

# Structure and Properties of a Novel Square-Pyramidal Cluster: Heptahydridopentadecacarbonylpentarehenate Dianion

Buh-Ching Jiang, Haw-Chiung Horng, Fen-Ling Liao, and Cheu Pyeng Cheng\*

Department of Chemistry, National Tsing Hua University, Hsin-Chu 30043, Taiwan

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$[\text{H}_4\text{Re}_3(\text{CO})_9^-][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$  (**1**) in chloroform solution containing DMF undergoes cluster transformation, yielding  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$  (**2**) and  $[\text{H}_5\text{Re}_4(\text{CO})_{12}^-][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$  (**3**). The anionic cluster in **2** is the first example of a 74-e square-pyramidal penta-transition-metal cluster without a non-hydride interstitial atom. The seven hydrides in the anion of **2** bridge all edges of the square-pyramidal pentarehenium cluster except one edge in the base. These hydrides are fluxional with  $\Delta H^\ddagger = 15.0(\pm 0.4)$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = 3.8(\pm 1.6)$  eu. The yields of **2** and **3** depend on the concentration of DMF. When  $[\text{DMF}] > 1$  M, **2** and **3** are not formed. At  $[\text{DMF}]$  around 0.15 M, the formation of **2** is favored, while at concentration around 0.03 M, **3** is favored. The rate law for the formation of **2** is that rate =  $k_f[\mathbf{1}]^2$ ,  $k_f = 9.7 \times 10^{-4}$  mM<sup>-1</sup> h<sup>-1</sup>. The proposed mechanisms for the formation of **2** and **3** are presented. **2** also undergoes cluster transformation in dichloromethane solution, and the pathways are dependent on the concentrations of DMF and **2**. At very low concentration ( $2.1 \times 10^{-5}$  M) of **2**, it transforms to  $[\text{H}_7\text{Re}_6(\text{CO})_{18}^-][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$ . In the presence of DMF ( $1 \times 10^{-3}$ ), **2** ( $2.2 \times 10^{-5}$  M) transforms to **1**. However, at moderate concentration ( $4.3 \times 10^{-3}$  M) of **2**, it transforms to a mixture of **1** and **3**. The mechanisms for these transformations are proposed.

## Introduction

Unsaturated clusters are known to have a high chemical reactivity. We are particularly interested in unsaturated rhenium clusters, which exhibit interesting chemistry. For example,  $\text{H}_4\text{Re}_4(\text{CO})_{12}$ ,<sup>1–4</sup> which has a tetrahedral geometry with two delocalized double bonds and four face-bridging hydrides, reacts readily with various donor ligands, including common coordinating solvents such as acetone, THF, DMF, and various alcohols. The reaction between  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  and methanol follows a clean fifth-order reaction (first order in  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  and fourth order in methanol), as reported in our previous paper.<sup>2</sup> The product of this fifth-order reaction is  $[\text{H}_4\text{Re}_3(\text{CO})_9^-][\text{Re}(\text{CO})_3(\text{MeOH})_3^+]$ .<sup>3</sup> In the solid state, the structure of  $[\text{H}_4\text{Re}_3(\text{CO})_9^-][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$  indicates that the unusual trirhenium anionic cluster possesses a metal–metal double bond and a coordinatively unsaturated site on the other rhenium atom not involved in the double bond.<sup>4</sup> To stabilize this highly unsaturated anionic cluster, two clusters are associated antiprismatically to form a dimer in which

a hydride bridging the double bond is located in the area of the coordinatively unsaturated site of the other associated cluster. The solution structure of  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  is completely different from that in the solid state. All spectroscopic data indicate that the cluster has a highly symmetric structure:  $(\mu_3\text{-H})(\mu_2\text{-H})_3(\text{CO})_9^-$ .

In this publication, we report the chemical properties of this highly unsaturated anionic cluster  $\text{H}_4\text{Re}_3(\text{CO})_9^-$ . Special attention is focused on the cluster skeletal transformation. When  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  was treated with acetone in dichloromethane solution,  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$  could be isolated. <sup>1</sup>H NMR investigation indicates that  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  is an intermediate. It is reasonable to expect that the associated dimer of  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  in the solid state may be formed in solution, which then may simply lose one hydride to form  $\text{H}_7\text{Re}_6(\text{CO})_{18}^-$ . However, this expectation is completely wrong. Instead, we found that two molecules of  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  form the novel square-pyramidal pentarehenium anionic cluster  $\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}$ , which can then be transformed to  $\text{H}_7\text{Re}_6(\text{CO})_{18}^-$ . Furthermore, we reported here that the concentration of DMF which serves as a coordinating ligand is critical in directing the skeletal transformation pathways.

## Results and Discussion

**A. Formation of the Novel Square-Pyramidal Anionic Cluster  $\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}$ .** The reaction between  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  and *N,N*-dimethylformamide (DMF) yields  $[\text{H}_4\text{Re}_3(\text{CO})_9^-][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$  (**1**) quantitatively.<sup>4</sup> In chloroform or dichloromethane solution with

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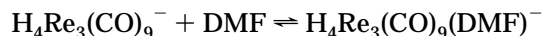
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high DMF concentration (> 1 M), **1** does not undergo any cluster skeletal transformation, because the anionic cluster  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  is coordinated by DMF:<sup>6</sup>

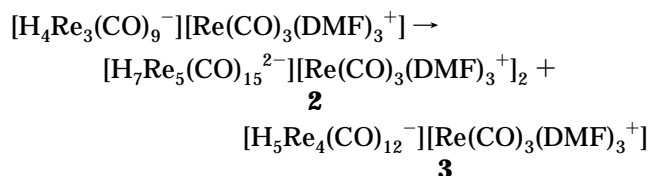


This DMF-coordinated cluster, with its extra ligand coordinated to the rhenium atom not connected to others by a Re–Re double bond, is isostructural with  $\text{H}_4\text{Re}_3(\text{CO})_{10}^-$ <sup>7</sup> and  $\text{H}_4\text{Re}_3(\text{CO})_9(\text{PPh}_3)^-$ .<sup>8</sup>

