0.24 g (19%) of product. ^1H NMR: δ 1.10 (m, 3), 2.14 (m, 2). ^{31}P NMR: δ -33.7 (4), -34.5 (1). FAB-MS: m/z 2466 ($\text{M}^+ - \text{I}$). Anal. Calcd for $\text{C}_{30}\text{H}_{75}\text{I}_2\text{P}_5\text{Re}_6\text{Se}_8$: C, 13.83; H, 2.91; I, 9.79; P, 5.97; Re, 43.08; Se, 24.36. Found: C, 13.83; H, 2.86; I, 9.71; P, 6.08; Re, 43.17; Se, 24.30.

$[\text{Re}_6\text{Se}_8(\text{PET}_3)_6\text{I}_2]$. This compound was prepared following the preceding preparation but with use of 20 instead of 6 equiv of Et_3P per mol of initial cluster. This mixture was refluxed under dinitrogen for 3 days and filtered. Sufficient ether was added to the cooled filtrate to cause separation of the product as a yellow-orange precipitate, leaving a colorless solution. This material was collected by filtration, washed with ether (3×25 mL), and dried *in vacuo* to afford the yellow-orange product in quantitative yield. ^1H NMR: δ 1.13 (q, 3), 2.20 (q, 2). ^{31}P NMR: δ -31.3. FAB-MS: m/z 2584 ($\text{M}^+ - \text{I}$).

***cis*- $[\text{Re}_6\text{Se}_8(\text{PET}_3)_4(\text{MeCN})_2](\text{BF}_4)_2$.** A solution of 0.080 g (0.41 mmol) of AgBF_4 in 2 mL of acetonitrile was added to a solution of 0.28 g (0.11 mmol) of *cis*- $[\text{Re}_6\text{Se}_8(\text{PET}_3)_4\text{I}_2]$ in 10 mL of dichloromethane. A yellow precipitate formed within seconds; the mixture

Table 1. Crystal Data^a and Structure Refinement for $(\text{Bu}_4\text{N})[\text{fac-}\text{Re}_6\text{Se}_8(\text{PEt}_3)_3\text{I}_3]$ (**2**), $\text{trans-}[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4\text{I}_2]\cdot 2\text{CHCl}_3$ (**3**), $\text{cis-}[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4\text{I}_2]\cdot 2\text{CHCl}_3$ (**4**), $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5\text{I}]\cdot 2\text{CH}_2\text{Cl}_2$ (**5**), and $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_6](\text{BF}_4)_2\cdot 2\text{CHCl}_3$ (**6**)

	2	3	4	5	6
formula	$\text{C}_{34}\text{H}_{81}\text{I}_3\text{NP}_3\text{Re}_6\text{Se}_8$	$\text{C}_{26}\text{H}_{62}\text{Cl}_6\text{I}_2\text{P}_4\text{Re}_6\text{Se}_8$	$\text{C}_{26}\text{H}_{62}\text{Cl}_6\text{I}_2\text{P}_4\text{Re}_6\text{Se}_8$	$\text{C}_{32}\text{H}_{79}\text{Cl}_4\text{I}_2\text{P}_5\text{Re}_6\text{Se}_8$	$\text{C}_{38}\text{H}_{92}\text{B}_2\text{Cl}_6\text{F}_8\text{P}_6\text{Re}_6\text{Se}_8$
formula wt	2726.49	2714.02	2714.02	2763.28	2870.14
space group	<i>Pnma</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P1</i>
Z	4	2	4	2	1
a, Å	26.089(10)	13.296(6)	14.693(5)	13.0015(2)	11.9566(1)
b, Å	14.871(4)	15.874(5)	19.509(9)	18.8072(2)	12.9861(2)
c, Å	15.195(6)	13.594(5)	20.673(7)	25.6105(2)	13.1240(2)
α, deg					66.168(1)
β, deg		104.59(3)	100.35(3)	90.236(1)	80.952(1)
γ, deg					77.250(1)
V, Å ³	5895(4)	2777(2)	5829(4)	6262.3(1)	1812.7(3)
d _{cal} , g/cm ³	3.072	3.246	3.092	2.931	2.629
μ, mm ⁻¹	18.89	19.81	18.87	17.51	14.39
R ₁ ^b (wR ₂ ^c), %	7.07 (13.66)	6.15 (12.94)	4.83 (9.71)	7.74 (17.78)	3.33 (8.86)

^a Obtained at 223 K (**2**, **3**, and **4**) and 213 K (**5**, **6**) with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. ^b $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^c $wR_2 = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w(|F_o|)^2]\}^{1/2}$.

Table 2. Crystal Data^a and Structure Refinement for $\text{cis-}[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{MeCN})_2](\text{SbF}_6)_2$ (**7**), $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{MeCN})](\text{BF}_4)_2$ (**8**), $[\text{Re}_6\text{Se}_8(\text{MeCN})_6](\text{BF}_4)_2\cdot 4\text{MeCN}$ (**9**), and $[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}](\text{BF}_4)_4\cdot 4\text{CH}_2\text{Cl}_2$ (**10**)

	7	8	9	10
formula	$\text{C}_{28}\text{H}_{66}\text{F}_{12}\text{N}_2\text{P}_4\text{Sb}_2\text{Re}_6\text{Se}_8$	$\text{C}_{32}\text{H}_{78}\text{B}_2\text{F}_8\text{NP}_3\text{Re}_6\text{Se}_8$	$\text{C}_{20}\text{H}_{30}\text{B}_2\text{F}_8\text{N}_{10}\text{Re}_6\text{Se}_8$	$\text{C}_{64}\text{H}_{158}\text{B}_4\text{Cl}_8\text{F}_{16}\text{P}_{10}\text{Re}_{12}\text{Se}_{16}$
formula wt	2775.09	2554.30	2332.54	5366.20
space group	<i>P1</i>	<i>P4₃2₁2</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
Z	2	8	4	2
a, Å	12.9026(5)	16.4250(1)	17.1791(4)	13.6328(3)
b, Å	14.9643(6)	16.4250(1)	23.7422(5)	25.6772(6)
c, Å	16.7183(7)	45.7441(1)	11.8633(3)	18.1560(1)
α, deg	85.459(1)			
β, deg	68.856(1)		95.952(1)	95.233(1)
γ, deg	83.776(1)			
V, Å ³	2990.1(2)	12340.9(1)	4812.7(1)	6329.1(2)
d _{cal} , g/cm ³	3.082	2.750	2.993	2.816
μ, mm ⁻¹	18.02	16.62	21.13	16.37
R ₁ ^b (wR ₂ ^b), %	6.65 (19.68)	3.92 (8.51)	10.79 (28.81)	7.56 (15.2)

^a Obtained at 213 K with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. ^b For definitions, cf. Table 1.

was stirred with exclusion of light for 12 h and filtered. The filtrate was concentrated to an orange-red residue, which was dissolved in 5 mL of dichloromethane; the solution was stirred for 5 min and filtered through a plug of Celite. The filtrate was collected and concentrated *in vacuo* to near dryness. The residue was triturated with ether to give the product as 0.23 g (84%) of an ochre-colored solid. ¹H NMR: δ 1.07 (q, 3), 1.14 (q, 3), 2.11 (q, 2), 2.22 (q, 2), 2.89 (1). ³¹P NMR: δ -24.3, -27.6. IR (KBr): ν_{CN} 2286, 2321 cm⁻¹. FAB-MS: *m/z* 2387 ($\text{M}^+ - \text{BF}_4$).

