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# Site-Differentiated Hexanuclear Rhenium(III) Cyanide Clusters $[Re_6Se_8(PEt_3)_n(CN)_{6-n}]^{n-4}$ ($n = 4, 5$) and Kinetics of Solvate Ligand Exchange on the Cubic $[Re_6Se_8]^{2+}$ Core

**Thomas G. Gray and R. H. Holm***

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

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The site-differentiated, cyanide-substituted hexanuclear rhenium(III) selenide clusters *cis*- and *trans*-$[Re_6Se_8(PEt_3)_4(CN)_2]$ and $[Re_6Se_8(PEt_3)_5(CN)]^+$ have been prepared from heterogeneous reactions of the corresponding iodo clusters with AgCN in refluxing chloroform. Isolated yields are 68%, 46%, and 64% for *cis*-$[Re_6Se_8(PEt_3)_4(CN)_2]$, *trans*-$[Re_6Se_8(PEt_3)_4(CN)_2]$, and $[Re_6Se_8(PEt_3)_5(CN)]^+$, respectively. The new compounds are air- and water-stable and are characterized by X-ray diffraction crystallography, $^{31}$P NMR and IR spectroscopies, and FAB mass spectrometry. In related work, the solvent exchange rates of two site-differentiated monosolvate clusters, $[Re_6Se_8(PEt_3)_5(MeCN)](SbF_6)_2$ and $[Re_6Se_8(PEt_3)_5(Me_2SO)](SbF_6)_2$, in neat solvents were measured by $^1$H NMR. These clusters are substitutionally inert; $k \approx 10^{-5}$–$10^{-6}$ s$^{-1}$ at 318 K. Activation parameters indicate a dissociative ligand exchange mechanism; $\Delta H^{\ddagger}$ values obtained from least-squares fitting of temperature-dependent kinetics data exceed $RT$ by a factor of ca. 50 over the temperature range studied. These results demonstrate that the substitutional lability encountered in a previous study of cluster photophysics (Gray, T. G.; Rudzinski, C. M.; Nocera, D. G.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 5932) cannot result from ground-state thermal reactions.

## Introduction

The concept of the site-differentiated cluster is long appreciated by bioinorganic investigators,[1,2] but remains less familiar in more broadly oriented metallocluster research.[3,4] By "site-differentiation" is meant the controlled and steadfast occupancy of one or more of the exopolyhedral ligand-binding sites of a cluster, such that all further reactions of the remaining few ligands occur *regioselectively*. Site differentiation presupposes that substitutionally inert nucleophiles satisfy the ligation requirements of several metal atoms simultaneously; the site(s) left over bind more labile ligands.[1] Cluster-centered ligand substitution chemistry is thus simplified, and new synthetic[5–7] and spectroscopic[8] opportunities thereby emerge.

We hold that rational means of site differentiation in transition element clusters are imperative to nonserendipitous, systematic advancement of metallocluster chemistry. Two strategies for site-differentiating metal aggregates are obvious: (i) ligand-derived and (ii) cluster-enforced site-differentiation. Cubane-type $[Fe_4S_4]$ and $[L_nMFe_3S_4]$[2,9] and cuboidal $[Fe_3S_4]$[10] clusters exemplify strategy i. Such clusters, being composed of first-row transition element ions, are substitutionally labile and can become moreso upon reduction of the cluster core.[11] In these species, site-differentiation relies upon the cavitand concept[12] of ligand design. This concept relies on elaborated organic ligands, specially designed to capture the $Fe_3$ face of an $[Fe_4S_4]$ or $[MFe_3S_4]$ cuboid. The ligand conformation in the bound cluster approximates the

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* Author to whom correspondence should be addressed. E-mail: holm@chemistry.harvard.edu.

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lowest-energy conformation of the free ligand. The cavitand concept has not yet been applied to single clusters of nuclearity exceeding four, but certainly pertains to larger entities. In this laboratory, the most successful such ligand has been 1,3,5-tris((4,6-dimethyl-3-mercaptophenyl)thio)-2,4,6-tris(*p*-tolylthio)benzene(3−), abbreviated $LS_3$.[12,13] A number of other 1:3 site-differentiating ligands have also been described.[14−17]

A new approach to site-differentiation in synthetic $[Fe_4S_4]$ clusters involves de-novo-designed peptides. Recent work from this laboratory describes a helical, 63-mer peptide designed at once to site-differentiate an $[Fe_4S_4]$ cluster and to induce bridging, through a cysteinate residue, to a nearby nickel(II) center.[18] The resulting supramolecular assembly was prepared as an analogue of the spectroscopic A site of the enzyme carbon monoxide dehydrogenase. In this entity, as in $LS_3$ complexes, site-differentiation is ligand-imposed.