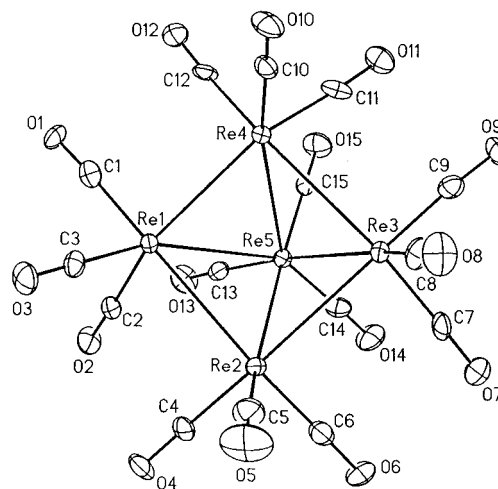
It was found that the chloroform solution of **1** with a DMF concentration of 0.13 M turned from yellow to reddish yellow on standing for 24 h at 298 K. A yellow crystalline precipitate, **2**, can be obtained from this solution. The <sup>1</sup>H NMR spectrum of **2** indicates that it has seven hydrides in two signals with a ratio of 3:4 and six equivalent coordinated DMF molecules. The FAB mass spectrum of **2** reveals the presence of a fragment of  $\text{H}_m\text{Re}_5(\text{CO})_{15}$ . On the basis of these spectroscopic data, **2** is assigned to be  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{Re}(\text{CO})_3(\text{DMF})_3^+]_2$ . Disorder in the crystal of **2** prevents us from determining its structure. However, the structure of this pentarhenium anionic cluster is confirmed by the structure of  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NET}_4^+]_2$  (**4**), in which the cation of **2** is replaced by the tetraethylammonium ion.

When the reaction is followed by <sup>1</sup>H NMR, besides **2**, only one other product was identified. The red color in the reacting solution is due to the compound **3**, which has a hydride signal at –10.4 ppm and  $\lambda_{\text{max}} = 463$  nm. Spectroscopic data indicate that **3** contains the known anionic cluster  $\text{H}_5\text{Re}_4(\text{CO})_{12}^-$ .<sup>9</sup> Since the only cation in the reaction solution is  $\text{Re}(\text{CO})_3(\text{DMF})_3^+$ , we assign **3** to be  $[\text{H}_5\text{Re}_4(\text{CO})_{12}^-][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$ .  $\text{H}_5\text{Re}_4(\text{CO})_{12}^-$  has also been prepared in this laboratory by the reaction between  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  and *N*-methylbenzamide in chloroform. After treatment with  $\text{NET}_4\text{BF}_4$ , we obtained  $[\text{H}_5\text{Re}_4(\text{CO})_{12}^-][\text{NET}_4^+]$ , which was characterized by a variety of spectroscopic methods, including X-ray diffraction, to have data identical with the literature data.<sup>9</sup> The UV–vis and <sup>1</sup>H NMR data of this compound are the same as those of **3**.

Therefore, in the chloroform solution with DMF, **1** is transformed into the two clusters **2** and **3**, with **2** containing the novel square-pyramidal anionic cluster  $\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}$  as shown in section B. The same reaction also occurs in dichloromethane solution, but **2** is more soluble in this solvent than in chloroform.



**B. Structure of  $\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}$ .** The structure of the anionic cluster of **4** (Figure 1) consists of five



**Figure 1.** ORTEP drawing of the anion of  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NET}_4^+]_2 \cdot \text{C}_2\text{H}_4\text{Cl}_2$ . The cation and 1,2-dichloroethane are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

**Table 1. Significant Bond Distances and Bond Angles of the Anionic Cluster in  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NET}_4^+]_2$  (**4**)<sup>a</sup>**

Bond Distances (Å)		
Re1–Re2 3.181(1)	Re1–Re4 3.046(1)	Re1–Re5 3.279(1)
Re2–Re3 3.236(1)	Re2–Re5 3.209(1)	Re3–Re4 3.216(1)
Re3–Re5 3.206(1)	Re4–Re5 3.265(1)	
Bond Angles (deg)		
Re2–Re1–Re4 91.4(1)	Re2–Re1–Re5 59.5(1)	Re4–Re1–Re5 62.0(1)
Re1–Re2–Re3 89.2(1)	Re1–Re2–Re5 61.8(1)	Re3–Re2–Re5 59.7(1)
Re2–Re3–Re4 87.4(1)	Re2–Re3–Re5 59.7(1)	Re4–Re3–Re5 61.1(1)
Re1–Re4–Re3 92.0(1)	Re1–Re4–Re5 62.5(1)	Re3–Re4–Re5 59.3(1)
Re1–Re5–Re2 58.7(1)	Re1–Re5–Re3 88.0(1)	Re1–Re5–Re4 55.5(1)
Re2–Re5–Re3 60.6(1)	Re3–Re5–Re4 87.0(1)	

<sup>a</sup> **4** contains a molecule of 1,2-dichloroethane solvent.

rhenium atoms in a square-pyramidal arrangement. Each rhenium atom is coordinated by three mutually perpendicular ( $\angle\text{C–Re–C} = 85.7\text{--}91.5^\circ$  (average  $88.9^\circ$ ), linear carbonyl groups ( $\angle\text{Re–C–O} = 174\text{--}179^\circ$ ). The significant bond distances and angles are given in Table 1. Except for the Re1–Re4 distance, the Re–Re bond distances are within the narrow range 3.181–3.279 Å, which is typical for a hydride-bridged Re–Re single-bond distance.<sup>1c,10</sup> The Re1–Re4 distance of 3.046 Å is a typical for a simple Re–Re single bond as in  $\text{Re}_2(\text{CO})_{10}$  (3.041 Å).<sup>11</sup> Therefore, it is reasonable to assume that the seven hydrides bridge all Re–Re edges except Re1–Re4. The four basal rhenium atoms Re1–Re4 form a slightly distorted square. The triangles formed by the apical rhenium atom and every pair of adjacent basal rhenium atoms are nearly equilateral. It is noteworthy that the Re1–Re5 and Re4–Re5 bond distances are decidedly longer than the others.

The above structure indicates that **2** contains a pentarhenium anionic cluster, which is unusual in the sense that it does not contain any interstitial atom other than hydride (Figure 1). Since the discovery of the first square-pyramidal pentanuclear carbonyl cluster  $\text{Fe}_5\text{C-}$

(6) The equilibrium constants are 492 and  $52.5 \text{ M}^{-1}$  at 193 and 233 K, respectively; details will be published elsewhere.