[Re₆Se₈(PEt₃)₅(MeCN)](BF₄)₂. A solution of 97.5 mg (0.038 mmol) of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5\text{I}]$ in 3 mL of dichloromethane was treated with 0.18 mL of a 0.51 M solution of AgBF₄ in acetonitrile. A yellow precipitate formed instantly. The mixture was stirred with exclusion of light for 3 h and filtered. Ether was diffused into the orange-red filtrate overnight to cause separation of the product as 77.2 mg (80%) of an orange-red crystalline solid. ¹H NMR: δ 1.05 (q, 3), 1.12 (q, 12), 2.08 (q, 2), 2.18 (q, 8), 2.91 (1). ³¹P NMR: δ -27.7 (4), -31.2 (1). IR (KBr): ν_{CN} 2284, 2317 cm⁻¹. FAB-MS: *m/z* 2468 ($\text{M}^+ - \text{BF}_4$). Anal. Calcd for $\text{C}_{32}\text{H}_{78}\text{B}_2\text{F}_8\text{NP}_3\text{Re}_6\text{Se}_8$: C, 15.05; H, 3.08; N, 0.55; P, 6.06; Re, 43.74; Se, 24.73. Found: C, 14.94; H, 3.16; N, 0.52; P, 6.02; Re, 43.88; Se, 24.64.

[Re₆Se₈(MeCN)₆](BF₄)₂. A solution of 0.257 g (1.32 mmol) of AgBF₄ in 4 mL of acetonitrile was added to a solution of 0.650 g (0.200 mmol) of $(\text{Bu}_4\text{N})_3[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]$ in 4 mL of dichloromethane. The mixture was stirred with exclusion of light for 12 h. The orange-red supernatant was decanted from the yellow precipitate. Addition of ether to the supernatant resulted in formation of a light yellow precipitate. This solid was collected and dissolved in 2 mL of acetonitrile, and the solution was filtered through a plug of Celite. Diffusion of ether into the orange filtrate afforded the product as 0.31 g (72%) of yellow-orange needle-like crystals. ¹H NMR (CD₃CN): δ 2.69. IR (KBr): ν_{CN} 2287, 2317 cm⁻¹. FAB-MS: *m/z* 2081 ($\text{M}^+ - \text{BF}_4$). Anal. Calcd

for $\text{C}_{12}\text{H}_{18}\text{B}_2\text{F}_8\text{N}_6\text{Re}_6\text{Se}_8$: C, 6.65; H, 0.84; B, 1.00; N, 3.87; Re, 51.51; Se, 29.13. Found: C, 6.53; H, 0.89; B, 0.96; N, 3.81; Re, 51.65; Se, 29.19.

[Re₁₂Se₁₆(PEt₃)₁₀](SbF₆)₄. A Pyrex ampule (i.d. × o.d. × l = 8 × 12 × 150 mm) was charged with 100 mg (0.036 mmol) of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{MeCN})](\text{SbF}_6)_2$ (prepared from $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5\text{I}]$) by metathesis with AgSbF₆ in dichloromethane/acetonitrile and heated under dynamic vacuum in an oil bath. After 24 h at 180 °C, a greenish-black solid was obtained. This material was dissolved in dichloromethane to give a dark green solution. Ether was introduced into this solution over 3 days, causing separation of the product as 92.5 mg (94%) of shiny brownish-green parallelepiped. ¹H NMR (CD₃CN): δ 0.99–1.21 (m), 2.17–2.39 (m). ³¹P NMR (CD₃CN): δ -15.01 (2), -19.52 (2), -22.57 (1). Electrospray MS: *m/z* 1169 ($[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^{4+}$).

Designation of Clusters. The clusters of principal interest in this work are designated as shown below. For simplicity, compounds that are salts are referred to by their cluster number in the following section and in Tables 1–4.

<i>fac-}[\text{Re}_6\text{Se}_8(\text{PEt}_3)_3\text{I}_3]^{-}</i>	2
<i>trans-}[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4\text{I}_2]</i>	3
<i>cis-}[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4\text{I}_2]</i>	4
$[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5\text{I}]^{1+}$	5
$[\text{Re}_6\text{Se}_8(\text{PEt}_3)_6]^{2+}$	6
<i>cis-}[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{MeCN})_2]^{2+}</i>	7
$[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{MeCN})]^{2+}$	8
$[\text{Re}_6\text{Se}_8(\text{MeCN})_6]^{2+}$	9
$[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^{4+}$	10

X-ray Structure Determinations. Structures were determined for the compounds in Tables 1 and 2. X-ray quality crystals of **2** were obtained by slow evaporation from an acetone/toluene solution. Other crystals were grown at room temperature by layering ether on concentrated chloroform (**3**, **4**, **6**) or dichloromethane (**5**, **7**, **8**, **10**)