Site-differentiation in cubic $[Re_6Q_8]$ clusters (Q = S, Se)[19] represents an extreme example of strategy ii, where cluster inertness to ligand substitution maintains stereochemical integrity of the ligand sphere. As such, site-differentiation relies on the intrinsic properties of the cluster itself, not on its ligands. In this laboratory, site-differentiation is impelled on the $[Re_6Q_8]^{2+}$ core by thermal reactions with triethylphosphine in DMF. These reactions, which require prolonged heating, produce mixtures of clusters, site-differentiated with tightly bound phosphine ligands. Product distributions are controllable through the loading of triethylphosphine and the reaction duration. For example, reaction of $(Bu_4N)_3[Re_6S_8Br_6]$ with 50 equiv of $PEt_3$ for 8 h, in refluxing DMF, yields *mer*- and *fac*-$(Bu_4N)[Re_6S_8(PEt_3)_3Br_3]$ in 33% and 5% yields, respectively; refluxing for 36 h yields *cis*- and *trans*-$[Re_6S_8(PEt_3)_4Br_2]$, in 43% and 19% respective yields; 60 h of refluxing, under the same conditions, produces $[Re_6S_8(PEt_3)_5Br]Br$ in 58% yield.[20] A parallel series of reactions exists for selenium−iodine analogues $[Re_6Se_8(PEt_3)_nI_{6-n}]^{(n-4)+}$.[6] Notably, no circumstance is observed where the $Re-PEt_3$ linkage ruptures, either thermally or photolytically, in fluid solution. In solid samples, heating to 500 °C under vacuum is required to decomplex $PEt_3$ from the $[Re_6Se_8]^{2+}$ core.[5] So tenaciously do $[Re_6Q_8]^{2+}$ clusters retain triethylphosphine that mixed-ligand entities are air- and water-stable, and the as-prepared mixtures of these clusters are straightforwardly separated by silica gel flash-column chromatography.

No other cluster system is as synthetically versatile in producing type ii site-differentiated species as is $[Re_6Q_8]^{2+}$ (Q = S, Se). The reduced, group 6 halide clusters[21] $[Mo_6X_{14}]^{2-}$[22] and $[W_6X_{14}]^{2-}$[23,24] are isoelectronic with $[Re_6Q_8X_6]^{2-}$ clusters (X = Cl, Br, I), but their substitution chemistry is nonsystematic and is dominated by persubstitution of the six apical halide ligands,[25,26] obviating site-differentiation. A similar situation prevails for the edge-bridged niobium and tantalum halide clusters,[26] and interstitially stabilized $Zr_6$ species.[27] Recently, tungsten sulfide clusters, also site-differentiated with phosphine ligands, have appeared.[28] Further, no polynuclear metal carbonyl cluster exhibits a profusion of site-differentiated derivatives comparable to that of $[Re_6Q_8]^{2+}$.

The purpose of this work is 2-fold. We seek first to extend the range of site-differentiation of $Re_6Q_8$ clusters to encompass cyanide-bound species. This development complements the range of compounds prepared from the hexacyano clusters of Fedorov,[29] Ibers,[30] Long,[31] Kim,[32] and their respective co-workers. Second, we quantify the inertness of the $[Re_6Se_8]^{2+}$ core in well-defined solvent exchange reactions, and therefrom draw conclusions concerning the mechanism of ligand substitution in such clusters. Resultant kinetics parameters also resolve a standing issue concerning certain lability observed in hexasolvate clusters upon photoexcitation. New cyanide-ligated clusters and solvate clusters are designated as in Chart 1.

**Chart 1.** Designation of Clusters

| | |
|---|---|
| *cis*-$[Re_6Se_8(PEt_3)_4(CN)_2]$ | **1** |
| *trans*-$[Re_6Se_8(PEt_3)_4(CN)_2]$ | **2** |
| $[Re_6Se_8(PEt_3)_5(CN)](BPh_4)$ | **3** |
| $[Re_6Se_8(PEt_3)_5(solv)](SbF_6)_2$ | **4**,[a] **5**[b] |

[a] solv = MeCN.[5] [b] solv = $Me_2SO$.

