O₂ activation by transition metal complexes is an attractive research topic from the standpoint of bioinorganic and synthetic chemistry. Activation of O₂ by transition metal complexes is well-known, and rare in the field of metal carbonyl complexes. Paramagnetic derivatives of metal carbonyls characteristically exist as clusters, and this field has matured over the previous decades. The structures of these clusters, as well as their redox and substituted derivatives, can be predicted using simple electron-counting rules. While a relatively large number of manganese carbonyl clusters are known, manganese carbonyl chalcogenide clusters are scarce, especially with regard to selenium carbonyl complexes. In the present study, we describe a new family of manganese carbonyl selenide clusters, Mn–Se–CO.“

When Se₈ was treated with Mn₂(CO)₁₀ at a molar ratio of 1:2.6 in concentrated KOH/MeOH solutions, the novel cluster [Se₆Mn₆(CO)₁₈(O)]⁴⁻ (1) was formed in a moderate yield (Scheme 1). X-ray analysis showed that 1 was composed of two Se₂Mn₃(CO)₉ units that were linked by a μ₃-η¹,η¹,η¹,η¹-S₂Se⁵⁻ ligand, in which three Mn atoms were capped above and below by two μ₁-Se²⁻ atoms with an inversion center located at the midpoint of the Se–Se bond (Figure 1a). While one of three Mn atoms of the Se₂Mn₃(CO)₉ unit exhibited a distorted octahedral geometry, the other two Mn centers were seven-coordinated with a direct Mn–Mn interaction. Cluster 1 can be considered a result of the coupling reaction of two [Se₂Mn₃(CO)₉]⁻ units and one Se₂²⁻ unit, which was confirmed by the reaction of [Se₂Mn₃(CO)₉]⁻ with a 1/8 equiv of Se₈ in a concentrated KOH/MeOH solution. Conversely, cluster 1 could be reconverted back to [Se₆Mn₆(CO)₁₈(O)]⁴⁻ upon treatment with [Cu(MeCN)₃][BF₄] in MeCN.

Differential pulse voltammetry measurement indicated that [Et₄N]₁][I] underwent two quasi-reversible oxidations at ~0.398 V (W₇/₂ = 212 mV), suggesting that 1 could be oxidized by two electrons. As a consequence, the reactivity of cluster 1 toward O₂ was investigated. Interestingly, 1 was found to react readily with 0.5 equiv of O₂ (see Supporting Information) in MeCN to give the O-inserted cluster [Se₆Mn₆(CO)₁₈(O)]⁴⁻ (2). X-ray analysis revealed that 2 consisted of two Se₂Mn₆(CO)₉ units bridged by an O atom (Figure 1b). The average Se–O distance of 2 was 1.99(1) Å which can be considered a normal single bond (the sum of the covalent radii for Se and O is 1.90 Å), and the Se–O–Se bond angle was 106.2(3)°, which is indicative of the tetrahedral geometry around the O center. Cluster 2 evidently resulted from the insertion of an O atom into the Se–Se bond of 1, which served as a two-electron reductant toward O₂. The isomeric μ₂-Se₂O was observed in [Ir(Se₂O)(dppe)₂]⁺ from [Ir(Se₃)(dppe)₂]⁺ with peracetic acid. Although thiolates and polythiolate complexes have been shown to undergo S-oxidation with O₂ and some dichalcogenido metal carbonyl complexes exhibited the oxidative addition of small organic molecules or metal fragments across the E–E bond. In place of oxygen, selenium was also found to oxidize 1. Thus with either a 1/8 or a 1/2 equiv of Se₈ in MeCN, the Se-rich cluster [Se₁₀Mn₆(CO)₁₈(O)]⁴⁻ (3) was produced (Scheme 1). As depicted in Figure 1c, cluster 3 possessed two (μ₁-μ₂-Se₂)₂Mn₆(CO)₁₈ moieties that were bridged by a Se₂²⁻ unit with an inversion center located at the midpoint of the central Se–Se bond and gave a dumbbell-like conformation. The six Mn atoms in 3 were nonbonded (Mn···Mn, 3.665(3) to 4.244(3) Å) and held together by five Se₂²⁻ units to give rise to three different bonding modes: μ₁-μ₂,μ₁-μ₁,μ₂-μ₂; μ₁-μ₁,μ₂-μ₂,μ₁-μ₂; and μ₁-μ₂,μ₂-μ₂,μ₁-μ₁. The formation of 3 can be described as involving the insertion of Se atoms into the Se–Mn and Mn–Mn bonds of the Se₂Mn₃(CO)₉ 3 fragments of 1, accompanied by the Se–Se bond formation. Cluster 3 could also be reconverted back to 1 by the addition of Mn₂(CO)₁₀ in concentrated KOH/MeOH solutions.