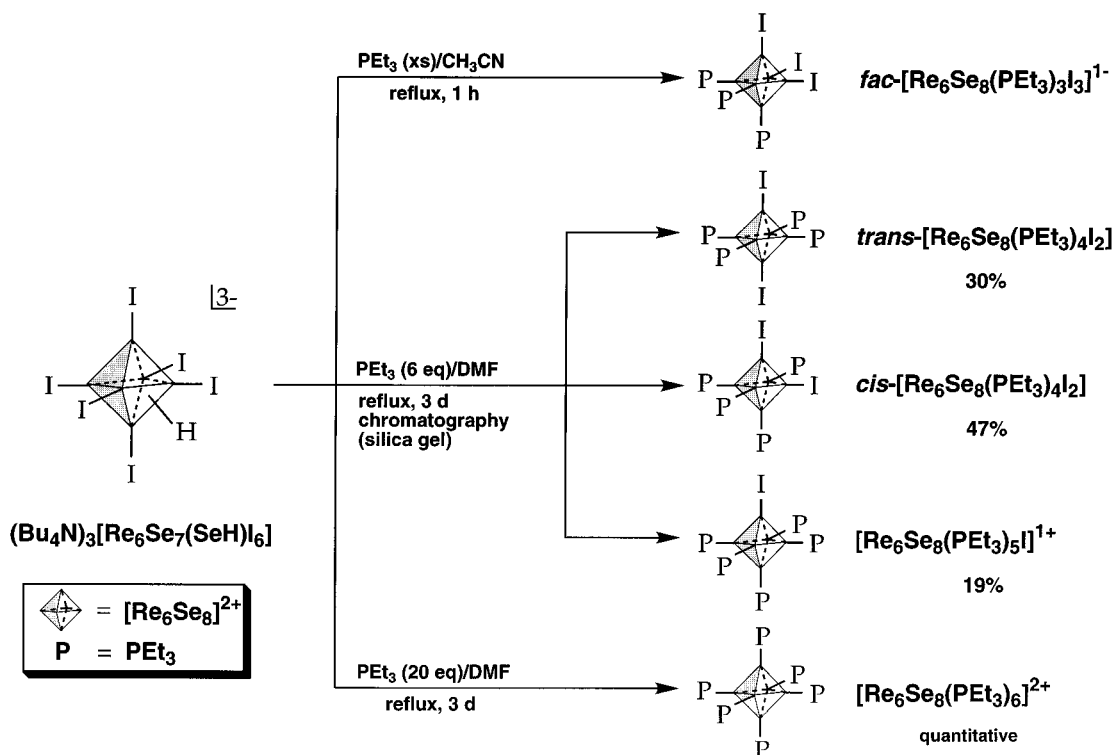


Figure 1. Summary of terminal ligand substitution reactions of $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$ affording the clusters $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_n\text{I}_{6-n}]^{(n-4)+}$ ($n = 3-6$).

solutions. Crystals of **9** were produced by vapor diffusion of ether in a concentrated acetonitrile solution. All crystals were orange-red with a block-type morphology except those of **9** (yellow-orange needles) and **10** (dark green spearheads). Crystals were coated with Apiezon L grease, attached to glass fibers, transferred to a Nicolet P3 (**2-4**) or a Siemens SMART (all others) diffractometer, and cooled in a dinitrogen stream. Lattice parameters were obtained from a 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.

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. In the structures of **2-4**, the thermal parameters for light atoms ($Z < 8$) were refined isotropically, while those for heavier atoms were refined anisotropically. For all other structures, thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included in the refinement of the structure of **2**. For all other structures, 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 **2**, the butyl arms of Bu_4N^+ and the ethyl arms of the Et_3P ligands are all disordered over two positions. One $[\text{SbF}_6]^{1-}$ anion in the structure of **7** was constrained and refined as a rigid octahedron. In each of the structures of **9** and **10**, one tetrafluoroborate anion was constrained and refined as a rigid tetrahedron. The large R_1 and wR_2 residual factors for the structure of **9** are due to the poor crystal quality, likely arising from its high solvent content. Crystallographic data are listed in Tables 1 and 2. Further details of the structure determinations are deposited as Supporting Information.¹⁹

Other Physical Measurements. NMR spectra were recorded on a Bruker AM 500 spectrometer. Chemical shifts of $^3\text{P}\{^1\text{H}\}$ spectra were referenced to external 85% H_3PO_4 (negative values upfield). Infrared

spectra were recorded on a Nicolet Impact 400D FT instrument using samples in KBr pellets.

Results and Discussion

As the first step in extending the molecular chemistry of $[\text{Re}_6\text{Q}_8]^{2+}$ clusters, we have examined the substitution reactions of $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$ with Et_3P . This cluster is more readily prepared than the unprotonated form;¹¹ its Bu_4N^+ salt is soluble in the solvents utilized for these reactions. Triethylphosphine was employed because of its anticipated non-lability under subsequent reaction conditions. The six terminal iodide ligands projecting from the vertices of $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$ are each potentially displaceable by Et_3P , engendering a family of ten stereochemically distinct cluster species with formulae $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_n\text{I}_{6-n}]^{(n-4)+}$ ($n = 0-6$).

Synthesis and Structures of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_n\text{I}_{6-n}]^{(n-4)+}$ ($n = 3-6$). The synthetic procedures employed are summarized in Figure 1. Addition of Et_3P to a solution of the starting cluster caused an immediate color change from dark greenish-brown to reddish-brown, the solution color of the unprotonated cluster. Adjustment of reaction conditions resulted in different extents of substitution. Thus, treatment of $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$ with excess phosphine in refluxing acetonitrile for 1 h gave trisubstituted **2** in low yield (<10%). The short reaction time was required in order that the substitution not proceed further; the low yield was in part a consequence of the difficulty in separating $(\text{Bu}_4\text{N})[\mathbf{2}]$ from other reaction products. Under the much more forcing conditions of excess phosphine in refluxing DMF for 3 days, fully substituted **6** was obtained in quantitative yield. Anion exchange of $[\mathbf{6}]_2$ with AgBF_4 in dichloromethane afforded quantitatively crystalline $[\mathbf{6}](\text{BF}_4)_2$, which was used in an X-ray structure determination. Intermediate extents of substitution were realized by reaction with 6 equiv of Et_3P in refluxing DMF for 3 days followed by chromatography on silica gel. In this way, tetrasubstituted isomers **3** (30%) and **4** (47%) and pentasubstituted **5** (19%) were obtained in essentially quantitative total yield. In the separation, *trans* isomer **3** was

(19) See paragraph at the end of the article for Supporting Information available.

