Inorg. Chem. **1999,** *38,* 4888−4895

Synthesis and Structures of Solvated Monoclusters and Bridged Di- and Triclusters Based on the Cubic Building Block $[Re_6(\mu_3\text{-}Se)_8]^{2+}$

Zhiping Zheng, Thomas G. Gray, and R. H. Holm*

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138

Received May 25, 1999

The cluster formulated as $[Re_6Se_7(SeH)I_6]^{3-}$ has been previously shown to undergo ligand substitution reactions to generate the family $[Re_6Se_8(PEt_3)_nI_{6-n}]^{(n-4)+}$ ($n = 3-6$), several members of which form solvate clusters upon treatment with Ag(I) in acetonitrile. Here it is demonstrated that additional de-iodination reactions afford solvate clusters useful in building up bridged cluster arrays. In dichloromethane/solv (5:1 v/v) in the presence of 2 equiv of $AgSbF_6$ at room temperature, *trans*-$[Re_6Se_8(PEt_3)_4I_2]$ forms *trans*-$[Re_6Se_8(PEt_3)_4(solv)_2]^{2+}$ (solv = MeCN (**5**), DMF (**6**), Me_2SO (**7**)). The hexaiodo cluster with 6 equiv of $AgSbF_6$ gives the fully solvated clusters $[Re_6Se_8(solv)_6]^{2+}$ (solv = DMF (**9**), Me_2SO (**10**), py (**11**)). In refluxing chlorobenzene for 3 days, $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ (**1**) and 4,4′-bipyridine (4,4′-bpy) yield $[Re_6Se_8(PEt_3)_5(4,4'\text{-bpy})]^{2+}$ (**12**); similarly, *cis*- and *trans*-$[Re_6Se_8(PEt_3)_4(MeCN)_2]^{2+}$ afford the *cis*- and *trans*-**14** isomers, respectively, of $[Re_6Se_8(PEt_3)_4(4,4'\text{-bpy})_2]^{2+}$. Clusters **1** and **12** (or **1** and 1/2 equiv of 4,4-bpy) under the same conditions afford the bridged dicluster $\{[Re_6Se_8(PEt_3)_5]_2(4,4'\text{-bpy})\}^{4+}$ (**15**). The related diclusters $\{[Re_6Se_8(PEt_3)_5]_2(L{-}L)\}^{4+}$ (L−L = 4,4′-$py_2C_2H_2$ (**16**), 4,4′-$py_2C_2H_4$ (**17**) (4,4′-$py_2C_2H_2$ = *trans*-1,2-bis(4-pyridyl)ethylene, 4,4′-$py_2C_2H_4$ = *trans*-1,2-bis(4-pyridyl)ethane)) are obtained by analogous methods. Reaction of **14** and 2 equiv of **1** in refluxing dichloromethane produces the linear tricluster $\{[Re_{18}Se_{24}(PEt_3)_{14}(4,4'\text{-bpy})_2\}^{6+}$. All clusters were isolated as SbF_6^- salts in yields of ca. 60−90% and were characterized by their ^1H and ^{31}P NMR spectra and by mass spectrometry. In addition, the structures of 10 clusters (**5**−**7**, **9**−**12**, **14**−**16**) were confirmed by X-ray structure determinations. All clusters are based on the cubic $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core whose dimensions are insensitive to the nature and substitution pattern of the ligands. All substitution reactions, as indicated, proceed with retention of stereochemistry. Appropriate choice of solvate cluster leads to the unambiguous formation of **14**−**17**, and should allow the construction of these and other cluster array shapes with variable bridging ligands. On the basis of voltammetric and EPR properties, clusters originally described as the monoprotonated species $[Re_6Se_7(SeH)I_6]^{3-}$ and $[Re_6S_7(SH)Br_6]^{3-}$ are reformulated as the oxidized 23-electron clusters $[Re_6Se_8I_6]^{3-}$ and $[Re_6S_8Br_6]^{3-}$.

Introduction

The chemistry of the cubic clusters $[Re_6Q_8X_6]^z$ (Q = S, Se, Te) is in a stage of rapid development. Originally, the cluster cores $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ were found in extended solids such as $Re_6Q_8X_2$ (X = Cl, Br)[1−4] and Re_5Te_{15}[5,6] where intercluster bridging is extensive. Solids containing *molecular* clusters can be obtained by high-temperature synthesis using the procedure of dimensional reduction[7,8] or by combination of simple reactants in the appropriate stoichiometry.[7−15] Such clusters are, therefore, readily accessible and can be subjected to a variety of studies. Of particular interest in this laboratory are their photophysical and reactivity properties. In the latter context, we have shown that terminal halides in the clusters $[Re_6S_8Br_6]^{4-}$ and $[Re_6Se_8I_6]^{4-}$ are replaceable by triethylphosphine under forcing conditions (typically in refluxing DMF for several days) and are separated and isolated by chromatography. In this way, the series $[Re_6S_8(PEt_3)_nBr_{6-n}]^{(n-4)+}$ ($n = 2-6$)[16] and $[Re_6Se_8(PEt_3)_nI_{6-n}]^{(n-4)+}$ ($n = 3-6$)[17] have been obtained, including nearly all diastereomers of the $n = 2-4$ species. We have further demonstrated that iodide ligands can be removed by Ag(I) in rapid reactions to afford the solvated species $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$, *cis*-$[Re_6Se_8(PEt_3)_4(solv)_2]^{2+}$ (solv = MeCN, DMF,

---

(1) Leduc, P. L.; Perrin, A.; Sergent. *Acta Crystallogr.* **1983**, *C39*, 1503.
(2) Speziali, N. L.; Berger, H.; Leicht, G.; Sanjinés, R.; Chapuis, G.; Lévy, F. *Mater. Res. Bull.* **1988**, *23*, 1597.
(3) Fischer, C.; Fiechter, S.; Tributsch, H.; Reck, G.; Schultz, B. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1752.
(4) Note a recent improved synthesis of phases $Re_6Q_8Br_2$ (Q = S, Se, Te): Yarovoi, S. S.; Mironov, Y. I.; Mironov, Y. V.; Virovets, A. V.; Federov, V. E.; Paek, U.; Shin, S. C.; Seo, M.-L. *Mater. Res. Bull.* **1997**, *32*, 1271.
(5) Klaiber, F.; Petter, W.; Hulliger, F. *J. Solid State Chem.* **1983**, *46*, 112.
(6) Federov, V. E.; Podberezskaya, N. V.; Asanov, I. P. *Mater. Res. Bull.* **1986**, *21*, 1335.
(7) Long, J. S.; Williamson, A. S.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 226.
(8) Long, J. R.; McCarty, L. S.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4603.
(9) Slougui, A.; Mironov, Y. V.; Perrin, A.; Federov, V. E. *Croat. Chim. Acta* **1995**, *68*, 885.
(10) Mironov, Y. V.; Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 2709.
(11) Slougui, A.; Ferron, S.; Perrin, A.; Sergent, M. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 1001.
(12) Fedin, V. P.; Federov, V. E.; Imoto, H.; Saito, T. *Polyhedron* **1997**, *16*, 1615.
(13) Mironov, Y. V.; Cody, J. A.; Albrecht-Schmitt, T. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 493.
(14) Naumov, N. G.; Virovets, A. V.; Podberezskaya, N. V.; Federov, V. E. *J. Struct. Chem.* **1997**, *38*, 857.
(15) Fedin V. P.; Virovets, A. A.; Sykes, A. G. *Inorg. Chim. Acta* **1998**, *271*, 228.
(16) Willer, M. W.; Long, J. R.; McLauchlan, C. C.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 328.
(17) Zheng, Z.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 2163.

10.1021/ic9906050 CCC: $18.00

Me_2SO, pyridine), and $[Re_6Se_8(MeCN)_6]^{2+}$.[17,18] All halide and solvate clusters have been characterized by ^1H and ^{31}P NMR and many by X-ray structure determinations, which reveal no chemically significant dependence of $[Re_6Q_8]^{2+}$ core dimensions on the nature of the ligands.