## Results and Discussion

**Cyanide-Terminated Clusters.** The heterogeneous reaction of *cis*- or *trans*-$[Re_6Se_8(PEt_3)_4I_2]$ with AgCN in refluxing chloroform affords the corresponding cyano-terminated clusters **1**−**3** in moderate isolated yields. Triethylphosphine ligands preserve cluster stereochemistry. X-ray diffraction quality crystals of **1** and **2** are obtained overnight by layering diethyl ether upon concentrated dichloromethane solutions of the cluster compounds at room temperature; crystals of **3** form upon standing for 4 h in chloroform solution after anion metathesis with $NaBPh_4$.

Figures 1, 2, and 3 depict the crystal structures of **1**−**3**, respectively. Salient crystallographic data are collected in Table 1. Cluster metrical features of **1**−**3** are closely similar

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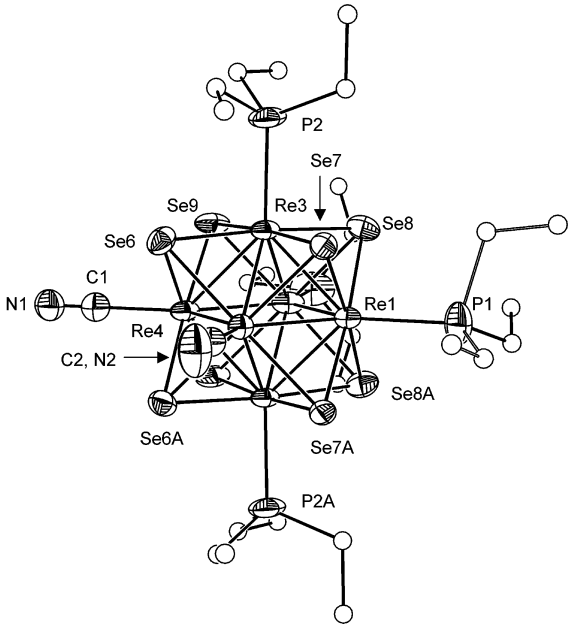

**Figure 1.** Structure of *cis*-$[Re_6Se_8(PEt_3)_4(CN)_2]$ (**1**) showing 50% probability ellipsoids. For clarity, triethylphosphine carbon atoms are depicted as spheres of arbitrary radii. This cluster has imposed centrosymmetry. A partial atom-labeling scheme is shown.

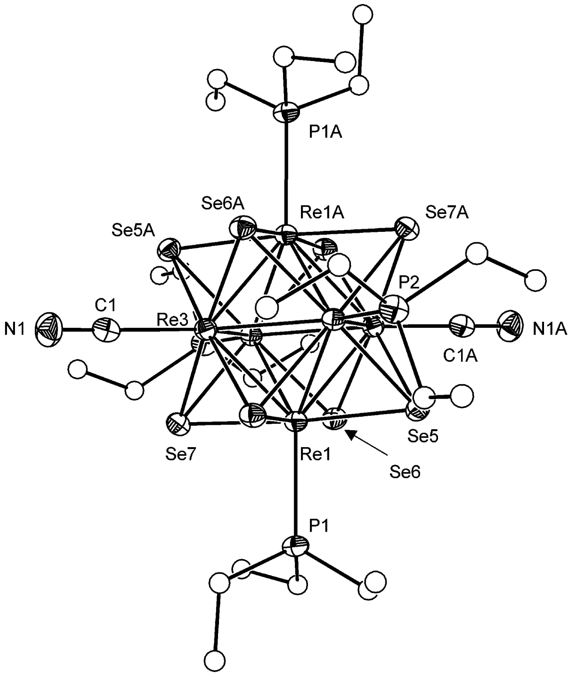

**Figure 2.** Structure of *trans*-$[Re_6Se_8(PEt_3)_4(CN)_2]$ (**2**) showing 50% probability ellipsoids. For clarity, triethylphosphine carbon atoms are depicted as spheres of arbitrary radii. This cluster has imposed centrosymmetry. A partial atom-labeling scheme is shown.

to those of related $[Re_6Se_8]^{2+}$ species.[6] In all cases, the $[Re_6Se_8]$ core structures closely approach $O_h$ symmetry; any symmetry-breaking deviations in the structures reported here and those described previously are asystematic. Mean values of terminal ligand bond distances are summarized in Table 2. The Re−P bond lengths range from 2.47 to 2.49 Å; when previous data[5−7] are included, the interval is 2.44−2.51 Å. Measured Re−C bond lengths and corresponding bond angles are unexceptional.[29−32]