Clusters 1 and 2 are both 104-electron species and cluster 3 is a 102-electron species, which all obey the 18-electron rule. Surprisingly, the magnetic measurements showed that [Et₄N]₁][I], [Et₄N][I]₂, and [Et₄N][I]₃ had effective magnetic moments, µₑffective = 2.98, 2.47, and 2.79 µ₅ at 300 K, respectively, which were close to the spin-only value (µ₀ = 2.83 µ₅) predicted for a simple S = 1 species (Figure S1). The slow decrease of µₑffective with the decreasing temperature was due to antiferromagnetic interactions between the Mn₃ units and the Se–Se bond. This is in agreement with the calculated spin density distribution, in which the Mn₃ units were rich in ±1/2 spin density (Figure S2).
interaction. Paramagnetic behavior of 1–3 was also shown by broadening of the 1H NMR signals of their [Et₄N]⁺ salt.⁷b Although electron-precise, clusters 1–3 are paramagnetic, a rare property for metal carbonyl clusters.⁵c,⁷b,¹¹,¹² Clusters 1–3 represent the first examples of electron-precise paramagnetic main-group transition metal carbonyl clusters.

The formation of 2 can be related to the higher-energy SOMO of 1 (Figure S2a), which had a large component on the antibonding interaction of the p orbitals of the Se₂-linkage. It is suggested that this orbital interacts with the π* orbitals of the O₂ molecule in its initial reaction with 1. The insertion of the p-like orbital of one of two oxygen atoms into the Se–Se bond gave the O-bridged cluster 2. On the other hand, the lower-energy SOMO of 1 received major contributions from the s and d orbitals of the Mn atoms and from the p orbital of the Se atoms of the two Se₂Mn₃(CO)₉ units, in which the overlaps between the terminal Mn atom and the two nearby Se or Mn atoms were not significant (Figure S2b). Hence, it is postulated that this orbital is a reactive site for the reaction of cluster 1 with Se₈ to give the Se-inserted cluster 3. Since we had no evidence for the Se analogue of 2, we calculated the relevant binding energies for 2 and its analogous Se-bridged cluster, which showed that the binding energy of 2 was stronger than its proposed Se-bridged cluster by more than 150 kcal/mol, which supports our experimental results. Furthermore, our calculations indicated that the unpaired electrons of 1 were significantly localized on both the terminal Mn and the central Se atoms. The central Se–O–Se fragment in 2 carried significant unpaired spin density (Figure S3).

In summary, an electron-precise, but paramagnetic, hexamanganese carbonyl selenide cluster [Se₆Mn₉(CO)₁₈]⁺ (1) was prepared, which afforded a versatile synthon for the activation of O₂ and Se₂ under mild conditions. The selectivity and their bonding properties are further elucidated by theoretical calculations.

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Supporting Information Available: Experimental details for synthesis, characterization, and X-ray structure determinations (in CIF format) of [Et₄N][1], [Et₄N][2], and [Et₄N][3]. Computational details for 1–3. This material is available free of charge via the Internet at http://pubs.acs.org.

References