The foregoing halide and solvate clusters constitute a basis set of potential building blocks. Applications include the formation of differently substituted single clusters, ligand-bridged multicluster arrays whose shapes depend on the stereochemistry of the linked clusters, and condensed clusters of higher nuclearity. For example, thermolysis of $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ removes acetonitrile and affords the centrosymmetric dicluster $[Re_{12}Se_{16}(PEt_3)_{10}]^{4+}$, in which two cluster cores are condensed by means of an $Re_2(\mu_4\text{-}Se)_2$ rhomboidal interaction.[17] Under the same conditions, *cis*-$[Re_6Se_8(PEt_3)_4(MeCN)_2]^{2+}$ yields *trans*-$[Re_{12}Se_{16}(PEt_3)_8(MeCN)_2]^{4+}$.[18,19] More recently, we have extended substitution reactions in the $[Re_6Se_8(PEt_3)_n I_{6-n}]^{(n-4)+}$ series ($n = 0, 4$) to include new types of solvated clusters and the first examples of ligand-bridged double clusters. The details of this work, including X-ray structure proofs, are provided here.

Experimental Section[20]

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. ^1H and ^{31}P NMR spectra of all compounds were determined in CD_3CN solution. Because of the small scale of the preparations, compounds were not analyzed. Their identity was established by a combination of NMR and mass spectrometric results and X-ray structure determinations. Fortuitously, the mass of SbF_6 (235.7) is almost exactly twice that of PEt_3 (118.2). In formulating compositions for various m/z values obtained in the low-resolution measurements reported here, we have tended to utilize SbF_6 rather than $2PEt_3$ because of the tight binding property of the phosphine to the $[Re_6Se_8]^{2+}$ core. All compounds were >95% pure by an NMR criterion.

***trans*-$[Re_6Se_8(PEt_3)_4(MeCN)_2](SbF_6)_2$.** A solution of 0.035 g (0.10 mmol) of $AgSbF_6$ in 2 mL of acetonitrile was added to a solution of 0.10 g (0.041 mmol) of *trans*-$[Re_6Se_8(PEt_3)_4I_2]$[17] in 10 mL of dichloromethane. A yellow precipitate formed within seconds; the mixture 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 0.10 g (89%) of an orange-red solid. ^1H NMR: δ 1.11 (t, Me), 2.22 (q, CH_2), 2.71 (s, MeCN). ^{31}P NMR: δ −17.9. FAB-MS: m/z 2774 (M^+).

***trans*-$[Re_6Se_8(PEt_3)_4(DMF)_2](SbF_6)_2$.** A solution of 0.019 g (0.055 mmol) of $AgSbF_6$ in 2 mL of DMF was added to a solution of 0.054 g (0.022 mmol) of *trans*-$[Re_6Se_8(PEt_3)_4I_2]$ in 10 mL of dichloromethane. A yellow precipitate formed within seconds; the mixture 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 0.048 g (78%) of an orange-red solid. ^1H NMR: δ 1.14 (t, Me), 2.28 (q, CH_2), 2.77 (s, NMe), 3.00 (s, NMe), 8.09 (s, HCO). ^{31}P NMR: δ −16.4. FAB-MS: m/z 2838 (M^+).

***trans*-$[Re_6Se_8(PEt_3)_4(OSMe_2)_2](SbF_6)_2$.** A solution of 0.019 g (0.055 mmol) of $AgSbF_6$ in 2 mL of DMSO was added to a solution of 0.054 g (0.022 mmol) of *trans*-$[Re_6Se_8(PEt_3)_4I_2]$ in 10 mL of dichloromethane. A yellow precipitate formed within seconds; the mixture 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 0.053 g (85%) of an orange-red solid. ^1H NMR: δ 1.11 (t, Me), 2.24 (q, CH_2), 2.49 (s, Me). ^{31}P NMR: δ −17.7. FAB-MS: m/z 2612 ($[M - SbF_6]^+$).

$[Re_6Se_8(DMF)_6](SbF_6)_2$. A solution of 0.085 g (0.25 mmol) of $AgSbF_6$ in 2 mL of DMF was added to a solution of 0.10 g (0.031 mmol) of $(Bu_4N)_3[Re_6Se_8I_6]$[8] in 10 mL of dichloromethane. A yellow precipitate formed within seconds; the mixture 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/DMF (4:1 v/v); the solution was stirred for 5 min and filtered through a plug of Celite. Ether was introduced to the filtrate over 1 d by vapor diffusion, causing separation of the product as 0.074 g (89%) of orange-red blocks. ^1H NMR: δ 2.90 (s, Me), 3.10 (s, Me), 8.53 (s, HCO). FAB-MS: m/z 2657 (M^+).

$[Re_6Se_8(OSMe_2)_6](SbF_6)_2$. A solution of 0.085 g (0.25 mmol) of $AgSbF_6$ in 2 mL of DMSO was added to a solution of 0.10 g (0.031 mmol) of $(Bu_4N)_3[Re_6Se_8I_6]$ in 10 mL of dichloromethane. A yellow precipitate formed within seconds; the mixture 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/Me_2SO (4:1 v/v); the solution was stirred for 5 min and filtered through a plug of Celite. Ether was introduced to the filtrate over 1 d by vapor diffusion, causing separation of the product as 0.068 g (82%) of orange-red needles. ^1H NMR: δ 2.50 (s, Me). FAB-MS: m/z 2688 (M^+).

$[Re_6Se_8(py)_6](SbF_6)_2$. To a solution of 0.329 g (0.098 mmol) of $(Bu_4N)_3[Re_6Se_8I_6]$ in 10 mL of dichloromethane was added 0.370 g (1.08 mmol) of $AgSbF_6$. This solution was treated with ca. 8 mL of pyridine, and the reaction mixture was stirred overnight. The resulting air-stable yellow suspension was twice filtered through Celite to give an orange filtrate which was evaporated to near-dryness. Diethyl ether was layered onto a concentrated acetonitrile solution of the residue, causing separation of the product over one week as 0.212 g (80%) of orange blocks. ^1H NMR: δ 9.69 (d, 2-H), 8.01 (t, 4-H), 7.40 (d, 3-H). FAB MS: m/z 2459 ($[M - SbF_6]^+$).

$[Re_6Se_8(PEt_3)_5(4,4'\text{-bpy})](SbF_6)_2$. A mixture of 0.240 g (0.0856 mmol) of $[Re_6Se_8(PEt_3)_5(MeCN)](SbF_6)_2$[17] and 4,4′-bipyridine (0.245 g, 1.57 mmol) was dissolved in 2 mL of dichloromethane. Chlorobenzene was added to the point of precipitation, and a minimal amount of dichloromethane was used to redissolve the precipitate. The reaction mixture was refluxed for 3 d to give an orange-red solution. Ether (20 mL) was added to produce an orange-red precipitate, which was collected and washed with ether (3 × 20 mL). This material was chromatographed on a silica gel column using dichloromethane/acetonitrile (6:1 v/v) as the eluting solvent. Two orange-red fractions were obtained, the first being $[Re_{12}Se_{16}(PEt_3)_{10}(4,4'\text{-bpy})](SbF_6)_4$ ($R_f = 0.53$, 0.022 g, 9%, vide infra). The second fraction ($R_f = 0.30$) was reduced in vacuo, and the residue was recrystallized from dichloromethane/ether to give the product as 0.16 g (62%) of orange-red blocks. ^1H NMR: δ 1.00−1.13 (m, Me), 2.10 (q, 3, CH_2), 2.24 (q, 12, CH_2); 7.59 (d, 1), 7.67 (d, 1), 8.76 (d, 1), 9.34 (d, 1, 2-H) (4,4′-bpy). ^{31}P NMR: δ −22.5 (4), −25.9 (1). ES-MS: m/z 1171 ($[Re_6Se_8(PEt_3)_5]^{2+}$), 1248 ($[M - 2SbF_6]^{2+}$).

