Inorg. Chem. **2007**, *46*, 8436–8438

Inorganic Chemistry
Communication

Cluster Carbonyls of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ Core

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Received March 24, 2007

The first $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core-containing cluster carbonyls, $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(CO)][SbF_6]_2$ and *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(CO)_2][SbF_6]_2$, were produced by reacting $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5I]I$ and *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4I_2]$, respectively, with $AgSbF_6$ in CO-saturated dichloromethane solutions. Spectroscopic and crystallographic studies suggest significant cluster-to-CO back-donation in these novel cluster derivatives and interesting electronic structures. Thermal and photolytic studies of the mono-carbonyl complex revealed its interesting and synthetically useful reactivity in producing new cluster derivatives.

Since the seminal discovery of high-critical-field superconductivity of the Chevrel phases,[1] considerable progress has been made in the study of hexanuclear transition metal clusters.[2−4] As their syntheses typically require high temperatures, the research of clusters of this type is generally regarded as the province of solid-state chemists, yet many of these clusters, when formed, are soluble in polar organic solvents and are quite amenable to synthetic manipulation. The structural integrity of the cluster core is maintained under normal chemical conditions, while the electronic structure and physical properties may be profoundly modified. In effect, these cluster cores are atom-like building blocks of expanded dimensions, with controllable stereochemistry and adjustable properties propitious to the development of novel, cluster-supported solution chemistry.[4]

One such cluster system receiving much recent interest features the hexarhenium chalcogenide core of $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ ($Q = S$, Se, Te).[5−10] It may be viewed as an octahedron of rhenium enclosed in a cube formed by the eight face-capping chalcogenido ligands (Figure 1). Unlike their well-known isomorphs of the earlier transition metal halides or chalcogenides, these clusters are stable to aerobic handling and vigorous synthetic conditions, yet labile enough that multiple-step, solution-phase ligand-substitution reactions on their terminally bound halides are easily accomplished.[11,12] The cluster core's relative inertness prohibits stereochemical scrambling, ensuring a fixed geometry for a given isomer. In effect, such stereoisomers form a complete kit of systematically altered building blocks and, therefore, are versatile synthons for the preparation of cluster-supported materials. Their superior synthetic utility has been demonstrated through the realization of a variety of super/supramolecular constructs[9] and porous framework solids.[13,14]

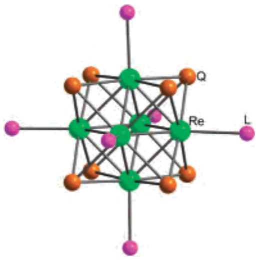

Figure 1. Structure of the $[Re_6(\mu_3\text{-}Q)_8]^{2+}$ ($Q = S$, Se) cluster core with terminal ligands (L).

Nevertheless, the use of the cluster in these developments is largely structural rather than functional. Conspicuously underdeveloped is the fundamental chemistry supported by the cluster core. We envision a new and potentially important chemistry wherein structurally well-defined and functionally interesting transition metal clusters, such as those discussed herein, act as surrogates for single metal centers in classical coordination and organometallic compounds. This is an essentially uncharted territory of cluster chemistry, one with great promise for developing new science and useful materi-

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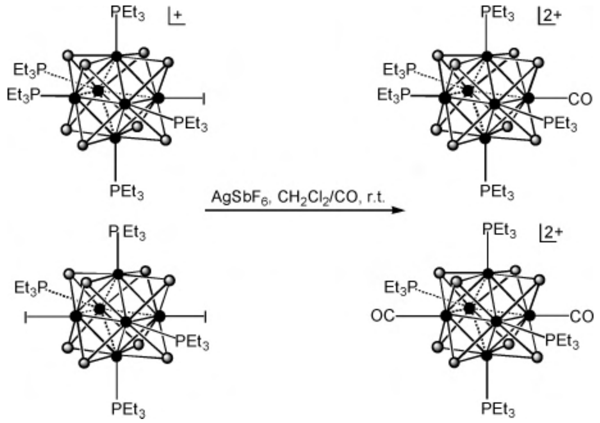
10.1021/ic700561q CCC: $37.00