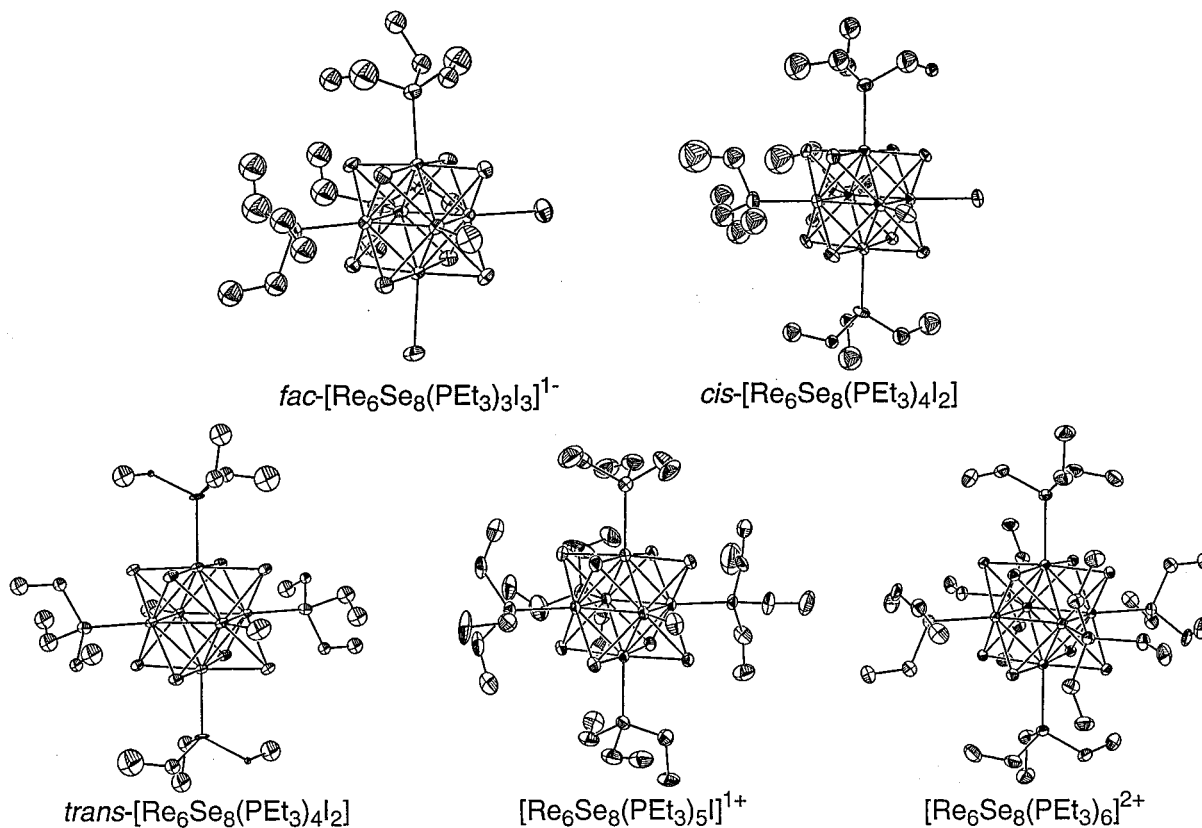
$$[\text{Re}_6\text{Se}_8(\text{PET}_3)_n\text{I}_{6-n}]^{(n-4)+} \quad (n = 3-6)$$


Figure 2. Structures of the clusters $[\text{Re}_6\text{Se}_8(\text{PET}_3)_n\text{I}_{6-n}]^{(n-4)+}$ ($n = 3-6$), with 50% probability ellipsoids. Dimensional differences within the set are insignificant (Table 3).

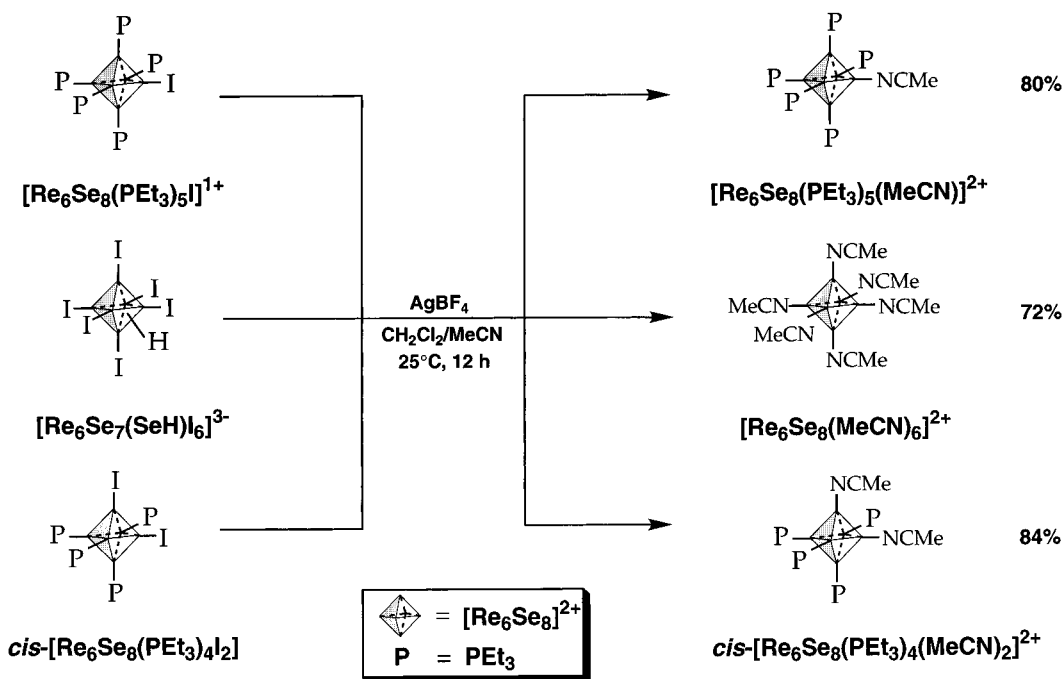


Figure 3. Summary of the preparations of $[\text{Re}_6\text{Se}_8(\text{PET}_3)_n(\text{MeCN})_{6-n}]^{2+}$ ($n = 0, 4, 5$).

eluted first with dichloromethane, followed by *cis* isomer **4** and then **5** in dichloromethane with increasing acetonitrile content. Under these conditions the order of elution is consistent with polarity and charge. Although the reaction was not optimized, **5** was isolated in 36% yield with use of 7 equiv of phosphine under the same conditions. The *cis* and *trans* isomers of $[\text{M}_6-$