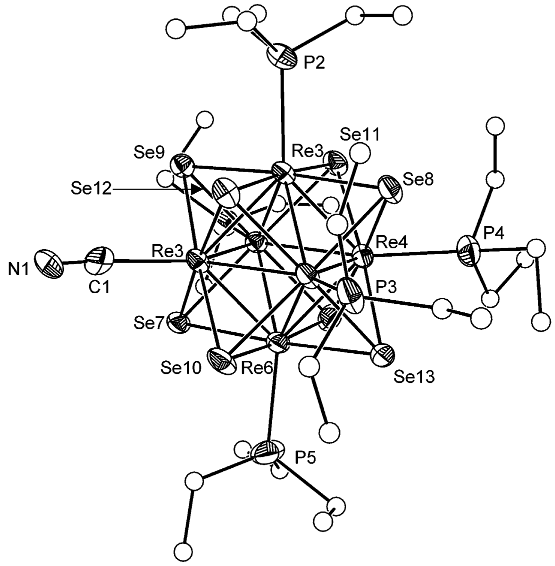

**Figure 3.** Structure of $[Re_6Se_8(PEt_3)_5(CN)]^+$ (**3**) showing 50% probability ellipsoids. For clarity, triethylphosphine carbon atoms are depicted as spheres of arbitrary radii. A mirror plane bisects the cluster through four Re atoms and the CN ligand. A partial atom-labeling scheme is shown.

$^{31}P$ NMR spectra of **1**−**3** are consistent with crystallographically determined stereochemistries. The cis cluster **1** exhibits equally intense resonances at $\delta$ −30.2 and −31.0 ppm; the trans isomer **2** exhibits a singlet at $\delta$ −30.5 ppm, whereas monocyano cluster **3** shows two $^{31}P$ resonances, in a 4:1 ratio, at $\delta$ −30.5 and −31.0 ppm, respectively.[30]

Infrared spectra exhibit $\nu_{CN}$ stretches at 2121−2123 cm$^{-1}$ for the three cyano clusters. These values exceed 2080 cm$^{-1}$ for cyanide ion in aqueous solution and indicate that back-donation to the CN $\pi^*$ orbitals, if any, is negligible.[23] Extended Hückel calculations on **1**−**3** accord with this view; they show that the highest occupied molecular orbitals of each cluster are dominated by d-orbital amplitude on Re. These orbitals, which are nondegenerate, derive from the $e_g$ HOMOs of $[Re_6Q_8X_6]^{4-}$ clusters in $O_h$ symmetry.[34,35] Figure 4 depicts a plot of these orbitals for the hypothetical model

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**Table 1.** Crystal Data[a] and Structure Refinement for Site-Differentiated Cyano Clusters

| | **1** | **2** | [**3**](BPh$_4$) |
|---|---|---|---|
| formula | $C_{26}H_{60}N_2Re_6Se_8P_4$ | $C_{26}H_{60}N_2Re_6Se_8P_4$ | $C_{55}H_{95}NBRe_6Se_8P_5$ |
| fw | 2273.59 | 2273.59 | 2684.96 |
| space group | *Ibam* | $P\bar{1}$ | $P2_1/n$ |
| $Z$ | 16 | 1 | 4 |
| $a$, Å | 18.5879(7) | 10.5369(9) | 21.2879(8) |
| $b$, Å | 35.3143(13) | 11.6919(10) | 13.3830(5) |
| $c$, Å | 18.0726(6) | 12.8561(11) | 26.6159(10) |
| $\alpha$, deg | | 71.208(2) | |
| $\beta$, deg | | 82.033(2) | 111.383(2) |
| $\gamma$, deg | | 70.620(2) | |
| $V$, Å$^3$ | 11863.2(7) | 1413.5(2) | 7060.8(5) |
| $d_{calc}$, g/cm$^3$ | 2.657 | 2.671 | 2.526 |
| $\mu$, mm$^{-1}$ | 17.324 | 18.075 | 14.517 |
| $\theta$ range, deg | 1.15−22.50 | 1.93−27.67 | 1.06−28.47 |
| $R_1$,[b] $wR_2$[c] | 0.0508, 0.1441 | 0.0304, 0.0881 | 0.0852, 0.2142 |

[a] Obtained with graphite-monochromatized Mo K$\alpha$ ($\lambda = 0.71073$ Å) radiation at 213 K. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$.