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(CO)<sub>15</sub>,<sup>12</sup> all subsequent reports on homopentamuclear Fe,<sup>12,13</sup> Ru,<sup>14,15</sup> Os,<sup>14,16,17</sup> Ir,<sup>18</sup> and Re<sup>19,20</sup> clusters state that they contain interstitial atoms or ligands, such as C,<sup>12,13b,14,19</sup> N,<sup>13a</sup> P(OCH<sub>3</sub>),<sup>16</sup> PMe,<sup>20</sup> PPh,<sup>18</sup> S<sup>17</sup> and CCPH.<sup>15</sup> These interstitial atoms or ligands invariably coordinate to at least four basal atoms and are believed to stabilize the clusters. Almost all other heteronuclear square-pyramidal transition-metal clusters, such as MFe<sub>4</sub>C(CO)<sub>16</sub> (M = Cr, Mo),<sup>21</sup> MFe<sub>4</sub>C(CO)<sub>14</sub><sup>-</sup> (M = Co,<sup>22</sup> Rh<sup>21</sup>), Ni<sub>2</sub>Ru<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>6</sub>(μ-CO)<sub>2</sub>(μ<sub>4</sub>-η<sup>2</sup>-CCPh),<sup>23</sup> Mo<sub>2</sub>-Co<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)(CO)<sub>10</sub>(μ<sub>5</sub>-N),<sup>24</sup> Os<sub>4</sub>Pt(CO)<sub>13</sub>(PPh<sub>3</sub>)(μ<sub>4</sub>-S),<sup>25</sup> and (Fe<sub>2</sub>Ru<sub>3</sub>(CO)<sub>14</sub>(μ<sub>4</sub>-O))<sub>2</sub>,<sup>26</sup> possess interstitial atoms or ligands coordinated to the basal atoms as well. To the best of our knowledge, there are only three known cases which do not contain an interstitial atom coordinated to all basal atoms, namely, HAu<sub>2</sub>-Ru<sub>3</sub>(CO)<sub>9</sub>(COMe)(PPh)<sub>2</sub>,<sup>27</sup> Mo<sub>5</sub>Cl<sub>13</sub><sup>2-</sup>,<sup>28</sup> and H<sub>4</sub>Zr<sub>5</sub>Cl<sub>12</sub>(PR<sub>3</sub>) (R<sub>3</sub> = Me<sub>3</sub>, Et<sub>3</sub>, Me<sub>2</sub>Ph).<sup>29</sup> However, these three exceptional clusters have an electron count different from 74 e, which is the value predicted by Wade's rule for a nido pentamuclear cluster.<sup>30</sup> Therefore, H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup> is the first 74-e square-pyramidal cluster without a non-hydride interstitial atom.

It has been pointed out that the presence of the basal interstitial atom contributes to the stability of the 74-e square-pyramidal cluster by the interactions of the orbitals of the interstitial atom with the skeletal orbitals of the cluster.<sup>31</sup> The existence of H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup> indicates that the skeletal orbitals of a square-pyramidal cluster can interact with hydrides in ways that are different from those with a non-hydride interstitial atom. In the series of hydridocarbonylrhenium clusters H<sub>5</sub>Re<sub>4</sub>(CO)<sub>12</sub><sup>-9</sup>, H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>, and H<sub>7</sub>Re<sub>6</sub>(CO)<sub>18</sub><sup>-5</sup>, the number of hydrides in each cluster is the same as the

**Table 2. Line Widths of the Hydride NMR Signals of [H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>][Re(CO)<sub>3</sub>(DMF)<sub>3</sub>]<sub>2</sub> (2) and Exchange Rate Constants as a Function of Temperature<sup>a,b</sup>**

T/K	H <sub>a</sub> at -11.7 (4H) ppm		H <sub>b</sub> at -17.4 (3H) ppm		
	Δν <sub>1/2</sub> /Hz	k <sub>ex</sub> (a)/s <sup>-1</sup>	Δν <sub>1/2</sub> /Hz	k <sub>ex</sub> (b)/s <sup>-1</sup>	k <sub>ex</sub> /s <sup>-1</sup>
293	36.5	108	46.3	139	35.4(0.9)
283	16.8	46.5	21.1	60.0	15.3(0.4)
273	7.6	17.6	8.3	19.8	5.4(0.7)
263	3.2	3.8	4.5	7.9	1.7(0.5)
253	2.6	c	2.8	c	

<sup>a</sup> The line width data were measured in a CD<sub>2</sub>Cl<sub>2</sub> solution using a 400 MHz NMR instrument. <sup>b</sup> k<sub>ex</sub>(a), k<sub>ex</sub>(b), and k<sub>ex</sub> are the exchange rate constants defined in the text. <sup>c</sup> Rate constants from widths are expected to be unreliable.

number of skeletal orbitals. This may indicate the importance of the interactions among hydrides and skeletal orbitals in stabilizing these Re clusters.

**C. Fluxional Behavior of the Hydrides of H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>.** According to the X-ray structure of **4**, one expects to see two hydride signals (2:1) for the three hydrides H<sub>b</sub> bridging the basal edges and another two hydride signals (2:2) for the hydrides H<sub>a</sub> bridging the bonds between apical and basal rhenium atoms for the anionic cluster H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>. However, experimental results revealed that only two sharp hydride signals (3:4) were observed down to 183 K. This indicates that the three H<sub>b</sub> atoms must exchange rapidly among themselves. H<sub>a</sub> cannot participate in this exchange; otherwise broadening of both H<sub>b</sub> and H<sub>a</sub> signals could be detected. This rapid exchange among H<sub>b</sub> atoms is not unique. The hydrides in both H<sub>7</sub>Re<sub>6</sub>(CO)<sub>18</sub><sup>-5</sup> and H<sub>5</sub>Re<sub>4</sub>(CO)<sub>12</sub><sup>-9</sup> are not equivalent, as revealed by their X-ray structures. However, both clusters exhibit a single hydride peak down to 183 K.