***cis*-$[Re_6Se_8(PEt_3)_4(4,4'\text{-bpy})_2](SbF_6)_2$.** A mixture of 0.025 g (0.0088 mmol) of *cis*-$[Re_6Se_8(PEt_3)_4(MeCN)_2](SbF_6)_2$[17] and excess 4,4′-bipyridine (0.10 g, 0.64 mmol) in 5 mL of chlorobenzene was stirred and refluxed for 4 d. Ether was added to the resultant red-brown solution, causing the precipitation of a light brown solid. The precipitate was collected, washed with ether (3 × 15 mL), and dissolved in 5 mL of dichloromethane, affording an orange-red solution. Ether was introduced

---

[18] Zheng, Z.; Holm, R. H. *Inorg. Chem.* **1997**, *36*, 5173.

[19] Note that the related cluster $[Re_9S_{11}Br_6]^{2-}$, based on confacial Re_6 octahedra, has recently been claimed: Federov, V. E.; Elsegood, M. R. J.; Yaravoi, S. S.; Mironov, Y. V. *J. Chem. Soc., Chem. Commun.* **1998**, 1861.

[20] Abbreviations: py, pyridine; 4,4′-bpy, 4,4′-bipyridine; ES, electrospray; FAB, fast atom bombardment; 4,4′-$py_2C_2H_2$, *trans*-1,2-bis(4-pyridyl)ethylene; 4,4′-$py_2C_2H_4$, 1,2-bis(4-pyridyl)ethane.

Table 1. Crystal Data[a] and Structure Refinement for Solvated Clusters

	[**5**]$(SbF_6)_2$	[**6**]$(SbF_6)_2$	[**7**]$(SbF_6)_2 \cdot 2Me_2SO$	[**9**]$(SbF_6)_2$	[**10**]$(SbF_6)_2$
empirical formula	$C_{28}H_{66}F_{12}N_2P_4$-$Re_6Sb_2Se_8$	$C_{30}H_{73}F_{12}N_2O_2P_4$-$Re_6Sb_2Se_8$	$C_{32}H_{84}F_{12}O_4P_4$-$Re_6S_4Sb_2Se_8$	$C_{18}H_{42}F_{12}N_6O_6$-$Re_6Sb_2Se_8$	$C_{16}H_{48}F_{12}O_8$-$Re_6S_8Sb_2Se_8$
fw	2775.08	2838.16	3005.49	2658.96	2845.40
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
Z	2	2	2	3	1
a, Å	12.826(3)	12.458(3)	11.805(2)	12.550(2)	9.337(2)
b, Å	17.121(3)	15.661(3)	12.065(2)	12.550(2)	11.578(2)
c, Å	13.230(3)	16.121(3)	24.985(5)	27.039(5)	13.498(3)
α, deg			102.39(3)		100.36(3)
β, deg	104.66(3)	97.87(3)	93.74(3)		94.52(3)
γ, deg			91.05(3)		95.38(3)
V, Å^3	2811(1)	3116(1)	3466(1)	3688(1)	1422.4(5)
d_{calcd}, g/cm^3	3.280	3.025	2.880	3.592	3.322
μ, mm^{-1}	19.17	17.30	15.68	21.29	19.13
θ range, deg	1.98−22.5	1.65−22.5	1.67−23.0	2.02−22.5	1.54−22.5
R_1,[b] wR_2[c]	0.0678, 0.1845	0.0617, 0.1407	0.0602, 0.1472	0.0337, 0.0818	0.0490, 0.1175

[a] Obtained with graphite-monochromatized Mo Kα ($\lambda = 0.710\ 73$ Å) radiation at 293 K. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$.

over 1 d by vapor diffusion, causing separation of the product as 0.023 g (87%) of orange-red needles. ^{1}H NMR: δ 1.05−1.17 (m, 36, Me), 2.19 (q, 3, CH_2), 2.30 (q, 3, CH_2); 7.63 (d, 1), 7.68 (d, 1), 8.76 (d,1), 9.50 (d, 1, 2-H) (4,4′-bpy). ^{31}P NMR: δ −19.0 (1), −21.8 (1). FAB-MS: m/z 2769 ($[M - SbF_6]^+$).

***trans*-[Re$_6$Se$_8$(PEt$_3$)$_4$(4,4′-bpy)$_2$](SbF$_6$)$_2$.** A mixture of 0.14 g (0.051 mmol) of *trans*-$[Re_6Se_8(PEt_3)_4(MeCN)_2](SbF_6)_2$[17] and excess 4,4′-bipyridine (0.10 g, 0.64 mmol) in 10 mL of chlorobenzene was stirred and refluxed for 2 d. Ether was added to the red-brown solution, causing the precipitation of a light brown solid. The precipitate was collected, washed with ether (3 × 15 mL), and dissolved in 5 mL of dichloromethane, affording an orange-red solution. Ether was introduced over 1 d by vapor diffusion, causing separation of the product as 0.13 g (84%) of orange-red needles. ^{1}H NMR: δ 1.15 (t, 9, Me), 2.34 (q, 6, CH_2); 7.58 (d, 1), 7.69 (d, 1), 8.77 (br), 9.27 (d, 1, 2-H) (4,4′-bpy). ^{31}P NMR: δ −18.3. FAB-MS: m/z 2771 ($[M - SbF_6]^+$).

{[Re$_6$Se$_8$(PEt$_3$)$_5$]$_2$(4,4′-bpy)}(SbF$_6$)$_4$. To a solution of 0.028 g (9.9 μmol) of $[Re_6Se_8(PEt_3)_5(MeCN)](SbF_6)_2$ in 10 mL of dichloromethane was added a solution of 0.84 mg (5.4 μmol) of 4,4′-bipyridine in 0.5 mL of dichloromethane. Chlorobenzene was added to the point of precipitation, and a minimal amount of dichloromethane was used to redissolve the precipitate. The mixture was refluxed for 3 d to give an ochre-colored solution. Ether (20 mL) was added to produce a brown precipitate which was collected, washed with ether (3 × 15 mL), and dissolved in 5 mL of acetonitrile. The solution was stirred for 5 min and filtered through a plug of Celite. Ether was introduced over 1 d by vapor diffusion, causing separation of the product as 0.023 g (81%) of red-brown blocks. ^{1}H NMR: δ 1.03 (t, 9, Me), 1.10 (t, 36, Me), 2.09 (q, 6, CH_2), 2.24 (q, 24, CH_2); 7.57 (d, 4, 3-H), 9.41 (d, 4, 2-H). ^{31}P NMR: δ −22.3 (4), −25.8 (1). ES-MS: m/z 1169 ($[Re_6Se_8(PEt_3)_5]^{2+}$), 1248 ($[Re_6Se_8(PEt_3)_5(4,4'\text{-bpy})]^{2+}$), 2653 ($[M - 2SbF_6]^{2+}$).

{[Re$_6$Se$_8$(PEt$_3$)$_5$]$_2$(4,4′-py$_2$C$_2$H$_2$)}(SbF$_6$)$_4$. To a solution of 0.292 g (0.102 mmol) of $[Re_6Se_8(PEt_3)_5(MeCN)](SbF_6)_2$ in 50 mL of dichloromethane/chlorobenzene (1:1 v/v) was added 1.09 mL (0.0545 mmol) of a freshly prepared 0.050 M solution of *trans*-bis(4-pyridyl)ethylene in dichloromethane. The reaction mixture was refluxed for 3 d, producing an orange solution which was evaporated to dryness. The residue was dissolved in a minimal volume of acetonitrile. The solution was filtered, and the filtrate was layered with benzene and allowed to stand for 3 d. The product was collected as 0.230 g (70%) of orange block-shaped crystals. ^{1}H NMR: δ 1.00 (t, 9, Me) 1.05 (t, 36, Me), 2.04 (q, 6, CH_2), 2.18 (q, 24, CH_2), 7.25 (d, 4, 3-H), 7.32 (s, =CH, 2), 9.07 (d, 4, 2-H). ^{31}P NMR: δ −19.8 (4), −22.7 (1). FAB-MS: m/z 5570.5 ($M^+ - SbF_6$), 2758.6 ($[Re_6Se_8(PEt_3)_5(4,4'\text{-}py_2C_2H_2)(SbF_6)]^+$).