Scheme 1. Synthesis of $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(CO)][SbF_6]$ and *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(CO)_2][SbF_6]_2$



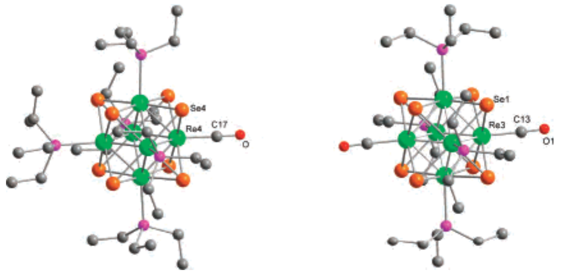


Figure 2. Crystal structure and partial labeling of the cationic clusters of **1** (left) and **2** (right). Selected interatomic distances (Å) and bond angles (deg): **1**, Re4−C17, 2.02(4), C17−O, 1.19(5), Re4−C17−O, 178(3); and **2**, Re3−C13, 1.98(1), C13−O1, 1.15(1), Re3−C13−O1, 178(1). H atoms are omitted for clarity. Color legends: Re (green), Se (orange), P (purple), O (red), gray (C).

als due to the unique structural and functional features of metal clusters.

Our initial efforts in this vein yielded two novel cluster-based organometallic compounds, $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(CO)][SbF_6]_2$ (**1**$\cdot[SbF_6]_2$) and *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4(CO)_2][SbF_6]_2$ (**2**$\cdot[SbF_6]_2$). They are the first carbonyl compounds of the hexarhenium cluster system and, most likely, of any hexanuclear metal chalcogenide clusters.

The preparation was achieved by reacting at room temperature the previously reported site-differentiated clusters, $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5I]I$ and *trans*-$[Re_6(\mu_3\text{-}Se)_8(PEt_3)_4I_2]$,[11] with $AgSbF_6$ in CO-saturated dichloromethane solutions (Scheme 1). The products were obtained as light brown crystalline solids in nearly quantitative yields (Supporting Information).

Complexes **1** and **2** were characterized by using NMR, IR, and elemental analysis. In ^{31}P NMR spectra, peaks with the expected relative integration as mandated by the stereochemistry of the clusters are shown, but they are substantially downfield-shifted as compared with those of their respective starting complexes. This can be understood as being a consequence of the ligand substitution of I^- for CO. The ^{13}C NMR spectra display, in addition to the anticipated resonances of PEt_3, peaks of the carbonyl carbon at 246 and 259 ppm, respectively, for **1** and **2**.

The presence of the CO ligand(s) is further confirmed by infrared spectroscopy. CO stretching frequencies (ν_{CO}) of **1** and **2** are observed at 2068 and 2070 cm^{-1}, respectively. These values are sizably lower than that of free CO (2143 cm^{-1}), suggesting back-bonding interactions. However, we note that essentially all computation studies on the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ clusters agree that the highest occupied molecular orbitals (HOMOs) are of e_g character.[15−18] This effectively excludes any significant overlap of the cluster core orbital with the π^* orbital of CO and thus prohibits back-donation. The IR results apparently contradict such conclusions reached by the theoretical work. We also note that in a recent study Fedorov and co-workers suggested the possibility of the HOMOs being a triply degenerate t_{2u} set, which by symmetry is suitable for back-donation to the CO π^* orbital.[19] Additionally, the oft overlooked Se atoms may play a vital role in the interaction of the cluster core with a ligand such as CO, or they may themselves interact directly with the ligand. Hence, there is a clear need to conduct more theoretical studies in order to gain a better understanding of the electronic structures of these clusters. To this end, computations are currently underway.