The line widths of the two hydride NMR peaks of **2** increase with temperature (Table 2). At 293 K, the width of H<sub>a</sub> is about 75% that of H<sub>b</sub>. This *width* information indicates that H<sub>a</sub> and H<sub>b</sub> exchange with each other under slow exchange conditions. This exchange process can be analyzed according to the equation

$$1/T_2(\text{obs},i) = 1/T_2(\text{int},i) + k_{\text{ex}}(i) \quad i = a, b$$

T<sub>2</sub>(obs,i) and T<sub>2</sub>(int,i) are the observed and intrinsic (no exchange) spin-spin relaxation times for hydride H<sub>i</sub> (i = a, b). k<sub>ex</sub>(i) is the exchange rate constant. The rate constants obtained from analyzing the line width data with the assumption that (πT<sub>2</sub>(int,i))<sup>-1</sup> = 2.0 Hz for both H<sub>a</sub> and H<sub>b</sub> are collected in Table 2. In the last column of Table 2, the exchange rate constant k<sub>ex</sub>, which is the mean of the inverse of the lifetimes of the sites, is calculated by the relation<sup>32</sup>

$$k_{\text{ex}} = (7/2)(k_{\text{ex}}(\text{a})/3 + k_{\text{ex}}(\text{b})/4)$$

Analysis of the rate constant according to the absolute rate theory k<sub>ex</sub> = (kT/h)exp(-ΔG<sup>‡</sup>/RT) yields the activation parameters ΔH<sup>‡</sup> = 15.0(±0.4) kcal mol<sup>-1</sup> and ΔS<sup>‡</sup> = 3.8(±1.6) eu. The small activation entropy is consistent with an intramolecular hydride exchange mechanism.

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**Table 3. Yields<sup>a</sup> of [H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>][Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup>]<sub>2</sub> (**2**) and [H<sub>5</sub>Re<sub>4</sub>(CO)<sub>12</sub><sup>-</sup>][Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup>] (**3**) as a Function of Concentration of DMF<sup>b</sup>**

[DMF]/M	yield of <b>2</b> /%	yield of <b>3</b> /%
0.025	<i>c</i>	55.6
0.05	38.4	46.9
0.1	47.8	33.1
0.2	42.8	4.4
1.0	<i>c</i>	<i>c</i>

<sup>a</sup> Yields (based on Re) are <sup>1</sup>H NMR yields. <sup>b</sup> Reaction conditions: H<sub>4</sub>Re<sub>4</sub>(CO)<sub>12</sub> (5.0 mg, 4.6 μmol) in 0.5 mL of CD<sub>2</sub>Cl<sub>2</sub> at ambient temperature in the presence of various DMF concentrations. Yields were determined after 24 h reaction time based on the integrated intensities of the hydride NMR signal (measured at 223 K) in comparison with that of internal standard of toluene. <sup>c</sup> Yields are negligible.

**Table 4. Rate of Formation of [H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>][Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup>]<sub>2</sub> (**2**) as a Function of the Concentration of [H<sub>4</sub>Re<sub>3</sub>(CO)<sub>9</sub><sup>-</sup>][Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup>] (**1**)<sup>a</sup>**

[ <b>1</b> ] <sup>b</sup> (mM)	Δ[ <b>2</b> ] <sup>c</sup> (mM)	rate <sup>d</sup> (mM/h)
27.5	1.42	0.71
26.4 <sup>e</sup>	1.16	0.58
15.6	0.49	0.245
14.5 <sup>e</sup>	0.53	0.265
11.3	0.26	0.13
11.1 <sup>e</sup>	0.29	0.14
5.6	0.080	0.040
5.3 <sup>e</sup>	0.080	0.040

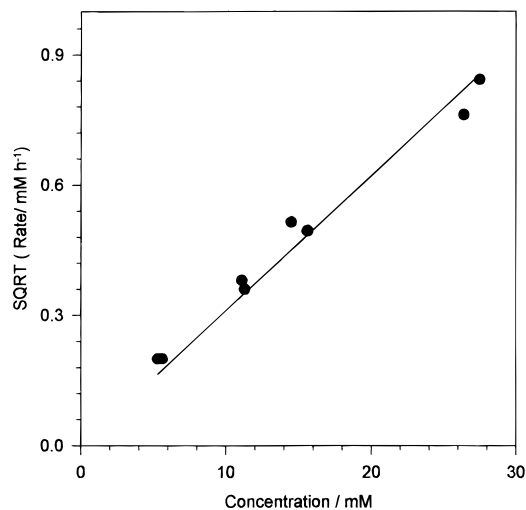
<sup>a</sup> Reaction conditions: [DMF] = 0.10 M in CD<sub>2</sub>Cl<sub>2</sub> with various concentrations of H<sub>4</sub>Re<sub>4</sub>(CO)<sub>4</sub> at 25 °C. <sup>1</sup>H NMR monitoring started after H<sub>4</sub>Re<sub>4</sub>(CO)<sub>4</sub> was completely converted to **1**. <sup>b</sup> Average of the concentrations at the beginning and the end of 2 h reaction period. <sup>c</sup> Concentration difference between the beginning and the end of 2 h reaction period. <sup>d</sup> Rate is evaluated according to Δ[**2**]/Δ*t*, Δ*t* = 2 h. <sup>e</sup> Data were obtained from the same sample, giving the data immediately above.

**D. Mechanism for the Formation of [H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>][Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup>]<sub>2</sub> (**2**) and [H<sub>5</sub>Re<sub>4</sub>(CO)<sub>12</sub><sup>-</sup>][Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup>] (**3**).** The <sup>1</sup>H NMR yields of **2** and **3** from **1** are dependent on the DMF concentrations (Table 3). At 0.2 M, the yields for both **2** and **3** are lower than those at 0.1 M. This may be because the fraction of stable H<sub>4</sub>Re<sub>3</sub>(CO)<sub>9</sub>(DMF)<sup>-</sup> increases at the expense of H<sub>4</sub>Re<sub>3</sub>(CO)<sub>9</sub><sup>-</sup>. When [DMF] is above 1 M, **2** and **3** were not detected within a 24 h period. When the concentration of DMF decreases, the pathway leading to **3** is accelerated and the pathway leading to **2** increases initially and then decreases. At a DMF concentration of 0.025 M, the yield of **2** is too small to be detected.