{[Re$_6$Se$_8$(PEt$_3$)$_5$]$_2$(4,4′-py$_2$C$_2$H$_4$)}(SbF$_6$)$_4$. To a solution of 0.097 g (0.034 mmol) of $[Re_6Se_8(PEt_3)_5(MeCN)](SbF_6)_2$ in 10 mL of chlorobenzene was added a solution of 3.1 mg (0.017 mmol) of 1,2-bis(4-pyridyl)ethane in 10 mL of dichloromethane. The mixture was refluxed for 3 d to give an ochre-colored solution. Ether (20 mL) was added to produce a light brown precipitate. The precipitate was dissolved in 5 mL of acetonitrile; the solution was stirred for 5 min and filtered through a plug of Celite. Ether was introduced over 1 d by vapor diffusion, causing separation of the product as 0.064 g (63%) of orange-red blocks. ^{1}H NMR: δ 1.01 (t, 9, Me), 1.10 (t, 36, Me), 2.11 (q, 6, CH_2), 2.23 (q, 24, CH_2), 3.03 (br, CH_2); 7.18 (d, 4, 3-H), 9.13 (d, 4, 2-H). ^{31}P NMR: δ −22.6 (4), −25.8 (1). FAB-MS: m/z 1703 ($[M - 3SbF_6]^{3+}$), 1260 ($[Re_6Se_8(PEt_3)_5(4,4'\text{-}py_2C_2H_4)]^{2+}$).

[Re$_{18}$Se$_{24}$(PEt$_3$)$_{14}$(4,4′-bpy)$_2$](SbF$_6$)$_6$. A mixture of 0.038 g (0.014 mmol) of *trans*-$[Re_6Se_8(PEt_3)_4(MeCN)_2](SbF_6)_2$ and 0.081 g (0.027 mmol) of $[Re_6Se_8(PEt_3)_5(4,4'\text{-bpy})](SbF_6)_2$ in 10 mL of chlorobenzene was stirred and refluxed for 4 d. Ether was added to the resultant red-brown solution, causing the precipitation of a light brown solid. The precipitate was collected and washed with ether (3 × 15 mL); the residue was chromatographed on a silica gel column using dichloromethane/acetonitrile (3:1 v/v) as the eluting solvent. The major fraction ($R_f = 0.76$) was collected and reduced in vacuo, and the residue was recrystallized from dichloromethane/ether to give the product as 0.085 g (73%) of orange-yellow needles. ^{1}H NMR: δ 1.02−1.16 (m, Me), 2.10 (m, CH_2), 2.24 (q, CH_2), 2.34 (q, CH_2); 7.55−7.57 (m), 9.30 (d, 2-H), 9.40 (d, 2-H). ^{31}P NMR: δ −17.9 (2), −22.2 (4), −25.7 (1). ES-MS: m/z 1922.0 ($[M - 4SbF_6]^{4+}$), 1708.2 ($[Re_{12}Se_{16}(PEt_3)_9(4,4'\text{-bpy})(SbF_6)]^{3+}$).

X-ray Structure Determinations. Structures were determined for the 10 compounds in Tables 1 and 2. Numerical designations of clusters are given in Chart 1. For simplicity, in this section compounds are referred to by their cation number. Suitable crystals were grown at room temperature by vapor diffusion of ether into concentrated dichloromethane (**5**, **6**, **12**), acetonitrile (**11**), dichloromethane/acetonitrile (**15**), dichloromethane/DMF (**9**), and dichloromethane/Me_2SO (**7**, **10**) solutions. Compounds **14** and **16** were crystallized by layering THF and benzene, respectively, on concentrated acetonitrile solutions. Block-shaped orange-red crystals were obtained in all cases. Crystals were coated with Apiezon L grease, attached to glass fibers, transferred to Nicolet P3 (**5**, **9**, **10**, **12**, **15**) and Siemens SMART (**6**, **7**, **11**, **14**, **16**) diffractometer. Lattice parameters were obtained from least-squares analysis of more than 30 carefully centered reflections. None of the crystals showed significant decay over the course of data collection. The raw intensity data were converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure amplitudes and their esd's using the program XDISK (**5**, **9**, **10**, **12**, **15**) or SAINT (**6**, **7**, **11**, **14**, **16**) of SHELXTL PLUS. An empirical absorption correction was applied to each data set by using the program XEMP, except for **15** where the procedure of Blessing[21] was used. Space group assignments are 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 were refined against all data using the SHELXTL 5.0 software package. For **9**, **11**, and **14**, the thermal parameters for all atoms were refined

---

(21) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

Table 2. Crystal Data[a] and Structure Refinement for Single and Bridged Clusters

	[**11**]$(SbF_6)_2$	[**12**]$(SbF_6)_2\cdot 2CH_2Cl_2$	[**14**]$(SbF_6)_2\cdot$THF	[**15**]$(SbF_6)_4$	[**16**]$(SbF_6)_4\cdot 8C_6H_6$
empirical formula	$C_{30}H_{30}F_{12}N_6$-$Re_6Sb_2Se_8$	$C_{41}H_{85}Cl_2F_{12}N_2$-$Re_6Sb_2Se_8$	$C_{38}H_{70}F_{12}N_2OP_4$-$Re_6Sb_2Se_8$	$C_{70}H_{158}F_{24}N_2P_{10}$-$Re_{12}Sb_4Se_{16}$	$C_{120}H_{208}F_{24}N_2P_{10}$-$Re_{12}Sb_4Se_{16}$
fw	2694.98	3052.24	2915.22	5778.44	6429.52
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Z	1	2	1	2	1
a, Å	13.9972(1)	16.9820(3)	10.6065(2)	12.6564(1)	12.8813(4)
b, Å	19.7337(3)	18.9644(4)	13.1141(3)	22.9957(1)	15.5023(5)
c, Å	39.9367(6)	23.2488(1)	16.7533(4)	23.5374(4)	24.4935(6)
α, deg		97.449(1)	111.83(1)		73.717(1)
β, deg	93.897(1)	96.387(1)	104.684(1)	103.036(1)	78.074(1)
γ, deg		96.211(1)	94.803(1)		68.940(1)
V, Å^3	11005.7(2)	7320.7(2)	2051.07(8)	6673.8(1)	4350.6(2)
d_{calcd}, g/cm^3	3.253	2.769	2.360	2.876	2.215
μ, mm^{-1}	19.468	14.82	13.141	16.17	12.41
T, K	213	293	213	213	213
θ range, deg	1.02−28.3	0.89−22.5	1.38−28.27	1.25−22.5	0.85−28.3
R_1,[b] wR_2[c]	0.0506, 0.1089	0.0649, 0.1255	0.0675, 0.1721	0.0627, 0.1101	0.0575, 0.1216

[a] See footnote *a* in Table 1.

Chart 1

$[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$	**1**[17]
cis-$[Re_6Se_8(PEt_3)_4(solv)_2]^{2+}$	**2** (MeCN),[17] **3** (DMF),[18] **4** (Me_2SO)[18]
trans-$[Re_6Se_8(PEt_3)_4(solv)_2]^{2+}$	**5** (MeCN), **6** (DMF), **7** (Me_2SO)
$[Re_6Se_8(solv)_6]^{2+}$	**8** (MeCN),[17] **9** (DMF), **10** (Me_2SO), **11** (py)
$[Re_6Se_8(PEt_3)_5(4,4'\text{-bpy})]^{2+}$	**12**
cis-$[Re_6Se_8(PEt_3)_4(4,4'\text{-bpy})_2]^{2+}$	**13**
trans-$[Re_6Se_8(PEt_3)_4(4,4'\text{-bpy})_2]^{2+}$	**14**
$\{[Re_6Se_8(PEt_3)_5]_2(4,4'\text{-bpy})\}^{4+}$	**15**
$\{[Re_6Se_8(PEt_3)_5]_2(4,4'\text{-}py_2C_2H_2)\}^{4+}$	**16**
$\{[Re_6Se_8(PEt_3)_5]_2(4,4'\text{-}py_2C_2H_4)\}^{4+}$	**17**
$[Re_{18}Se_{24}(PEt_3)_{14}(4,4'\text{-bpy})_2]^{6+}$	**18**

anisotropically. In other structures, carbon atoms were refined isotropically, while heavier atoms were described anisotropically. In all cases, 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 **5**, the anion was constrained and refined as a rigid octahedron, while for **12** dichloromethane solvate molecules were treated as rigid tetrahedra with a fixed C−Cl distance of 1.78 Å. The asymmetric unit of **12** contains two formula weights, and those of **5**, **6**, **10**, **14**, and **15** half of the formula weight because of inversion symmetry. Compound **7** contains two independent half formula weights with inversion symmetry. The asymmetric unit of **9** contains one-sixth formula weight owing to symmetry. Crystallographic data are listed in Tables 1 and 2. See the paragraph at the end of this paper concerning the Supporting Information.