**Table 2.** Interatomic Distances (Å) for Clusters **1**−**3**

| | | | |
|---|---|---|---|
| Re−Re | 2.622(13)−2.650(4) | Re−P | 2.457(9)−2.490(7) |
| mean | 2.637(7) | mean | 2.474(9) |
| Re−Se | 2.497(9)−2.530(7) | Re−C | 2.08(3)−2.11(3) |
| mean | 2.513(8) | mean | 2.11(2) |

cluster *trans*-[$Re_6Se_8(PH_3)_4(CN)_2$], which represents **2**. A Mulliken gross overlap population analysis indicates that the cyanide valence orbitals are uninvolved (0% contribution) in these high-energy occupied orbitals; however, their exclusion is not symmetry-imposed.

**Kinetics of Thermal Solvent Exchange in [$Re_6Se_8(PEt_3)_5(solv)]^{2+}$ (solv = MeCN, Me$_2$SO).** We have observed that certain clusters, including solvated species, expel ligands under photolysis conditions at ambient temperature.[8] Precise data concerning thermal ligand elimination, which necessarily competes with photosubstitution, are required to distinguish ground-state from excited-state reactivity. We select the following ligand exchange reactions (1) of the site-differentiated clusters **4** and **5** for $^1$H NMR study.

$$[Re_6Se_8(PEt_3)_5(solv)](SbF_6)_2 + solv^* \rightarrow [Re_6Se_8(PEt_3)_5(solv^*)](SbF_6)_2 + solv \quad (1)$$

$$solv = MeCN, Me_2SO;\ solv^* = MeCN\text{-}d_3, Me_2SO\text{-}d_6\text{, respectively}$$

Decay of the bound solv $^1$H resonance was monitored with time at several temperatures. The reaction proceeds cleanly at all temperatures investigated. The bound acetonitrile $^1$H resonance ($\delta$ 2.75) decreases monotonically with time in CD$_3$CN; other resonances are unaffected; the Me$_2$SO-ligated cluster ($\delta$ 2.59) behaves analogously in Me$_2$SO-$d_6$. Chemical shifts of all $^1$H resonances are independent of temperature. The ligand exchange product, [$Re_6Se_8(PEt_3)_5(solv^*)](SbF_6)_2$, can be recrystallized quantitatively by layering diethyl ether onto the reaction mixture at 4 °C or room temperature. Solvent exchange is first order overall (eq 2). Reaction

$$rate = k[Re_6Se_8(PEt_3)_5(solv)]^{2+} \quad (2)$$

progress was monitored under pseudo-first-order conditions in [solv]. Plots of ln[$Re_6Se_8(PEt_3)_5(solv)]^{2+}$, as measured by the integrated area of the $^1$H NMR resonance of the bound acetonitrile, vs time, are linear to at least 3 half-lives; Figure 5 shows a representative example for the cluster [$Re_6Se_8(PEt_3)_5(MeCN)]^{2+}$ at 328 K. Rate constants as a function of temperature are summarized in Table 3. Activation parameters were determined by linear least-squares fitting to the Eyring eq 3[36] as shown in Figure 6. We find that $\Delta S^\ddagger$ =

$$\ln(k/T) = \ln(k_B/h) + \Delta S^\ddagger - \Delta H^\ddagger/RT \quad (3)$$

14.8 ± 1.0 cal K$^{-1}$ mol$^{-1}$ and $\Delta H^\ddagger = 30.6 \pm 1.4$ kcal mol$^{-1}$. Activation parameters for the related cluster [$Re_6Se_8(PEt_3)_5(Me_2SO)]^{2+}$ are similar (Table 3). These results indicate a dissociative ligand exchange of substantial activation barrier. From the structures of *cis*- and *trans*-[$Re_6Se_8(PEt_3)_4(OSMe_2)_2]^{2+}$,[6,7] the sulfoxide is O-bonded. Since, at 298 K, $RT = 0.59$ kcal mol$^{-1}$, we conclude that thermal ligand exchange at room temperature cannot account for the ligand lability which we have documented to occur in the presence of exciting radiation.[8]

## Summary

The following are the primary results and conclusions of this work.

(1) Cyanide can be regioselectively substituted for iodide in *cis*- and *trans*-[$Re_6Se_8(PEt_3)_4I_2$] and in [$Re_6Se_8(PEt_3)_5I$]I in heterogeneous reactions with AgCN. The resulting clusters are air- and water-stable. These clusters are also phosphorescent, and luminescence properties are detailed elsewhere.[37]

(2) Infrared spectra of clusters **1**, **2**, and **3** indicate negligible back-bonding from the [$Re_6Se_8]^{2+}$ core into cyanide $\pi$* orbitals.