The rates for the formation of **2** are investigated as a function of the concentration of **1** by <sup>1</sup>H NMR spectroscopy. These studies were carried out in the presence of 0.10 M DMF to maximize the rates of formation of **2**. The data in Table 4 indicate that, when the concentration of **1** increases, the rate also increases, but nonlinearly. Figure 2 shows clearly that the square root of the reaction rate is proportional to the concentration of **1**. Therefore, the rate law for the formation of **2** is

$$\text{rate} = k_f[\mathbf{1}]^2$$

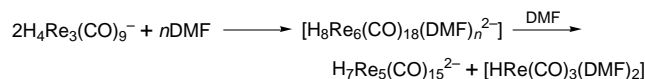
The rate constant is  $k_f = 9.7 \times 10^{-4} \text{ mM}^{-1} \text{ h}^{-1}$ , as calculated from the slope of the straight line in Figure 2. This rate law indicates that the formation of **2** requires an intermediate which is an associated complex



**Figure 2.** Square root of the rate of formation of [H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>][Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup>]<sub>2</sub> (**2**) as a function of the concentration of [H<sub>4</sub>Re<sub>3</sub>(CO)<sub>9</sub><sup>-</sup>][Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup>] (**1**) in CD<sub>2</sub>Cl<sub>2</sub> at 25 °C.

of two anionic clusters of **1**. We propose that this intermediate further reacts with DMF to release a one-rhenium species as in Scheme 1.

#### Scheme 1

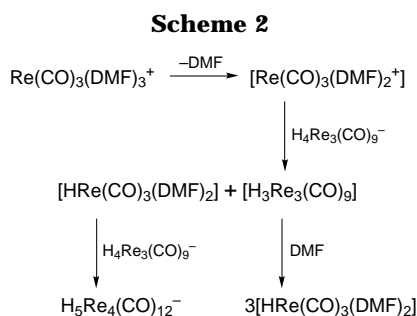


The presence of *n*DMF (*n* = 0, 1) in this scheme is to indicate that one of the two molecules of **1** may associate with DMF in forming the intermediate. The proposed intermediate then reacts with DMF to form **2**. This reaction is favored at reasonably high DMF concentration. On the other hand, the proposed intermediate [H<sub>8</sub>Re<sub>6</sub>(CO)<sub>18</sub>(DMF)<sub>*n*</sub><sup>2-</sup>] may lose a hydride to form H<sub>7</sub>Re<sub>6</sub>(CO)<sub>18</sub><sup>-</sup>. A possible hydride acceptor is [Re(CO)<sub>3</sub>(DMF)<sub>2</sub>]<sup>+</sup>, which can come from the cation Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup> by dissociation of one DMF. However, H<sub>7</sub>Re<sub>6</sub>(CO)<sub>18</sub><sup>-</sup> was not detected throughout a wide range of DMF concentration (Table 3). Therefore, this hydride transfer from the hexarhenium intermediate is not a favored reaction pathway. The proposed mononuclear species [HRe(CO)<sub>3</sub>(DMF)<sub>2</sub>] in Scheme 1 was not detected. This may be due to its high reactivity; it can either react with H<sub>4</sub>Re<sub>3</sub>(CO)<sub>9</sub><sup>-</sup> to form H<sub>5</sub>Re<sub>4</sub>(CO)<sub>12</sub><sup>-</sup> (see below) or combine to form **1**. This proposed mechanism is consistent with the trends in Table 3.

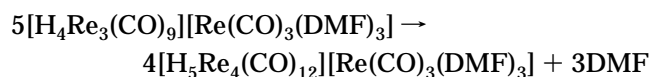
In Scheme 1, we assume that the cation of **1**, Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup>, does not participate in the formation of **2**, and this is clarified by the following experiment. <sup>1</sup>H NMR spectra of an acetone-*d*<sub>6</sub> solution (0.5 mL) of [H<sub>4</sub>Re<sub>3</sub>(CO)<sub>9</sub><sup>-</sup>][NET<sub>4</sub><sup>+</sup>] (35 mg, 37 μmol) indicate that H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup> and H<sub>5</sub>Re<sub>4</sub>(CO)<sub>12</sub><sup>-</sup> are formed rapidly in the initial stage of the reaction (within 60 min). In this experiment, acetone was used as solvent to overcome the solubility limitation. The weakly coordinating acetone must play the role of DMF in Scheme 1 in the formation of H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>. This experimental result indicates that indeed Re(CO)<sub>3</sub>(DMF)<sub>3</sub><sup>+</sup> does not participate in the formation of H<sub>7</sub>Re<sub>5</sub>(CO)<sub>15</sub><sup>2-</sup>.

Since the formation of **3** is favored at low DMF concentration, we propose that dissociation of a coordi-

nated DMF from the cation is the initial step in the formation of **3** as shown in Scheme 2.

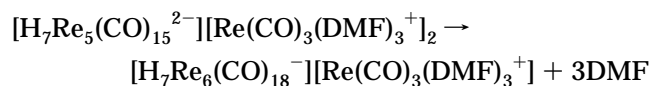


The resulting coordinatively unsaturated species  $[\text{Re}(\text{CO})_3(\text{DMF})_2^+]$  then abstracts a hydride from  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  to form  $[\text{HRe}(\text{CO})_3(\text{DMF})_2]$ , which then reacts with  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  to form **3**. The proposed intermediate  $[\text{H}_3\text{Re}_3(\text{CO})_9]$  further reacts with DMF to form more  $[\text{HRe}(\text{CO})_3(\text{DMF})_2]$  and consequently more **3**. The overall reaction is given by



Since DMF is released, this reaction is favored under the condition of low DMF concentration, consistent with the experimental results.