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). EPR spectra were measured at 4.2 K with a Bruker ESP 300-E spectrometer operating at X-band frequencies. Spin concentrations were determined from doubly integrated spectra using an aqueous $[Cu(EDTA)]^{2-}$ standard. FAB mass spectra were obtained with a JEOL SX-102 instrument using 3-nitrobenzyl alcohol as matrix. Electrospray mass spectra were recorded using a Platform 2 mass spectrometer (Micromass Instruments, Danvers, MA). Electrochemical measurements were performed with a PAR Model 263 potentiostat/galvanostat using a platinum working electrode. The supporting electrolyte was $(Bu_4N)(PF_6)$, 0.1 M in acetonitrile solution. Potentials were referenced to the SCE.

Results and Discussion

Cluster compounds prepared in this investigation have been characterized by ^1H and ^{31}P NMR spectroscopy, mass spectrometry, and X-ray structure determinations. The structures of 10 clusters (Tables 1 and 2) have been determined. Because metric features of the $[Re_6Se_8]^{2+}$ cores are not significantly dependent on the nature or substitution pattern of ligands, core dimensions of the representative cluster **10** (rather than data for the full set) are provided in Table 3 in terms of ranges and mean values of core parameters. Tabulations of interatomic distances and angles for closely related clusters are available elsewhere.[8,17,18] Suffice it to say that the core structures closely approach O_h symmetry, and that any deviations therefrom in the structures reported here and those described previously are nonsystematic. Mean values of terminal ligand bond distances are summarized in Table 4. The Re−P bond lengths fall in the narrow interval 2.47−2.49 Å; when previous data[17,18] are included, the range is 2.44−2.51 Å, with the large majority of distances in the interval found here. On the basis of very limited comparative values, terminal Re−N/O bond lengths and corresponding bond angles are normal.

Table 3. Interatomic Distances (Å) and Angles (deg) for $[Re_6Se_8(Me_2SO)_6]^{2+}$

Re−Se	2.514(2)−2.527(3)	Re−Re−Se	118.48(7)−119.26(7)
mean	2.519(5)	mean	118.9(2)
Re−Re	2.601(1)−2.609(1)	Re−Re−Se	58.60(6)−59.15(7)
mean	2.603(3)	mean	58.9(2)
Re−Re−Re[a]	59.87(4)−60.18(4)	Re−Se−Re	61.95(7)−62.54(6)
mean	60.0(1)	mean	62.1(2)
Re−Re−Re[b]	89.71(4)−90.29(5)	Se−Re−Se	89.60(9)−90.48(9)
mean	90.0(2)	mean	90.0(2)

[a] Within triangular faces. [b] Within an equatorial square.

Table 4. Terminal Ligand Bond Distances (Å) and Angles (deg)

ligand/cluster	av Re−P	Re−N/O	Re−N/O−C/S
MeCN			
5	2.470	2.09(2)	175(2)
DMF			
6	2.478	2.13(2)	125(2)
9		2.14(1)	128(1)
Me_2SO			
7	2.478(4)	2.11(2)	122.6(8)
		2.14(2)	122.3(8)
10		2.16(2)	119.6(8)−124.8(8)
4,4′-bpy/4,4′-$py_2C_2H_2$			
11	2.49(1)	2.22	
14	2.49(1)	2.22	
15	2.486(7)	2.22(1)	

Solvate Clusters. In this investigation we have sought clusters whose solvate ligands are sufficiently labile to allow substitution in regiospecific reactions that lead to bridged cluster arrays. Monosolvate cluster **1**, the *cis*-disolvates **2**−**4**, and the hexakis-

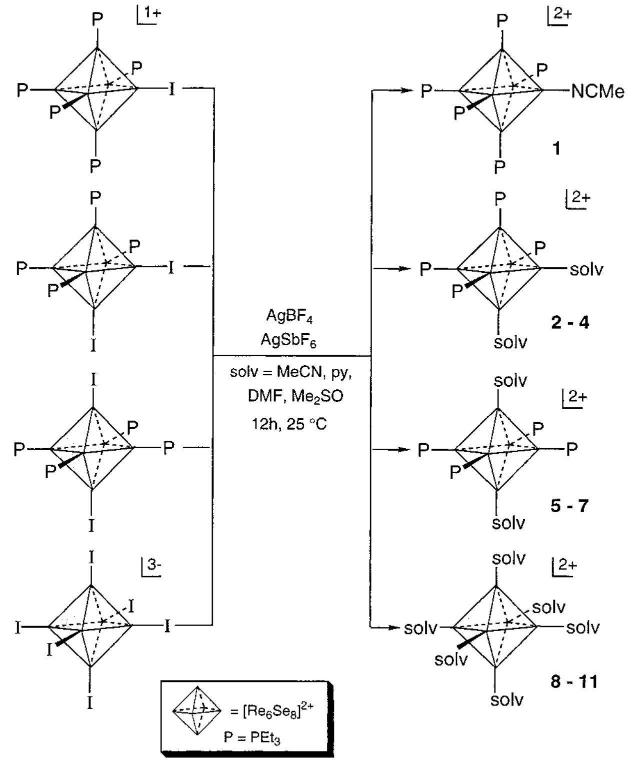

Figure 1. Synthesis of solvate clusters **1**−**11** by de-iodination reactions of $[Re_6Se_8(PEt_3)_5I]^+$, *cis*- and *trans*-$[Re_6Se_8(PEt_3)_4I_2]$, and $[Re_6Se_8I_6]^{4-}$ with Ag(I).

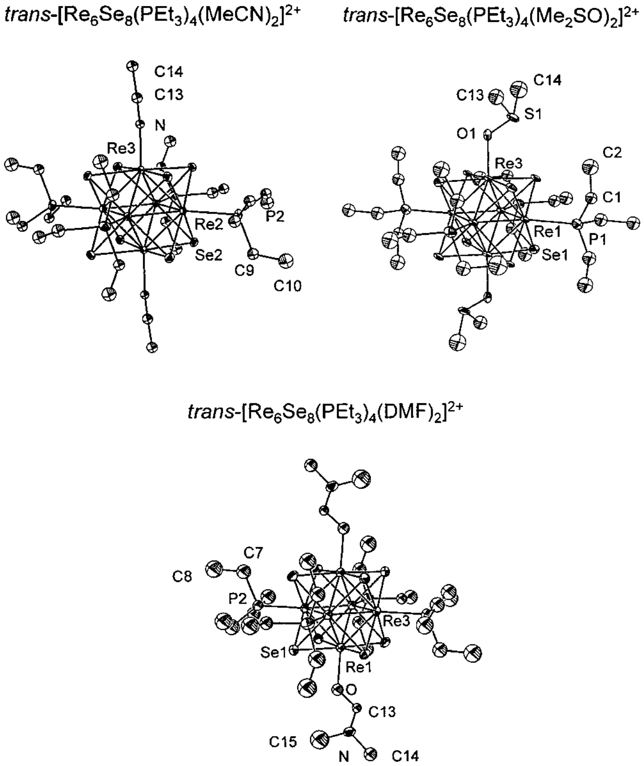

Figure 2. Structures of the solvate clusters *trans*-$[Re_6Se_8(PEt_3)_4(solv)_2]^{2+}$ [solv = MeCN (**5**), DMF (**6**), Me_2SO (**7**)] showing 50% probability ellipsoids and partial atom labeling schemes. Each cluster has imposed centrosymmetry.