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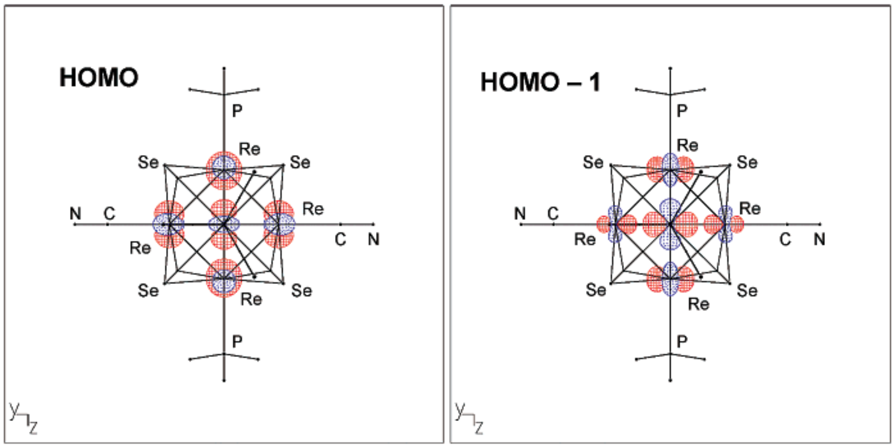

**Figure 4.** Extended Hückel HOMO and second HOMO of *trans*-$[Re_6Se_8(PH_3)_4(CN)_2]$, which serves as a model for **2**. A partial atom-labeling scheme is shown.

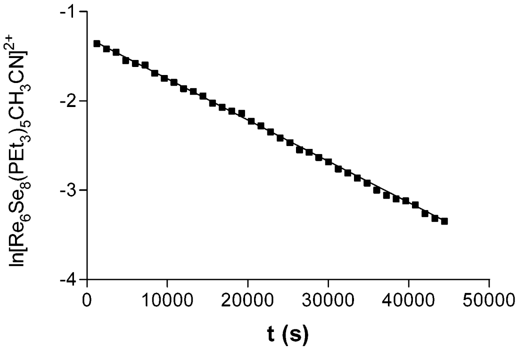

**Figure 5.** Graph of the logarithm of the integrated area of the bound MeCN $^1H$ NMR resonance of $[Re_6Se_8(PEt_3)_5(MeCN)](SbF_6)_2$ at $\delta$ 2.75 ppm, recorded at 55 °C in MeCN-$d_3$ at 10 min intervals.

**Table 3.** Kinetics Data for Solvate Exchange in $[Re_6Se_8(PEt_3)_5(solv)]^{2+}$

| solvent | $T$ (K) | $k$ ($s^{-1}$) | $\Delta H^‡$ (kcal $mol^{-1}$) | $\Delta S^‡$ (cal $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|
| MeCN | 318 | $9.0 \times 10^{-6}$ | $30.6 \pm 1.4$ | $14.8 \pm 1.4$ |
| | 323 | $1.9 \times 10^{-5}$ | | |
| | 328 | $4.7 \times 10^{-5}$ | | |
| | 333 | $7.9 \times 10^{-5}$ | | |
| | 338 | $2.2 \times 10^{-5}$ | | |
| | 343 | $5.8 \times 10^{-4}$ | | |
| DMSO | 313 | $7.5 \times 10^{-7}$ | $29.2 \pm 0.8$ | $6.7 \pm 0.2$ |
| | 318 | $1.6 \times 10^{-6}$ | | |
| | 323 | $3.3 \times 10^{-6}$ | | |
| | 328 | $6.7 \times 10^{-6}$ | | |
| | 333 | $1.3 \times 10^{-5}$ | | |
| | 338 | $2.6 \times 10^{-5}$ | | |
| | 343 | $4.9 \times 10^{-5}$ | | |