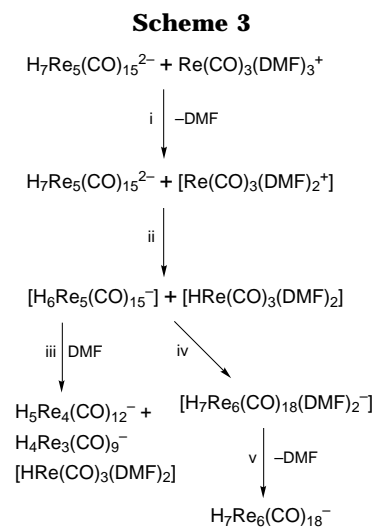
**E. Cluster Transformation of  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{Re}(\text{CO})_3(\text{DMF})_3^+]_2$ .** The cluster compound **2** can undergo further transformation. In a dichloromethane solution of **2** ( $2.1 \times 10^{-5}$  M), the UV-vis peak of **2** at 266 nm decreases with concomitant formation of an absorption peak at 342 nm with an isosbestic point at 323 nm. The half-life of **2** is approximately 30 min. The  $^1\text{H}$  NMR spectrum of the product (after being concentrated in a rotary evaporator) consists of four peaks at  $\delta$  7.96 (s, 3H, H, of DMF), 3.18 (s, 9H,  $\text{CH}_3$  in DMF), 3.01 (s, 9H,  $\text{CH}_3$  in DMF) and  $-16.8$  (s, 7H). The UV-vis and  $^1\text{H}$  NMR spectroscopic data indicate the presence of the known anionic cluster  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$  and the cation  $\text{Re}(\text{CO})_3(\text{DMF})_3^+$ . This transformation is summarized by



The dissociated free DMF was also detected by a  $^1\text{H}$  NMR spectrum. However, in dichloromethane solution in the presence of DMF ( $1.0 \times 10^{-3}$  M), the UV-vis spectrum of **2** ( $2.2 \times 10^{-5}$  M) disappeared with concomitant formation of a peak at 372 nm, the characteristic peak for  $\text{H}_4\text{Re}_3(\text{CO})_9^-$ . Again the half-life of **2** is approximately 30 min. This transformation of **2** back to **1** is also confirmed by  $^1\text{H}$  NMR. However, when the DMF concentration is above 0.1 M, **2** is stable indefinitely. On the other hand, when the concentration of **2** ( $4.3 \times 10^{-3}$  M) is high in dichloromethane without additional DMF, **2** is transformed into both **1** and **3** but not  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$  as indicated by the  $^1\text{H}$  NMR spectra. An intermediate with a hydride signal at  $-16.2$  ppm, which we were unable to isolate, was involved in this transformation. This observation indicates that the concentration of **2** has a large effect on its reaction. The fact that  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$  is not formed can be understood

on the basis of DMF concentration change. When **2** is transformed into **1**, **3**, or  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$ , the number of coordinated DMF molecules on a per rhenium per molecule basis decreases from 6/7 to 3/4, 3/5, and 3/7 for **1**, **3**, and  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$ , respectively. Therefore, the DMF concentration in the reaction mixture increases as a result of the transformation of **2** into **1**, **3**, or  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$ . This increased DMF concentration, which may become significant when the concentration of **2** is high, prevents further transformation of **2** into  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$ . Accordingly, **1** and **3** are the detected products at a high concentration of **2**. Therefore, the results of the cluster transformation of **2** depend critically on the concentration of both **2** and DMF.

Though the detail mechanisms of the cluster transformations of **2** are not completely known yet, experimental data are consistent with the mechanism in Scheme 3. Since  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NET}_4^+]_2$  does not



undergo any of the transformations of **2** on the same time scale, the cation  $\text{Re}(\text{CO})_3(\text{DMF})_3^+$  of **2** must play an important role. Because **2** is stable under the condition that  $[\text{DMF}] > 0.1$  M, it is logical to conclude that dissociation of DMF from the cation must be involved (step i). This dissociation is the same as that proposed in Scheme 2. After DMF dissociation, we propose that  $[\text{Re}(\text{CO})_3(\text{DMF})_2^+]$  is transformed to  $[\text{HRe}(\text{CO})_3(\text{DMF})_2]$  by hydride abstraction from  $\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}$  (step ii). The proposed intermediate  $[\text{H}_6\text{Re}_5(\text{CO})_{15}^-]$  may be responsible for the observed intermediate with a hydride signal at  $-16.2$  ppm. This intermediate is unsaturated; it can presumably react readily with either DMF or the other intermediate  $[\text{HRe}(\text{CO})_3(\text{DMF})_2]$ , depending on the reaction conditions. When there is a reasonable concentration of DMF,  $[\text{H}_6\text{Re}_5(\text{CO})_{15}^-]$  reacts with DMF and leads to fragmentation, yielding  $\text{H}_5\text{Re}_4(\text{CO})_{12}^-$ ,  $\text{H}_4\text{Re}_3(\text{CO})_9^-$ , and  $[\text{HRe}(\text{CO})_3(\text{DMF})_2]$  (step iii). When the DMF concentration is low, then only  $[\text{HRe}(\text{CO})_3(\text{DMF})_2]$  can react with  $[\text{H}_6\text{Re}_5(\text{CO})_{15}^-]$ , and this reaction yields  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$  (steps iv and v) after further dissociation of DMF.

When  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  reacts with acetone instead of DMF in chloroform solution,  $^1\text{H}$  NMR indicates the initial formation of  $\text{H}_4\text{Re}_3(\text{CO})_9^-$ , which then transforms to  $\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}$ . Subsequently,  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$  is formed. The whole reaction sequence leading to  $\text{H}_7\text{Re}_6(\text{CO})_{18}^{5-}$  is similar to that with DMF. The ease of conversion of

$\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}$  to  $\text{H}_7\text{Re}_6(\text{CO})_{18}^-$  in acetone, as observed experimentally,<sup>5</sup> is because acetone is a weaker ligand than DMF. According to Scheme 3, processes corresponding to steps iv and v are favored.

### Conclusion

The highly unsaturated cluster  $[\text{H}_4\text{Re}_3(\text{CO})_9]^-$  [ $\text{Re}(\text{CO})_3(\text{DMF})_3^+$ ] (**1**) can undergo skeletal transformation by two pathways. In the first pathway, which is favored in the presence of a reasonably high concentration of DMF, the novel cluster  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$  (**2**) is formed. **2** contains a square-pyramidal pentarhenium anionic cluster, which is the first example of a 74-e square-pyramidal cluster without a non-hydride interstitial atom. The rate of formation of **2** is second-order in **1**, suggesting the formation of an intermediate involving the association of two  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  groups. In the second pathway, which is favored in the presence of a low concentration of DMF,  $[\text{H}_5\text{Re}_4(\text{CO})_{12}^-][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$  (**3**) is formed. We propose that **3** is formed by the reaction of  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  with  $[\text{HRe}(\text{CO})_3(\text{DMF})_2]$ , which is formed from  $\text{Re}(\text{CO})_3(\text{DMF})_3^+$  by dissociating one DMF followed by a hydride abstraction.