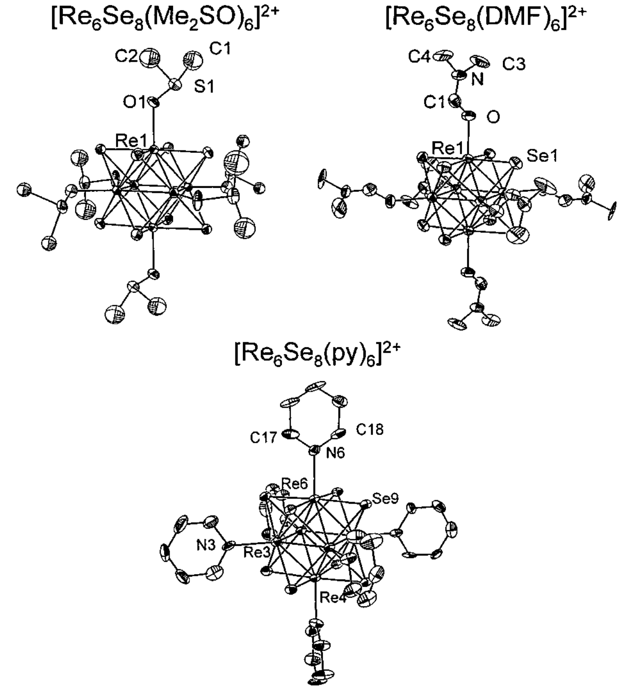

Figure 3. Structures of fully solvated clusters $[Re_6Se_8(DMF)_6]^{2+}$ (**9**), $[Re_6Se_8(OSMe_2)_6]^{2+}$ (**10**), and $[Re_6Se_8(py)_6]^{2+}$ (**11**) showing 50% probability ellipsoids and a partial atom labeling scheme. Cluster **9** has an imposed $\bar{3}$ axis coincident with a Se···Se core body diagonal; cluster **10** has imposed centrosymmetry.

(acetonitrile) species **8** have been reported previously. We have extended these reactions to include the *trans*-disolvates **5**−**7** and two further examples, **9** and **10**, of fully solvated clusters. In addition, the hexakis(pyridine) cluster **11** has been prepared. All new compounds were isolated as hexafluoroantimonate(V) salts and were subjected to X-ray structure determinations. Summarized in Figure 1 are the preparations of solvate clusters by iodide substitution of $[Re_6Se_8(PEt_3)_5I]^{1+}$,[17] *cis*- and *trans*-$[Re_6Se_8(PEt_3)_4I_2]$,[17] and $[Re_6Se_8I_6]^{3-}$ [8] using Ag(I) in dichloromethane solutions containing acetonitrile, DMF, Me_2SO, or pyridine. Yields of the *trans*-disolvates **5**−**7** and hexasolvates **9**−**11** are 79−89%. In the preparation of **1**−**7** in this and prior work,[17,18] we have found without exception that substitution reactions proceed with *retention of stereochemistry*, the phosphine ligands acting as nonlabile protecting groups. As demonstrated in some detail for the $[Re_6S_8(PEt_3)_nBr_{6-n}]^{(n-4)+}$ family in particular, product stereochemistry is readily established by ^{31}P NMR.[12] For example, the single resonance of *trans*-$[Re_6Se_8(PEt_3)_4I_2]$ (δ −33.0) is retained but shifted in disolvates **5** (δ −17.9), **6** (δ −16.4), and **7** (δ −17.7) in acetonitrile solutions.

Structures of disolvates **5**−**7** set out in Figure 2 confirm trans stereochemistry, here with imposed centrosymmetry. Structures of hexasolvate clusters **9**−**11** are depicted in Figure 3. These species and **8** are the simplest and most fundamental forms of $[Re_6Se_8]^{2+}$ clusters, and are expected to be useful precursors for various substituted clusters in future work. Very recently, the related cluster $[Re_6S_8(OH_2)_6]^{2+}$ was generated in aqueous acid solution by reaction of $[Re_6S_8Cl_6]^{4-}$ and $AgClO_4$.[15] The initial cluster could be reformed by reaction of the aquo cluster with HCl at 90 °C.

Bridged Clusters. Earlier we had reported the preparation of *cis*-$[Re_6Se_8(PEt_3)_4(py)_2]^{2+}$ from the reaction of the cis precursor **2** with excess pyridine in refluxing chlorobenzene.[18] The two equally intense ^{31}P NMR signals (δ −19.2 and −22.0 in acetonitrile) are consistent with the product formulation; the cluster was not characterized by a structure determination. With the intention of producing bridged cluster arrays in this and subsequent work, reactions with the bifunctional ligand 4,4′-bipyridine were examined under similarly forcing conditions in chlorobenzene. The results are summarized in Figure 4; all

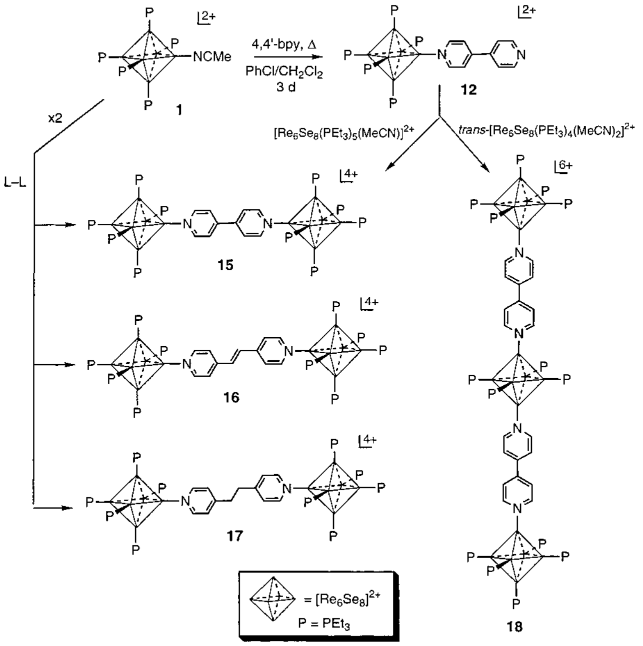

Figure 4. Formation of pyridyl-bridged diclusters from **1** + L–L = bpy (**15**), 4,4′-$py_2C_2H_2$ (**16**), and 4,4′-$py_2C_2H_4$ (**17**), and tricluster **18** from **12** + **5**. The conditions for the preparation of **15**–**18** are similar to those indicated for the reaction **1** → **12**.

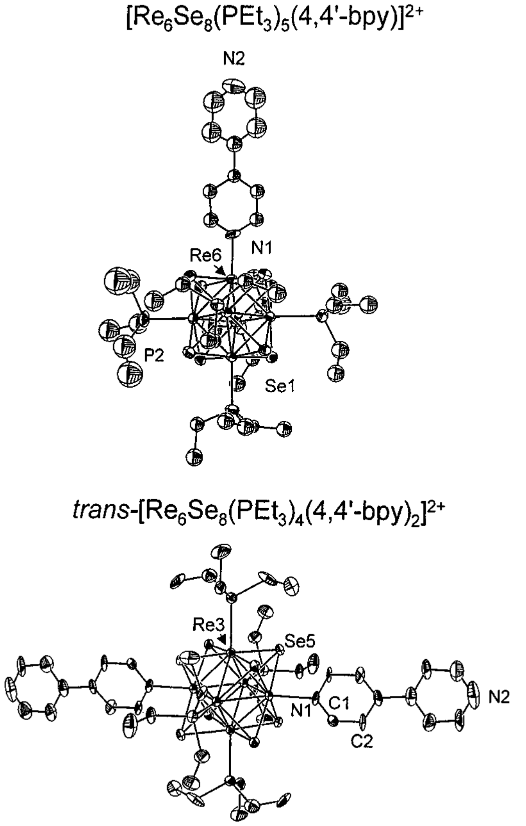

Figure 5. Structures of $Re_6Se_8(PEt_3)_5(4,4'\text{-bpy})]^{2+}$ (**12**) and *trans*-$[Re_6Se_8(PEt_3)_4(4,4'\text{-bpy})_2]^{2+}$ (**14**) showing 50% probability ellipsoids and partial atom labeling schemes. Cluster **14** has imposed centrosymmetry.