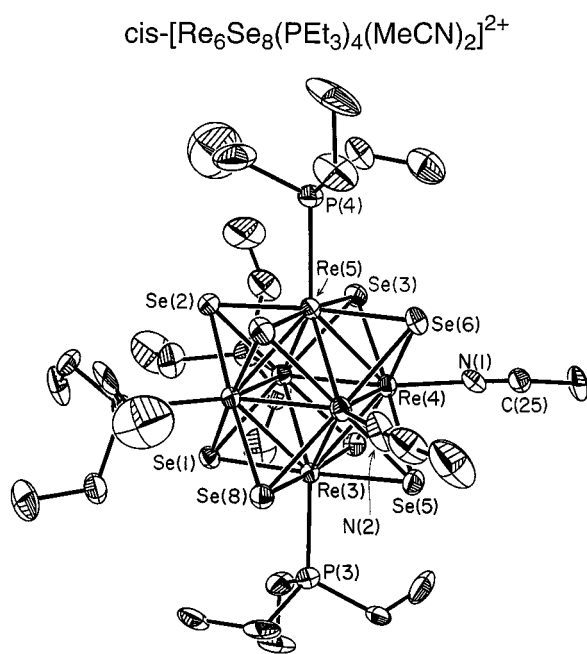
$\text{Cl}_{14}(\text{PR}_3)_4$ ($\text{M} = \text{Nb}, \text{Ta}$)²⁰ and of $[\text{Mo}_6\text{Cl}_{10}(\text{PR}_3)_4]^{2+}$ have been prepared previously by similar means. Clusters **2-6** are readily differentiated by their ³¹P spectra, whose resonances occur in

(20) (a) Klendworth, D. D.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 1151. (b) Imoto, H.; Hayakawa, S.; Morita, N.; Saito, T. *Inorg. Chem.* **1990**, *29*, 2007.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$, $(\text{Bu}_4\text{N})[\text{fac-Re}_6\text{Se}_8(\text{PET}_3)_3\text{I}_3]$ (**2**), $\text{trans-}[\text{Re}_6\text{Se}_8(\text{PET}_3)_4\text{I}_2]\cdot 2\text{CHCl}_3$ (**3**), $\text{cis-}[\text{Re}_6\text{Se}_8(\text{PET}_3)_4\text{I}_2]\cdot 2\text{CHCl}_3$ (**4**), $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5\text{I}]\text{I}\cdot 2\text{CH}_2\text{Cl}_2$ (**5**), and $[\text{Re}_6\text{Se}_8(\text{PET}_3)_6](\text{BF}_4)_2\cdot 2\text{CHCl}_3$ (**6**)

	$\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6^a$	2	3	4	5	6
Re–I	2.779(5)–2.801(5)	2.786(2)	2.747(4)	2.773(2)	2.768(2)	
mean	2.793(8)	2.774(3)		2.776(2)		
Re–P		2.780(8)	2.481(10)	2.458(9)	2.475(4)	2.478(14)
mean		2.442(10)	2.482(10)	2.460(9)	2.477(4)	2.478(14)
				2.473(8)	2.481(4)	2.481(2)
				2.484(8)	2.489(5)	
mean		2.449(9)	2.482(1)	2.469(12)	2.486(14)	2.479(1)
Re–Re	2.617(4)–2.635(4)	2.614(2)–2.637(2)	2.639(2)–2.646(2)	2.624(2)–2.646(2)	2.641(9)–2.662(10)	2.643(2)–2.648(2)
mean	2.625(5)	2.628(6)	2.641(3)	2.637(6)	2.651(7)	2.646(2)
Re–Se	2.505(6)–2.534(7)	2.500(2)–2.526(4)	2.509(4)–2.533(4)	2.499(4)–2.532(4)	2.515(2)–2.538(2)	2.507(5)–2.526(6)
mean	2.519(7)	2.509(7)	2.522(7)	2.517(8)	2.526(6)	2.516(5)
Re–Re–I	131.1(1)–139.0(1)	132.8(1)–137.0(1)	133.7(1)–136.5(1)	133.9(1)–136.0(1)	133.4(1)–135.3(1)	
mean	135.0(2)	134.9(17)	135.1(12)	134.9(6)	134.9(4)	
Re–Re–P		132.9(1)–137.1(1)	132.2(1)–137.6(1)	132.0(1)–138.0(1)	132.7(1)–137.6(1)	133.0(1)–137.1(1)
mean		135.0(19)	135.0(17)	135.0(18)	135.0(13)	135.0(13)
Re–Re–Re ^b	59.7(1)–60.4(1)	59.6(1)–60.4(1)	59.9(1)–60.2(1)	59.7(1)–60.3(1)	59.7(1)–60.2(1)	59.9(1)–60.1(1)
mean	60.0(2)	60.0(2)	60.0(1)	60.0(2)	60.0(2)	60.0(1)
Re–Re–Re ^c	89.7(1)–90.2(1)	89.8(1)–90.3(1)	89.8(1)–90.2(1)	89.6(1)–90.4(1)	89.6(1)–90.3(1)	90.0(1)–90.1(1)
mean	90.0(2)	90.0(2)	90.0(2)	90.0(2)	90.0(2)	90.0(1)
Re–Re–Se	58.1(2)–58.9(2)	58.2(1)–58.9(1)	58.1(1)–58.7(1)	57.9(1)–58.9(1)	58.0(1)–58.7(1)	58.1(1)–58.5(1)
mean	58.6(2)	58.4(2)	58.4(2)	58.4(2)	58.3(2)	58.3(1)
Re–Se–Re	62.3(1)–62.5(1)	62.7(1)–63.4(1)	62.9(1)–63.6(1)	62.7(1)–63.6(1)	63.0(1)–63.8(1)	63.2(1)–63.6(1)
mean	62.4(1)	63.1(2)	63.2(2)	63.2(3)	63.3(2)	63.4(1)
Se–Re–I	90.7(2)–92.8(2)	89.1(1)–94.6(1)	90.7(1)–93.4(1)	91.0(1)–93.1(1)	91.1(1)–92.2(1)	
mean	91.0(1)	91.9(16)	92.0(12)	91.9(7)	91.8(5)	
Se–Re–P		89.5(1)–94.6(1)	90.9(1)–94.4(1)	89.5(1)–94.6(1)	90.0(1)–94.0(1)	89.7(1)–94.6(1)
mean		92.1(19)	92.3(13)	92.0(17)	92.1(13)	92.1(13)
Se–Re–Se	89.7(1)–90.2(1)	89.4(1)–90.5(1)	89.4(1)–90.3(1)	88.7(1)–90.9(1)	88.9(1)–90.5(1)	89.7(1)–90.2(1)
mean	90.0(2)	89.9(4)	89.9(3)	89.9(6)	89.9(4)	89.9(2)

^a Reference 11. ^b Within triangular faces. ^c Within equatorial squares.

**Figure 4.** Structure of $\text{cis-}[\text{Re}_6\text{Se}_8(\text{PET}_3)_4(\text{MeCN})_2]^{2+}$, showing 50% probability ellipsoids and the atom labeling scheme.

the interval -31 to -36 ppm in chloroform solution. We have not pursued clusters with $n = 1$ and 2 as these are not of immediate utility in forming discrete cluster aggregates.