The electronically saturated cluster **2** can be further transformed to  $[\text{H}_7\text{Re}_6(\text{CO})_{18}^-][\text{Re}(\text{CO})_3(\text{DMF})_3^+]$  in low concentration ( $2.1 \times 10^{-5}$  M) of **2** without additional DMF. However, in the presence of a low concentration of DMF ( $1 \times 10^{-3}$  M), **2** converts back to **1**. **2** transforms to a mixture of **1** and **3**, when its concentration is  $4.3 \times 10^{-3}$  M. We postulate that the transformations of **2** go through the coordinatively unsaturated intermediate  $[\text{H}_6\text{Re}_5(\text{CO})_{15}^-]$ , which is formed by hydride transfer from  $\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}$  to  $[\text{Re}(\text{CO})_3(\text{DMF})_2^+]$ . The intermediate then reacts with  $[\text{HRe}(\text{CO})_3(\text{DMF})_2]$  to form  $\text{H}_7\text{Re}_6(\text{CO})_{18}^-$  or reacts with DMF to form **1** and **3**, depending on the reaction conditions.

It is clear that the reactions of both **1** and **2** are strongly dependent on DMF. At very high DMF concentration, both **1** and **2** do not undergo skeletal transformation. At low DMF concentration the cation  $\text{Re}(\text{CO})_3(\text{DMF})_3^+$  participates in the reactions by dissociating a DMF followed by a hydride abstraction to form the intermediate  $[\text{HRe}(\text{CO})_3(\text{DMF})_2]$ . This intermediate can react, in competition with DMF, with a stable cluster or an intermediate to form the various cluster products. Also at intermediate concentration, DMF can facilitate the fragmentation of a high-nuclearity intermediate which is formed from two  $\text{H}_4\text{Re}_3(\text{CO})_9^-$  groups. Thus, we have demonstrated the importance of the concentrations of cluster compounds and the weak coordinating ligand DMF in influencing the cluster skeletal transformation.

### Experimental Section

$\text{H}_4\text{Re}_4(\text{CO})_{12}$  was prepared from the reaction between  $\text{Re}_2(\text{CO})_{10}$  (from Strem Chemical Co.) and  $\text{H}_2$  in decane at 175 °C according to the literature method.<sup>1c</sup> *N,N*-dimethylformamide, dichloromethane, and chloroform were obtained from Aldrich Chemical Co. and purified according to the standard procedure.<sup>33</sup>

(33) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: New York, 1988.

**Table 5. Crystal Data for the Structural Analysis of  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NET}_4^+]_2 \cdot \text{C}_2\text{H}_4\text{Cl}_2$ .**

emp formula	$\text{C}_{33}\text{H}_{51}\text{Cl}_2\text{N}_2\text{O}_{15}\text{Re}_5$
fw	1717.7
cryst syst	monoclinic
space group	$P2_1/n$
lattice params	
<i>a</i> , Å	10.579(2)
<i>b</i> , Å	17.069(2)
<i>c</i> , Å	26.940(2)
β, deg	93.82(2)
<i>V</i> , Å <sup>3</sup>	4853.9(11)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> , g/cm <sup>-3</sup>	2.349
<i>F</i> <sub>000</sub>	3164
μ(Mo Kα), cm <sup>-1</sup>	149.514
temp, K	296
2θ <sub>max</sub> , deg	51.4
no. of meas rflns	21 701
no. of obsd rflns ( <i>I</i> > 2σ( <i>I</i> ))	17 170
no. of variables	515
<i>R</i> , <i>R</i> <sub>w</sub>	0.0414, 0.0510
max min in <i>D</i> map, e Å <sup>-3</sup>	+1.47, -1.44

**Physical Measurements.** NMR spectra were measured on a Bruker AM-400 or Varian Unity-400 spectrometer. IR spectra were recorded on a Jasco FTIR-300E spectrometer. UV-vis spectra were measured on a Perkin-Elmer Lambda-5 spectrometer. Elemental analysis of C, H, and N was obtained on a Perkin-Elmer 240C-2400 EA instrument.

**Synthesis of  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{Re}(\text{CO})_3(\text{DMF})_3^+]_2$  (**2**).** When *N,N*-dimethylformamide (30 μL, 390 μmol) was added to the chloroform solution (3.0 mL) containing  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  (30.0 mg, 27 μmol), the solution turned from red to yellow within 2 h. On standing, the color changed to reddish yellow. After 24 h, the yellow crystalline precipitate **2** was obtained. The precipitate was collected and washed with chloroform. After being dried in a vacuum oven (60 °C),  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{Re}(\text{CO})_3(\text{DMF})_3^+]_2$  (13.0 mg, 5.56 μmol) was obtained. Yield (based on Re): 36%. <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ , 223 K): δ 7.87 (s, 6H, H in DMF), 3.09 (s, 18H, CH<sub>3</sub> in DMF), 2.82 (s, 18H, CH<sub>3</sub> in DMF), -11.66 (s, 4H), -17.38 (s, 3H) ppm. <sup>13</sup>C NMR ( $\text{CD}_2\text{Cl}_2$ , 223 K): δ 33.7 (CH<sub>3</sub> in DMF), 33.9 (CH<sub>3</sub> in DMF), 167.3 (CO in DMF), 185.0 (3CO), 192.3 (3CO of  $\text{Re}(\text{CO})_3(\text{DMF})_3^+$ ), 193.6 (8CO) and 195.1 (4CO) ppm. IR (ν(CO),  $\text{CH}_2\text{Cl}_2$ ): 2048 (s), 2033 (s), 2006 (s), 1914 (br) cm<sup>-1</sup>. Mass (FAB): *m/z* 1355 (76.4%), 1357 (100%), 1359 (74.8%), and 1361 (27.7%) (theoretical for  $\text{H}_6\text{Re}_5(\text{CO})_{15}$ : 1353 (17.3%), 1355 (58.9%), 1357 (100%), 1359 (84.9%) and 1361 (28.8%). Anal. Calcd for  $\text{C}_{33}\text{H}_{49}\text{N}_6\text{O}_{27}\text{Re}_7([\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{Re}(\text{CO})_3(\text{DMF})_3^+]_2)$ : C, 20.04; H, 2.10; N, 3.60. Found: C, 20.05; H, 2.21; N, 3.64.