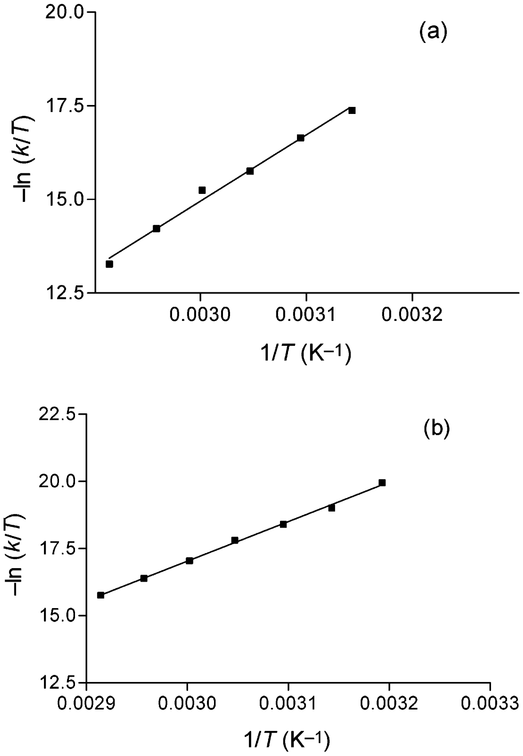

**Figure 6.** Eyring plots for solvent exchange in $[Re_6Se_8(PEt_3)_5(solv)]^{2+}$: (a) solv = MeCN; (b) solv = $Me_2SO$.

(3) The first terminal ligand substitution rates have been determined for $[Re_6Q_8]^{2+}$ clusters. Solvate ligand exchange of **4** and **5** in neat solvents is extremely slow ($k \approx 10^{-5}$–$10^{-6}$ $s^{-1}$at 318 K) and is dissociative, with a substantial barrier to Re–terminal ligand bond scission. Observed values of $\Delta H^‡$ exceed $RT$ by a factor of ca. 50 at ambient temperature, conclusively demonstrating that the lability previously encountered upon photoexcitation cannot be thermal in origin.

The results described here broaden the range of site-differentiated clusters to include soluble, metal–metal bonded polynuclear cyanide complexes. Also, the first quantitative kinetics data on $[Re_6Se_8]^{2+}$ ligand exchange are presented. These data indicate extreme inertness to ligand loss, and are qualitatively consistent with the very slow (~7 days) conversion of $[Re_6S_8(OH_2)_6]^{2+}$ to $[Re_6S_8Cl_6]^{4-}$ in 1 M HCl.[38] For approximate comparison with ligand exchange reactions of trivalent ions, we calculate from eq 3 $k = 3.9 \times 10^{-7}$ $s^{-1}$ (**4**) and $k = 7.5 \times 10^{-8}$ $s^{-1}$ (**5**) at 298 K. These data are in same regime as rate constants ($s^{-1}$) for $[CrL_6]^{3+}$ (L = $H_2O$, $2.4 \times 10^{-6}$; DMF, $3.3 \times 10^{-7}$; $Me_2SO$, $3.1 \times 10^{-8}$) and $[Ru(OH_2)_6]^{3+}$ ($3.5 \times 10^{-6}$),[39] but substantially less than for $[Rh(OH_2)_6]^{3+}$ ($2.2 \times 10^{-9}$) and $[Ir(OH_2)_6]^{3+}$ ($1.1 \times 10^{-10}$).[40] A further assessment of the kinetics characteristics

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of $[Re_6Q_8]^{2+}$ cores would be greatly aided by determination of the rate constant for aquo ligand exchange of $[Re_6Q_8(OH_2)_6]^{2+}$ in water. Substitutional inertness also concurs with older observations that network solids built upon the $[Re_6Q_8]^{2+}$ core (Q = S, Se) defy cluster excision.[41] Ligand substitution of $[Re_6Q_8]^{2+}$ cores is dissociative, and the loss of intercluster bonding in extended solids is energetically prohibitive. The kinetic stability of such solids, and also of newfangled, expanded Prussian blue-type materials, is now understandable in terms of the inherent propensities of the constituent clusters. In particular, steric impenetrability of extended cluster solids need not be the only factor promoting their stability.[42]

Excited-state lability, previously documented,[8] offers relief from the ground-state inertness of $[Re_6Q_8]^{2+}$ species. We note that binding to rhenium(III) is expected to render solvate ligands relatively electropositive. Any consequent reactions with nucleophiles, combined with photodecomplexation, may potentially become catalytic. Ensuing photocatalytic schemes are likely manipulable through site-differentiation with photoinert triethylphosphine. The chemistry of site-differentiated clusters then affords, not for the first time, new experimental prospects.