Structure proofs of clusters **2–6** were obtained by single-crystal X-ray diffraction. The structures are collected in Figure

2. Each contains a Re_6 octahedron concentric with a Se_8 cube whose atoms cap the triangular octahedral faces. The structure and bonding patterns of this core have been described previously.^{10,11} The *fac* (**2**), *trans* (**3**), and *cis* (**4**) isomeric forms and pentakis (**5**) and hexakis (**6**) phosphine substitutions are readily apparent. Dimensional data are reported in Table 3, mainly as ranges and mean values because of the close similarity in values over the set of clusters. No significant variance is observed in the face-capped octahedral geometry of the $[\text{Re}_6\text{Se}_8]^{2+}$ cores, nor in Re–I/P bond lengths and Se–Re–I/P bond angles. In turn, these dimensions do not differ significantly from those in $\text{Cs}_4\text{Re}_6\text{Se}_8\text{I}_6$.¹¹ The mean value of 92° for the Se–Re–I/P angles indicates that the Re atom is situated nearly in the Se_4 mean plane of each core face.

Synthesis and Structures of $[\text{Re}_6\text{Se}_8(\text{PET}_3)_n(\text{MeCN})_{6-n}]^{2+}$ ($n = 0, 4, 5$). With the desired phosphine-substituted clusters in hand, reactions leading to clusters with more labile ligands in desired substitution patterns were undertaken. The scheme employed, set out in Figure 3, proceeds by removal of iodide from **4**, **5**, and $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$ with AgBF_4 followed by binding of acetonitrile from solvent to afford **7** (84%), **8** (80%), and fully solvated **9** (72%),²² respectively, in the indicated yields. The compounds were identified spectroscopically and confirmed by X-ray diffraction. Among the more interesting spectroscopic observations is the downfield shift of ^{31}P resonances upon substitution of iodide with a nitrile. The shifts of **7** are displaced by 9.8 and 8.1 ppm compared to **4**, while those of **8** are moved by 3.3 and 6.0 ppm vs those of **5**. Evidently, replacement of electron-rich iodide with neutral nitrile ligand(s) reduces electron density at the phosphorus atoms. Further, the methyl resonances

(21) (a) Saito, T.; Nishida, M.; Yamagata, T.; Yamagata, Y.; Yamaguchi, Y. *Inorg. Chem.* **1986**, *25*, 1111. (b) Ehrlich, G. M.; Deng, H.; Hill, L. I.; Steigerwald, M. L.; Squattrito, P. J.; DiSalvo, F. J. *Inorg. Chem.* **1995**, *34*, 2480.

(22) A similar fully solvated cluster core, $[\text{Mo}_6\text{Cl}_8(\text{MeCN})_6]^{4+}$, has been produced in small quantities by an alternative method: Ehrlich, G. M.; Warren, C. J.; Haushalter, R. C.; DiSalvo, F. J. *Inorg. Chem.* **1995**, *34*, 4284.

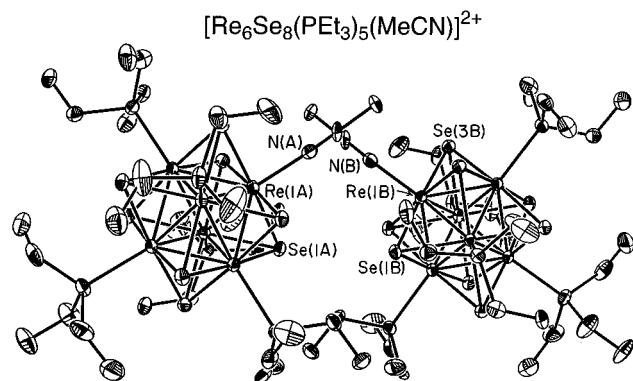


Figure 5. Structure of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{MeCN})]^{2+}$, showing 50% probability ellipsoids and the orientation of adjacent cluster molecules in the crystalline BF_4^- salt that is apparently favorable for dicluster formation: $\text{Re}(1\text{A})\cdots\text{Re}(1\text{B}) = 6.84 \text{ \AA}$, $\text{Re}(1\text{B})\cdots\text{Se}(1\text{A}) = 5.70 \text{ \AA}$, $\text{Re}(1\text{A})\cdots\text{Se}(3\text{B}) = 8.67 \text{ \AA}$. The two clusters are related by a crystallographically imposed 2-fold rotation axis.

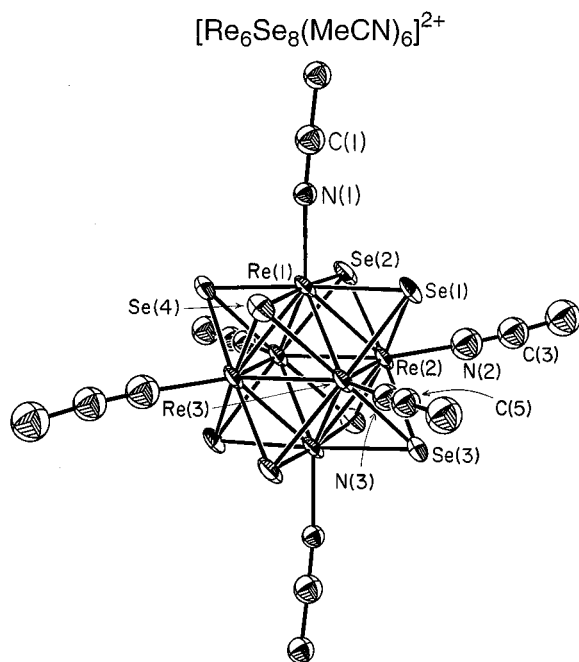


Figure 6. Structure of $[\text{Re}_6\text{Se}_8(\text{MeCN})_6]^{2+}$, showing 50% probability ellipsoids and the atom labeling scheme.

of **7** (2.89 ppm), **8** (2.91 ppm), and **9** (2.69 ppm) are appreciably shifted downfield compared to free acetonitrile (1.95 ppm). Over the course of months, coordinated acetonitrile did not exchange with CD_3CN solvent, as seen from no change in the ^1H NMR signal intensities of **7–9**. Crystal structures are presented in Figures 4–6. Individual values, ranges, and mean values of selected dimensions of **7** and **8** are collected in Table 4. Core dimensions and Re–P distances are essentially constant for the acetonitrile-ligated clusters and differ in no significant way from those of **2–6** (Table 3). The coordination of acetonitrile is nearly linear, the Re–N–C angles falling in the narrow range of $173(1)–177(2)^\circ$.