**Synthesis of  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NET}_4^+]_2$  (**4**).** DMF (100 μL, 1.3 mmol) was added to the dichloromethane solution (10.0 mL) containing  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  (100.0 mg, 92 μmol). After a reaction period of 20 h,  $\text{NET}_4\text{BF}_4$  (40 mg, 0.184 mmol) was added to the chloroform solution. The resulting reaction mixture was separated on a TLC plate of silica gel 60 F<sub>254</sub> (Merck) using acetone/1,2-dichloroethane (1/2 volume ratio) as eluent. The product  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NET}_4^+]_2$  (13.0 mg, 8.0 μmol) was isolated at *R*<sub>f</sub> 0.26. Yield (based on Re): 11%. <sup>1</sup>H NMR (*d*<sub>6</sub>-acetone, 223 K): δ 3.34 (q, 16H, *J* = 7.26 Hz, CH<sub>2</sub> in  $\text{NET}_4^+$ ), 1.30 (tt, 24H, *J* = 7.26, 1.89 Hz, CH<sub>3</sub> in  $\text{NET}_4^+$ ), -11.7 (s, 4H), -17.4 (s, 3H) ppm. <sup>13</sup>C NMR ( $\text{CD}_2\text{Cl}_2$ , 223 K): δ 7.5 (CH<sub>3</sub> in  $\text{NET}_4^+$ ), 52.8 (CH<sub>2</sub> in  $\text{NET}_4^+$ ), 185.9 (3CO), 193.5 (8CO), and 195.1 (4CO) ppm. IR (ν(CO), KBr pellet): 2002 (s), 1916 (br), and 1892 (br) cm<sup>-1</sup>. A single crystal of  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NET}_4^+]_2$  was obtained from the 1,2-dichloroethane solution by the slow evaporation method. The single crystal of **4** also contains one  $\text{C}_2\text{H}_4\text{Cl}_2$  solvent molecule.

**Synthesis of  $[\text{H}_5\text{Re}_4(\text{CO})_{12}^-][\text{NET}_4^+]$ .** *N*-Methylbenzamide (37.4 mg, 276 μmol) was added to the chloroform solution (5.0 mL) containing  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  (50.0 mg, 46 μmol). After a reaction period of 24 h at 22 °C,  $\text{NET}_4\text{BF}_4$  (10 mg, 46 μmol) was added to the reaction mixture. After 30 min of stirring

followed by stripping off solvent, a dark red oily residue was obtained. When 2 mL of dichloromethane was added to this residue, a yellow crystalline precipitate, which was identified to be  $[\text{H}_4\text{Re}_3(\text{CO})_9][\text{NEt}_4^+]$ , could be isolated by filtration. The volume of the dichloromethane dark red filtrate was then reduced to 0.5 mL. On addition of 4 mL of chloroform to the solution, dark red crystalline  $[\text{H}_5\text{Re}_4(\text{CO})_{12}][\text{NEt}_4^+]$  (17 mg, 14.0  $\mu\text{mol}$ ) precipitated out on standing. Yield (based on rhenium): 30.4%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  3.16 (q, 8H,  $J = 7.32$  Hz,  $\text{CH}_2$  in  $\text{NEt}_4^+$ ), 1.32 (tt, 12H,  $J = 7.26, 1.95$  Hz,  $\text{CH}_3$  in  $\text{NEt}_4^+$ ),  $-10.4$  (s, 5H) ppm.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.7 ( $\text{CH}_3$  in  $\text{NEt}_4^+$ ), 53.0 ( $\text{CH}_2$  in  $\text{NEt}_4^+$ ), 190.5 ppm. IR ( $\nu(\text{CO})$ ,  $\text{CH}_2\text{Cl}_2$ ): 2015 (s), 1938 (s)  $\text{cm}^{-1}$ . UV-vis ( $\text{CH}_2\text{Cl}_2$ ): 462.5 ( $\epsilon = 3737$   $\text{cm}^{-1} \text{M}^{-1}$ ) nm. X-ray diffraction data: unit cell  $P2_1/c$ , monoclinic,  $a = 18.424(5)$  Å,  $b = 8.764(2)$  Å,  $c = 17.962(5)$  Å,  $\beta = 91.79^\circ$ . These spectroscopic data are identical with the literature reported values.<sup>9</sup>

**X-ray Crystallography.** A single crystal of  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NEt}_4^+]_2$  (**4**) was sealed in epoxy resin. Diffraction intensity data were collected on a Siemens Smart CCD diffractometer using monochromic  $\text{Mo K}\alpha$  radiation (0.7107 Å) from a graphite single crystal at 23 °C. Intensity data were collected in 1271 frames with increasing  $\omega$  (width of 0.3° per frame). Absorption correction was based on 3037 symmetry-

equivalent reflections using the SHELXTL-PC package ( $T_{\text{min}}, T_{\text{max}} = 0.360, 0.940$ ). The general data collection and results are summarized in Table 5. The structure was solved by direct methods. All non-hydrogen atoms were subsequently located from a Fourier map and then anisotropically refined by full-matrix least squares. All hydrogen atoms were placed in the ideal positions according to the riding model with isotropic  $U$  values in structure factor calculations.  $R$  and  $R_w$  values after least-squares refinement are also reported in Table 5. All calculations were performed on a Micro VAX III computer with the Siemens SHELXTL PLUS (VMS) program.

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**Supporting Information Available:** Complete tables of crystal data, bond distances and bond angles, atomic coordinates, and thermal parameters and an additional ORTEP drawing for  $[\text{H}_7\text{Re}_5(\text{CO})_{15}^{2-}][\text{NEt}_4^+]_2$  (**4**) (11 pages). Ordering information is given on any current masthead page.

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