## 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. $^1H$ 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. Product identities were established by a combination of NMR and mass spectrometric results and X-ray structure determinations. All compounds were >95% pure by an NMR criterion. The compound $[Re_6Se_8(PEt_3)_5(MeCN)](BF_4)_2$ was prepared as described;[5] $[Re_6Se_8(PEt_3)_5(OSMe_2)](SbF_6)_2$ was obtained by the method for *trans*-$[Re_6Se_8(PEt_3)_4(OSMe_2)_2](SbF_6)_2$[7] but starting with $[Re_6Se_8(PEt_3)_5I]I$.[5]

***cis*-$[Re_6Se_8(PEt_3)_4(CN)_2]$.** To a 50 mL Schlenk flask equipped with a stir bar was added 0.5751 g of *cis*-$[Re_6Se_8(PEt_3)_4I_2]$ (23.23 $\mu$mol); the cluster was dissolved in dichloromethane to give a red solution. Silver cyanide (0.196 g, 0.1464 mmol, 6.30 equiv) was added, and the resulting orange suspension was refluxed in chloroform under dinitrogen purge for 12 h. The green suspension was filtered through Celite to give an air-stable orange solution. The filtrate was evaporated to near-dryness, the residue was dissolved in 1 mL of chloroform, and the solution was filtered through Celite. Diethyl ether was introduced by vapor diffusion at 4 °C over 48 h into the concentrated filtrate to produce orange-brown crystals. Yield: 0.358 g (68%). $^1H$ NMR ($CDCl_3$): $\delta$ 1.09 (q, 3), 1.13 (q, 3), 2.11 (q, 2), 2.22 (q, 2), 2.88 (1). $^{31}P$ NMR: $\delta$ −30.2, −31.0 ppm. IR (KBr): $\nu_{CN}$ 2121 $cm^{-1}$. FAB MS: 2274.4 ($M^+$).

***trans*-$[Re_6Se_8(PEt_3)_4(CN)_2]$.** To a 50 mL Schlenk flask equipped with a stir bar was added 0.1169 g of *trans*-$[Re_6Se_8(PEt_3)_4I_2]$[5] (47.22 $\mu$mol); the cluster was dissolved in dichloromethane to give an orange solution. Silver cyanide (0.10593 g, 0.7912 mmol, 4.03 equiv) was added, and the resulting orange suspension was refluxed in chloroform under nitrogen purge for 12 h. The green suspension was filtered through Celite to give an air-stable orange solution. The filtrate was evaporated to near-dryness, and the residue was dissolved in 4 mL of dichloromethane. Evaporation of the solution overnight gave gold-colored crystals, which were washed with diethyl ether (3 × 30 mL). Yield: 0.0496 g (46%). $^1H$ NMR ($CDCl_3$): $\delta$ 1.12 (t, Me), 2.22 (q, $CH_2$), 2.71 (s, MeCN). $^{31}P$ NMR: $\delta$ −30.4. FAB MS: 2274.4 ($M^+$). IR (KBr): $\nu_{CN}$ 2123 $cm^{-1}$.

**$[Re_6Se_8(PEt_3)_5(CN)](BPh_4)$.** $[Re_6Se_8(PEt_3)_5I]I$[5] (0.0615 g, 23.73 $\mu$mol) was dissolved in 20 mL of chloroform. AgCN (0.06154 g, 0.4596 mmol, 19 equiv) was added, and the resulting orange suspension was refluxed for 21 h under dinitrogen. The green suspension was filtered through Celite to give an air-stable orange solution. Solvent was removed, and the orange solid was dissolved in acetonitrile. An excess of sodium tetraphenylborate (0.9554 g, 2.792 mmol) was added, with immediate dissolution. The solution was stirred for 15 min in air and filtered through Celite to give an orange solution. Solvent was removed under vacuum, and the compound was redissolved in acetonitrile-$d_3$. Yield: 0.041 g (64%). $^1H$ NMR ($CDCl_3$): $\delta$ 1.05 (q, 3), 1.12 (q, 12), 2.08 (q, 2), 2.18 (q, 8), 2.91 (1). $^{31}P$ NMR: $\delta$ −30.1 (4), −31.0 (1). IR (KBr): $\nu_{CN}$ 2121 $cm^{-1}$.

**Other Physical Measurements.** NMR spectra were recorded on a Bruker AM 500 spectrometer. Chemical shifts of $^{31}P\{^1H\}$ NMR spectra are referenced to external 85% $H_3PO_4$ (negative values upfield). 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). X-ray diffraction data for compounds **1**−**3** were collected on a Siemens (Bruker) SMART CCD-based diffractometer. Structures were solved and refined using the procedures for other $[Re_6Se_8]^{2+}$ clusters that are detailed elsewhere.[7] Crystallographic data and agreement factors are contained in Table 1.

**Calculations.** Extended Hückel calculations were performed within the program Cacao[43] using default parameters.[44]

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

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