The foregoing observations of clusters **2–9**, and of $[\text{Re}_6\text{Se}_8\text{I}_6]^{4-}$ and $[\text{Re}_6\text{Se}_7(\text{SeH})\text{I}_6]^{3-}$,¹¹ lead to the recognition of certain properties. (i) The cubic $[\text{Re}_6\text{Se}_8]^{2+}$ core **1** remains virtually invariant structurally when protonated and bound by iodide, phosphine, and nitrile ligands alone or in combination. (ii) Binding sites are not electronically remote, as sensed by ^{31}P shifts in stereochemically equivalent clusters differing only in

SYNTHESIS OF A CLUSTER OF CLUSTERS: DICLUSTER

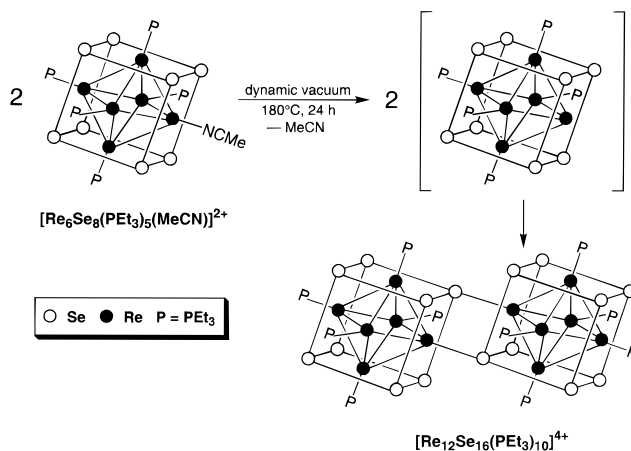


Figure 7. Schematic depiction of the synthesis concept leading to the dicluster $[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^{4+}$.

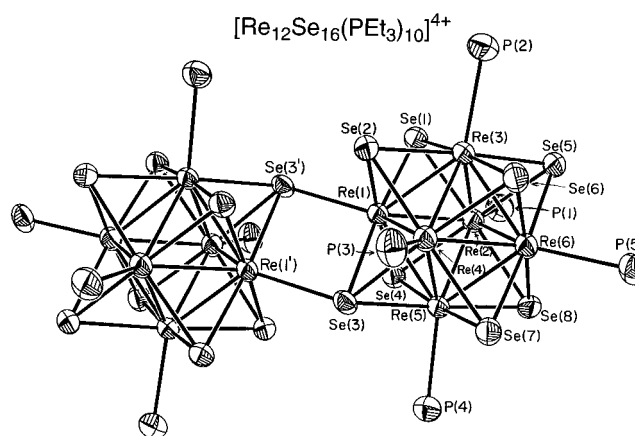


Figure 8. Structure of the dicluster $[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_{10}]^{4+}$ showing the atom labeling scheme and 50% probability ellipsoids. Primed and unprimed atoms are related by an inversion center; ethyl groups are omitted for clarity.

I^-/MeCN ligands. (iii) Nitrile ligands are potentially activated toward nucleophilic reagents by the electron-withdrawing nature of the core.

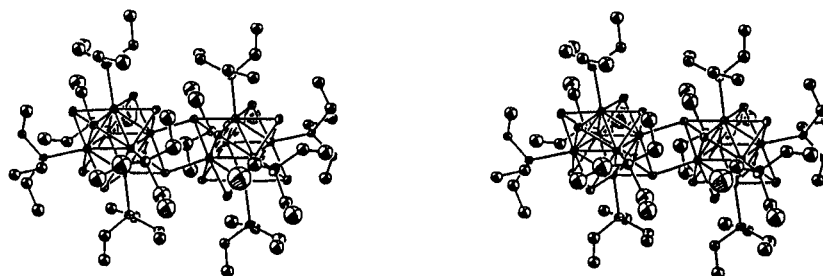
Synthesis of a Dicluster. One current concept for the synthesis of discrete oligomeric clusters containing the core $[\text{Re}_6\text{Q}_8]_n^{2n+}$ is generation of a coordinatively unsaturated $[\text{Re}_6\text{Q}_8]^{2+}$ cluster. This species could then oligomerize by formation of intercluster Re–Q bonds in Re_2Q_2 rhombs such as those present in $\text{Re}_6\text{Q}_8\text{Cl}_2$ ^{13,14} and related phases. The number and positions of unsaturated Re sites available for recoordination in an individual core would predispose the number of cores and the structure of the product oligomeric cluster. Acetonitrile-ligated clusters **7** and **8** have been prepared for this purpose. We have commenced investigation of this means of cluster buildup by selecting a dicluster as the initial objective. The synthesis concept is illustrated in Figure 7, from which it is seen that initial cluster **8** can give only one logical product when the acetonitrile ligand is removed.

Monoacetonitrile cluster **8** is a viable starting material for dicluster synthesis. The compound **[8](SbF₆)₂** was heated at 180°C for 24 h under dynamic vacuum. The orange-red crystalline material gradually turned brown and then greenish-black. It was crystallized from dichloromethane–ether to afford the product **[10](SbF₆)₄** as brownish-green crystals in 94% yield. The analogous reaction with the BF_4^- salt of **8** led to the same product in essentially quantitative yield. The synthesis is

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for *cis*-[Re₆Se₈(PEt₃)₄(MeCN)₂](SbF₆)₂ (**7**), [Re₆Se₈(PEt₃)₅(MeCN)](BF₄)₂ (**8**), and [Re₁₂Se₁₆(PEt₃)₁₀]BF₄·4CH₂Cl₂ (**10**)