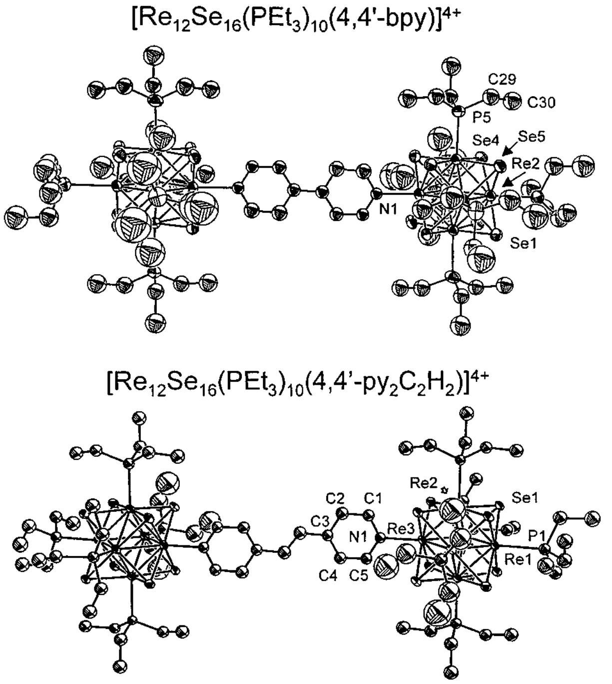

Figure 6. Structures of diclusters $\{[Re_6Se_8(PEt_3)_5]_2(4,4'\text{-bpy})\}^{4+}$ (**15**) and $\{[Re_6Se_8(PEt_3)_5]_2(4,4'\text{-}py_2C_2H_2)\}^{4+}$ (**16**) showing 50% probability ellipsoids and partial atom labeling schemes. Each dicluster has imposed centrosymmetry.

clusters were isolated as hexafluoroantimonate(V) salts. Treatment of **1** with 2 equiv of 4,4′-bpy gives **12** (62%), which displays two ^{31}P resonances in a 4:1 intensity ratio consistent with the X-ray structure of the cluster in Figure 5. The related reactions **2** → **13** (84%) and **5** → **14** (87%) proceed in high yield and provide other clusters with bridging potentiality. Two equally intense ^{31}P resonances for **13** and a single resonance for **14** are consistent with the indicated formulations. The identity of **13** has been additionally demonstrated by an X-ray structure determination (Figure 5). The extreme conditions required for acetonitrile/4,4′-bpy ligand substitution in good yield—refluxing chlorobenzene for 2–3 days—emphasize the considerable inertness of the $[Re_6Se_8]^{2+}$ core to terminal ligand replacement.

Cluster **12**, either in isolated form or prepared in situ, engages in further cluster binding to afford the bridged dicluster **15** (Figure 4). Thus, reaction of monosolvate cluster **1** with 0.55 equiv of 4,4′-bpy affords **15** (81%) having the desired bridge structure, as shown in Figure 6. The cluster is centrosymmetric, and the two pyridyl rings are coplanar. Cluster **1** and *trans*-1,2-bis(4-pyridyl)ethylene and 1,2-bis(4-pyridyl)ethane react analogously to give **16** (70%) and **17** (63%), respectively. The bridged nature of **16** was demonstrated by its X-ray structure (Figure 6). The dicluster is centrosymmetric; the 4,4′-$py_2C_2H_2$ ligand is planar. Retention of this structure in solution is demonstrated by NMR spectra (not shown). In the downfield region, the four equally intense ^1H resonances of **12** (δ 7.59, 7.67, 8.76, 9.34) are reduced to two in **15** (δ 7.57, 9.41), with that at δ 9.41 being the counterpart of the 2-H signal at δ 9.35 in **12**. The two ^{31}P signals of **12** in a 4:1 intensity ratio (δ −22.5, −25.9) are retained in **15** with insignificant chemical shift differences. Diclusters **16** (δ 7.25, 9.07) and **17** (δ 7.18, 9.13) also exhibit two pyridyl proton shifts similar to those of **15**. In the set **11**–**17**, 2-H protons undergo characteristic downfield shifts owing to the inductive effect of Re(III), and occur in the range δ 9.07–9.50 in acetonitrile.

Bridged clusters **15**–**17** maintain their structures in solution, as would be expected from the compelling conditions required to form them. Given the planar conformation of the bridge in **15**, the possibility of coupled electron transfer observed in a number of simple binuclear complexes with the same and related bridges[22,23] arises. In cyclic voltammetry, this species shows a redox step at $E_{1/2} = 1.10$ V (100 mV/s) in acetonitrile, essentially identical to that of single cluster **12** in the same solvent ($E_{1/2} = 1.05$ V). Oxidative coulometry at 1.3 V produced a color change from orange to light blue-green and $n = 2.0$ C, demonstrating simultaneous oxidation of both clusters. This behavior apparently arises as a consequence of the extended bridge, which in **15** places the bridged Re atoms at a distance of 11.61 Å. Oxidative coulometry of **1** at 1.3 V caused a similar color change and gave $n = 0.95$ C, indicating a one-electron process. However, the rhomb-bridged dicluster *trans*-$\{[Re_6Se_8(PEt_3)_4]_2(MeCN)_2\}^{4+}$, where individual clusters are in intimate contact through Re−Se bridges, exhibits two coupled oxidations at $E_{1/2} = 1.37$ and 1.59 V in acetonitrile.[18]

Other bridging patterns can be achieved by the choice of initial clusters. In one case, reaction of the trans disolvate **5** with 2 equiv of the 4,4′-bpy cluster **14** yields the quasilinear tricluster **18**. This species was identified by NMR spectroscopy; diffraction-quality crystals were not obtained. The ^{31}P spectrum consists of signals at δ −17.9 (2), −22.2 (4), and −25.7 (1). The first matches closely with that of **5** (δ −18.3) and the second and third with **12** (δ −22.5 (4), −25.9 (1)). The ^{1}H spectrum in the downfield region shows two equally intense 2-H signals at δ 9.30 and 9.40. Thus, the NMR evidence supports the formulation **18** in Figure 4. Additionally, the species $[M - 4SbF_6]^{4+}$ was detected in the electrospray mass spectrum.

Attempts to prepare a "molecular square" based on equimolar condensation of **2** with 4,4′-bipyridyl or *trans*-1,2-bis(4-pyridyl)-ethylene, or of **2** and **13**, resulted in mixtures of products. ^{1}H NMR spectra of the reaction mixture in acetonitrile indicated at least three soluble products; a fourth insoluble phase constitutes the majority of product and has resisted characterization. This insolubility may result from the accumulation of charge as dipositive monoclusters aggregate. Further work directed at anionically bridged cluster assemblies is underway in this laboratory.

Oxidized Clusters. During an investigation of the photophysics of Re_6Q_8 clusters[24] and in the synthetic work reported here, we have had occasion to revisit certain compounds previously formulated as $(Bu_4N)_3[Re_6Q_7(QH)X_6]$ (Q = S, Se; X = Cl, Br, I) and containing monoprotonated clusters.[8] The cation:anion ratio was established by X-ray structure determinations and elemental analysis,[8] leading to the postulated protonated clusters. The putative proton was considered to be associated with a chalcogenide atom; it was not detected in the structure determinations. The preparation of solvate clusters **8**−**11** utilizes as a starting material a compound initially described as $(Bu_4N)_3[Re_6Se_7(SeH)I_6]$.[8] It was obtained from the product of a solid-state reaction targeting $Cs_4Re_6Se_8I_6$ by cation metathesis with Bu_4NI in aqueous HI solution. The resulting precipitate was recrystallized from acetone/toluene containing a small quantity of $SOCl_2$; the product was obtained as a black crystalline solid. This compound is soluble in aprotic solvents and, therefore, is preferable as a starting material to $Cs_4Re_6Se_8I_6$, whose crystal structure reveals the presence of the authentic $[Re_6Se_8I_6]^{4-}$ cluster.[8] By similar means, compounds described as $(Bu_4N)_3[Re_6S_7(SH)X_6]$ were obtained.[8] With sulfide clusters, the corresponding series $(Bu_4N)_4[Re_6S_8X_6]$, obtained under basic workup conditions, was similarly authenticated. We describe several new results for the compounds originally reported as $(Bu_4N)_3[Re_6S_7(SH)Br_6]$ (bromide cluster) and $(Bu_4N)_3[Re_6Se_7(SeH)I_6]$ (iodide cluster).