The nearly identical CO stretching frequencies observed for **1** and **2** merit more discussion as well. First, comparable magnitude of cluster-to-CO back-donation may be inferred. A corollary is that the electronic perturbation to a CO ligand caused by the presence of a CO ligand trans to it on the same cluster core is negligible. It also suggests that individual Re(III) centers are largely capable of holding the charge to themselves and that delocalization of charges over the whole cluster core may not be significant enough for the core to be considered, in terms of electronic structure, as a “pseudo” metal ion. Otherwise, the competition for electron density from the same cluster core should lead to reduced back-donation and a larger value of ν_{CO} for **2**.

The structures of **1** and **2** were established crystallographically (Supporting Information). Shown in Figure 2 are the structures of the cationic clusters, in which the Re−CO moiety is unequivocally displayed. The bond lengths and angles of the core vary insignificantly relative to other derivatives of the same core with different ligand sets. The Re(III)−C bond distances are 2.02(4) (**1**) and 1.98(1) Å (**2**), but no literature data are available for comparison. The C−O bond distances [1.19(5) Å in **1** and 1.15(1) Å in **2**] are only slightly longer than that of a free CO (1.13 Å).[20] Therefore, definitive conclusions may not be drawn on this particular basis as to how much the bonding interactions in **1** and **2** actually differ; the situation is no different from those of other metal carbonyls.[21]

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Besides their fundamentally interesting properties, these novel cluster carbonyls may be suitable precursors to cluster-based functional materials. Specifically, the CO ligands may be driven off by thermal, as well as photolytic, means. Our preliminary studies showed that heating a small sample (ca. 5 mg) of **1** at 250 °C under dynamic vacuum caused a gradual color change from tan to dark green. The distinct CO stretching frequency is absent in the IR spectrum of this green crystalline solid. Its ^{31}P NMR spectrum reveals three sharp peaks whose relative integration and positions both match those of the previously reported fused dimer $[Re_{12}Se_{16}(PEt_3)_{10}](SbF_6)_4$,[11] obtained by thermally decomposing the pentatriethylphosphine-substituted nitrile solvate $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5(CH_3CN)][SbF_6]_2$.[11]

Interestingly, UV irradiation of **1** in a dichloromethane solution resulted in the isolation of a novel species identified by crystallography and mass spectrometry to be $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5Cl][SbF_6]_2$ (**3**, Supporting Information). The cluster core bears a formal charge of +3 and is therefore oxidized. Dichloromethane is likely the source of the chloro ligand. Presumably, a Cl radical generated by homoleptic cleavage of the C−Cl bond is trapped by the CO-free cluster moiety $[Re_6(\mu_3\text{-}Se)_8(PEt_3)_5]^{2+}$, the photolysis product of **1**. As one-electron oxidation of the $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ cluster core has long been established,[4,9] it is reasonable to believe that contribution of one electron from the cluster core leads to the formation of the Re−Cl bond and the oxidized product.

In summary, the first $[Re_6(\mu_3\text{-}Se)_8]^{2+}$ core-containing cluster carbonyls have been successfully produced and characterized. The unexpected spectroscopic findings regarding the Re−CO bonding interactions suggest that the bonding arguments commonly accepted for metal carbonyls are not upheld, thus inviting further investigation, in particular, through computations. Thermal and photolytic studies of the mono-carbonyl complex **1** have also been conducted, with which interesting reactions (cluster condensation and radical reaction) of these novel cluster compounds have been demonstrated. These promising preliminary results portend a wealth of this essentially uncharted coordination and organometallic chemistry supported by solid-state transition metal clusters, with many fundamentally stimulating and practically significant questions waiting to be answered.

Acknowledgment. This work was supported by the University of Arizona. The authors thank Professor D. L. Lichtenberger for the use of the photolysis setup and Ms. Eva Nichol for experimental assistance. The CCD-based diffractometer was purchased through an NSF grant (CHE-96103474).

Supporting Information Available: Details of synthesis and characterization of **1** and **2** and data for their crystal structural determination. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700561Q