	7	8	10
Re–N	2.110(2)	2.146(11)	
mean	2.121(14)		
Re–P	2.116(8)		
	2.469(5)	2.477(4)	2.467(8)
	2.476(4)	2.478(3)	2.485(8)
	2.484(4)	2.479(3)	2.490(8)
	2.488(5)	2.481(3)	2.495(9)
mean	2.479(8)	2.480(3)	2.509(9)
Re–Re	2.611(9)–2.650(9)	2.628(7)–2.656(7)	2.489(15)
mean	2.633(9)	2.641(8)	2.623(2)–2.670(2)
Re–Se ^a	2.506(2)–2.527(2)	2.509(14)–2.527(13)	2.643(12)
mean	2.517(5)	2.519(5)	2.510(3)–2.525(3)
Re–Re–N	133.0(1)–136.7(1)	131.4(1)–138.3(1)	2.516(4)
mean	134.8(13)	134.8(29)	
Re–Re–P	132.1(1)–138.1(1)	133.3(1)–136.6(1)	131.6(1)–138.8(1)
mean	135.1(14)	135.0(11)	135.0(19)
Re–Re–Re ^b	59.5(1)–60.4(1)	59.6(1)–60.3(1)	59.2(1)–60.9(1)
mean	60.0(3)	60.0(2)	60.0(4)
Re–Re–Re ^c	90.0(1)–90.6(1)	89.6(1)–90.3(1)	89.5(1)–90.7(1)
mean	90.0(3)	90.0(2)	90.0(4)
Re–Re–Se ^a	58.1(1)–58.9(1)	57.9(1)–58.7(1)	57.8(1)–58.6(1)
mean	58.5(2)	58.4(2)	58.3(2)
Re–Se–Re ^a	62.5(1)–63.6(1)	62.8(1)–63.7(1)	61.7(1)–64.1(1)
mean	63.1(3)	63.2(3)	63.3(5)
Se–Re–N	90.0(1)–93.6(1)	89.8(1)–94.6(1)	
mean	91.9(16)	92.7(25)	
Se–Re–P	89.5(1)–94.6(1)	90.1(1)–94.2(1)	89.5(1)–96.2(1)
mean	91.6(13)	92.1(11)	92.2(16)
Se–Re–Se ^a	89.0(1)–90.6(1)	88.9(1)–90.8(1)	89.2(1)–90.7(1)
mean	89.9(5)	89.9(5)	90.0(5)
Re–N–C	177(2)	173(1)	
mean	173(2)		
within Re ₂ Se ₂ rhomb	175(2)		
Re–Se			2.603(3)
			2.638(3)
mean			2.621(18)
Re–Se–Re			81.4(1)
Se–Re–Se			98.6(1)

^a Excluding Re₂Se₂ rhomb. ^b Within triangular faces. ^c Within equatorial squares.

**Figure 9.** Stereoview of the dicluster [Re₁₂Se₁₆(PEt₃)₁₀]⁴⁺ with 50% probability ellipsoids.

described for the SbF₆[−] salt because it proved somewhat easier to purify by recrystallization on a bulk scale. However, crystalline samples of [10](BF₄)₄ were also obtained, and the structure of the product cluster was established by an X-ray determination. The structure is presented in Figure 8 and a stereoview is available in Figure 9. The desired result has been achieved. Product **10** is a dicluster containing two [Re₆Se₈]²⁺ cores linked through the rhomb Re(1,1')Se(3,3') in a centrosymmetric structure. Selected metric data are included in Table 4. The bridging Re–Se distances (2.603(3), 2.638(3) Å) are about 0.1 Å longer than those within the core of **8** (mean 2.519(5) Å), the other six clusters prepared in this work (Tables 3 and 4), and Re₆Se₈Cl₂ (mean 2.52(1) Å).¹⁴ However, these bond lengths are essentially the same as those in the bridging rhombs of the two-dimensional phases Re₆Se₈Cl₂ (mean 2.62(1) Å)¹⁴ and CsRe₆Se₈I₃ (2.603(2) Å),¹¹ thus emphasizing the strength of the bridging interactions in **10**. The two compounds are dark

green and are freely soluble in solvents such as dichloromethane, acetonitrile, and acetone to give dark green solutions. The observation of three ³¹P NMR signals in the intensity ratio 2:2:1 for both compounds in chloroform solution is consistent with the solid state structure.

The origin of the high yield of **10** by thermolysis of **8** is clearly due to the preferential loss of acetonitrile rather than PEt₃. The phosphine ligands serve as protecting groups for their coordinated Re atoms. However, in the conversion of [8](BF₄)₂ we recognize another favorable factor, found in its crystal structure. The packing of clusters in the structure is such that they are organized in pairs with the Re sites featuring labile acetonitrile ligands in close proximity (Re(1A)···Re(1B)) = 6.84 Å, as illustrated in Figure 5. The arrangement likely facilitates the coupling of cluster cores in the solid state. When the acetonitrile ligands are released, two clusters may be brought into alignment with minimal rearrangement by translating and

rotating such that intercore bonds are formed between atoms Re(1A) and Se(3B) and atoms Se(1A) and Re(1B). While it is reasonable to suppose that neighboring clusters in the thermolyzed crystal react with each other, we cannot prove that this is the case. Nonetheless, the synthesis of **10** is directed by the structure of precursor **8** with its single labile ligand site. We observe that the bridging interactions produced in the formation of **10** are just those which are broken in the synthesis of $[\text{Re}_6\text{Se}_8]^{2+}$ clusters by dimensional reduction.¹¹ Furthermore, with its single rhombic linkage, the dicluster structure establishes the missing member in a series of frameworks composed of $[\text{Re}_6\text{Se}_8]^{2+}$ units linked to four ($\text{Re}_6\text{Se}_8\text{Cl}_2$), three ($\text{TlRe}_6\text{Se}_8\text{Cl}_3$), two ($\text{TlRe}_6\text{Se}_8\text{Cl}_4$ and $\text{CsRe}_6\text{Se}_8\text{X}_4$ ($\text{X} = \text{Cl}, \text{Br}$)), and zero ($\text{Tl}_5\text{Re}_6\text{Se}_8\text{Cl}_7$, *inter alia*) neighbors via Re_2Se_2 rhombs.^{10,11,14}

The synthesis concept is capable of extension. For example, a similar condensation of *cis* isomer **7** could lead to the tetracluster *cyclo*- $[\text{Re}_{24}\text{Se}_{32}(\text{PEt}_3)_{16}]^{8+}$, in which four clusters are held in a square-like arrangement. Analogously, conversion of **2** into *fac*- $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_3(\text{MeCN})_3]^{2+}$ might provide access to a cube-like octacluster, $[\text{Re}_{48}\text{Se}_{64}(\text{PEt}_3)_{24}]^{16+}$. These discrete multicluster aggregates would represent nanoscale pieces of a parent solid with a three-dimensional cluster framework of the type observed in the Chevrel phases $\text{A}_x\text{Mo}_6\text{Se}_8$.³ Indeed, it may

be possible to produce new materials exhibiting just such extended frameworks by similar means. Thus solids containing *trans* isomer **3** and fully solvated **9** could conceivably be thermolyzed and annealed to form one- and three-dimensional rhomb-linked frameworks of empirical formulae $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4]^{2+}$ and $[\text{Re}_6\text{Se}_8]^{2+}$, respectively. The results of additional synthetic experiments and the reactivity properties of single and oligomerized clusters will be the subjects of future reports.

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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 (109 pages). See any current masthead page for ordering and Internet access instructions.

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