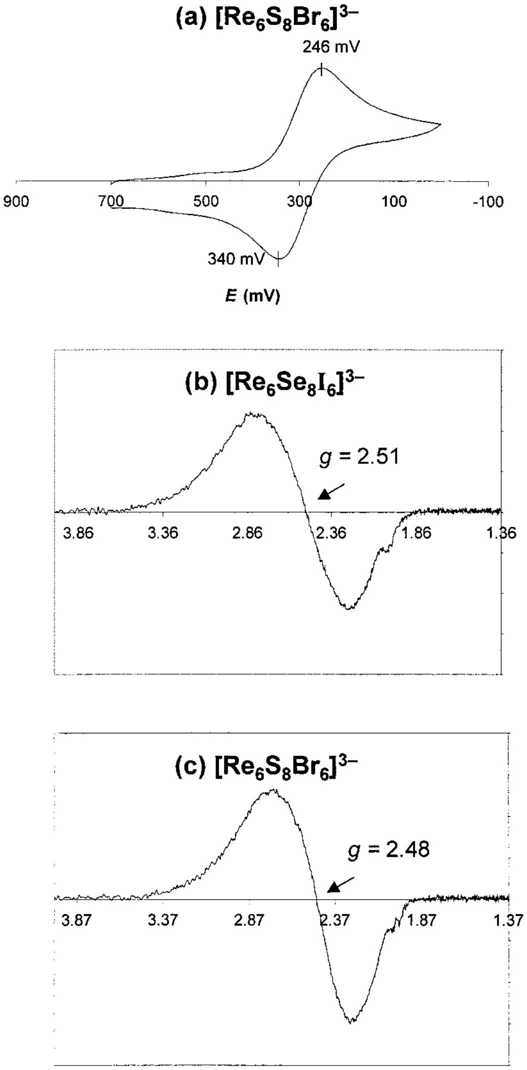

Figure 7. (a) Cyclic voltammogram (100 mV/s) of $(Bu_4N)_3[Re_6S_8Br_6]$ (bromide cluster) in acetonitrile. Peak potentials vs SCE are indicated. X-band EPR spectra (100 μW power) of (b) $(Bu_4N)_3[Re_6Se_8I_6]$ (iodide cluster) and (c) $(Bu_4N)_3[Re_6S_8Br_6]$ in DMF at 4.2 K.

As seen in Figure 7, the bromide cluster supports a chemically reversible redox couple with $E_2 = +0.29$ V and $i_{pc}/i_{pa} = 0.95$.[25] In the indicated scan direction, the initial reaction is reduction. The bromide and iodide clusters display broad EPR spectra in frozen DMF solution with apparent g values of 2.51 and 2.48, respectively, and weak features at $g \approx 2$ (Figure 7). These spectra are similar to those of the 23-electron clusters $[Mo_6Cl_{14}]^-$ ($g_\perp = 2.10$, $g_\parallel = 2.0$)[26] and $[W_6Br_{14}]^-$ ($g \approx 2.3$)[27] at 9−10 K. Concentrations of $S = 1/2$ species determined from EPR signal integrations are 0.53 mM for the bromide cluster and 0.65 mM for the iodide. These compare favorably with the known solution concentrations of 0.54 and 0.55 mM, respectively. Both clusters have been utilized as starting materials for the synthesis of halide−Et_3P mixed-ligand clusters requiring elevated temperatures.[16,17] Here the reaction of the bromide cluster was

---

[22] Crutchely, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273.

[23] Ward, M. D. *Chem. Soc. Rev.* **1995**, 121.

[24] Gray, T. G.; Rudzinski, C.; Nocera, D. G.; Holm. R. H. Submitted for publication.

[25] The voltammetry of the iodide cluster is more complicated, showing several irreversible oxidations, and is not included here.

[26] Maverick, A. W.; Najdzionek, J. S.; MacKenzie, D.; Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1878.

[27] Zietlow, T. C.; Schaaefer, W. P.; Sadeghi, B.; Nocera, D. G.; Gray, H. B. *Inorg. Chem.* **1986**, *25*, 2198. The g value is estimated from the published spectrum.

examined spectrophotometrically at ambient temperature in acetonitrile solution. Treatment with 40 equiv of Et_3P caused rapid development of the spectrum of authentic $[Re_6S_8Br_6]^{4-}$.[8] Further, addition of excess phosphine to solutions of the bromide and iodide clusters eliminated the EPR signals. From these observations, we conclude that the bromide and iodide clusters are actually $[Re_6S_8Br_6]^{3-}$ and $[Re_6Se_8I_6]^{3-}$, isoelectronic with the 23-electron $S = 1/2$ clusters $[Mo_6Cl_{14}]^{-}$ and $[W_6Br_{14}]^{-}$. In the case of the bromide cluster, phosphine substitution is preceded by reduction to $[Re_6S_8Br_6]^{4-}$. The oxidant in the acidic workup/crystallization conditions[8] remains to be identified.

Summary. The following are the principal results and conclusions of this investigation, and include certain findings from previous studies.[8,16,17,28]

(1) The clusters $[Re_6Se_8(PEt_3)_5I]^{+}$, *cis*- and *trans*-$[Re_6Se_8(PEt_3)_4I_2]$, and $[Re_6Se_8I_6]^{3-}$ undergo facile de-iodination reactions with Ag(I) in dichloromethane/solvent mixtures to afford the corresponding solvate clusters in good yield (Figure 1).

(2) The clusters $[Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ and *cis*- and *trans*-$[Re_6Se_8(PEt_3)_4(MeCN)_2]^{2+}$ (from the reactions in (1)) undergo substitution reactions under forcing conditions (refluxing chlorobenzene) with pyridine-type ligands. The occurrence of these reactions and their slow rate emphasize the affinity of the $[Re_6Se_8]^{2+}$ core for unsaturated nitrogen ligands. One application of this property is the formation of dendrimeric clusters based on pyridyl ligation.[28]

(3) The bridged diclusters $\{[Re_6Se_8(PEt_3)_5]_2(4,4'\text{-bpy})\}^{4+}$, $\{[Re_6Se_8(PEt_3)_5]_2(4,4'\text{-py}_2C_2H_2)\}^{4+}$, and $\{[Re_6Se_8(PEt_3)_5]_2(4,4'\text{-py}_2C_2H_4)\}^{4+}$ and the bridged tricluster $[Re_{18}Se_{24}(PEt_3)_{14}(4,4'\text{-bpy})_2]^{6+}$ have been prepared by the reactions in (2) (Figure 4). The structures of two diclusters have been proven by X-ray analysis. The clusters maintain their structures in solution. These observations augur well for the directed syntheses of *cluster*-based supramolecular assemblies. Note that existing types of metal-containing supramolecular assemblies are based on mononuclear coordination units.[29-35]

(4) All terminal ligand substitution reactions of the $[Re_6Se_8(PEt_3)_n]^{2+}$ units occur with retention of stereochemistry.

(5) Clusters previously described as the protonated 24-electron species $[Re_6S_7(SH)Br_6]^{3-}$ and $[Re_6Se_7(SeH)I_6]^{3-}$ are reformulated as the 23-electron clusters $[Re_6S_8Br_6]^{3-}$ and $[Re_6Se_8I_6]^{3-}$.

Acknowledgment. This research was supported by National Science Foundation Grant CHE 94-23830. T.G.G. holds a National Science Foundation Predoctoral Fellowship. We thank E. Tulsky for experimental assistance. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247.

Supporting Information Available: X-ray crystallographic data in CIF format for the 10 compounds in Tables 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9906050

---

(28) Wang, R.; Zheng, Z. *J. Am. Chem. Soc.* **1999**, *121*, 3549.

(29) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502.

(30) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267.

(31) Linton, B.; Hamilton A. D. *Chem. Rev.* **1997**, *97*, 1669.

(32) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417.

(33) Olenyuk, B.; Fechtenkötter, A.; Stang, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1707.

(34) Caulder, D. N.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185.

(35) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689.