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CO and CO_2 Fixation by Se−Ru−CO Hydride Clusters

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Supporting Information

ABSTRACT: The selective insertion of CO and CO_2 into the C−O and O−H bonds of alcohols by the Se−Ru−CO hydride clusters $[(\mu\text{-H})Ru_4(CO)_{10}Se_2]^-$ (**1**) and $[(\mu_3\text{-H})Ru_5(CO)_{14}Se]^-$ (**2**) was demonstrated by a cooperative effect of the protonic hydride, the electron-rich Ru atom, and the electronegative Se atom as well as the symmetry of the clusters. These reactions generated the first examples of Se-containing ruthenium carboxylate and alkylcarbonate clusters $[\{(\mu\text{-H})Ru_4(CO)_{10}Se_2\}_2\{Ru_2(CO)_4(\mu\text{-}\eta^1{:}\eta^1\text{-OOCR})\}]^{3-}$ (R = Me, **3**; Et, **4**) and $[\{(\mu\text{-H})Ru_4(CO)_{10}Se_2\}_2\{Ru_2(CO)_4(\mu\text{-}\eta^1{:}\eta^1\text{-OOCOR})\}]^{3-}$ (R = Me, **5**; Et, **6**), respectively. These results disclosed herein provide a new avenue for the capture and storage of CO and CO_2 and useful synthetic routes to novel $RCOO^-$- and $ROCOO^-$-bridged ruthenium selenide clusters.

Fixations of CO and CO_2 have recently attracted an extensive amount of attention mainly because they are key or potentially useful C_1 feedstocks for the production of valuable C-containing molecules.[1−3] Along these lines, the utilization of transition-metal complexes bearing appropriate ligands to facilitate CO and CO_2 activation has become an increasingly desirable target. Transition-metal hydrides are known to exhibit significant activity for the reduction of CO and CO_2.[3a−d,f,4,5] In contrast with most metal hydride complexes coordinated by electron-donating ligands, hydride complexes equipped with π-accepting ligands such as CO are known to have hydrides with enhanced acidity.[6] The function of the acidity of metal hydrides with regard to CO and CO_2 activation has become intriguing in light of limited studies. The most noted example is found in $HCo(CO)_4$, which is catalytically active for carbonylation of methanol (MeOH) to acetic acid under high pressure and temperature.[7] On the other hand, CO_2 activation by protonic metal hydride complexes has rarely been observed because of the formation of unstable metallocarboxylic acid species.[8] Additionally, carboxylation of MeOH by metal carbonyl complexes has only been reported in the case of $W(CO)(N_2)(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) to form the hydridomethylcarbonato complex $WH(\eta^1\text{-OCOOMe})(CO)(dppe)_2$.[9] To date, no examples of the insertion of CO_2 into alcohols by protonic hydride metal carbonyl complexes have been demonstrated. Apart from the CO ligand, the electronegative main-group elements could also fine-tune the electronic properties of metal hydride complexes and thereby exert an effect on their acidity and reactivity patterns.[10] While chalcogen-containing metal carbonyl hydrides have been widely reported, the cooperative effect of the hydride and chalcogen elements, as well as the transition metal for CO and CO_2 activation, has remained unexplored.[11] Besides, the cluster-like Ru_xSe_y nanoparticles have been known as efficient cathode materials in the direct MeOH fuel and exhibit higher electrocatalytic activities than Ru_xS_y and Ru_xTe_y.[12] Prompted by these, we have synthesized two Se−Ru−CO hydride octahedral clusters, $[(\mu\text{-H})Ru_4(CO)_{10}Se_2]^-$ (**1**) and $[(\mu_3\text{-H})Ru_5(CO)_{14}Se]^-$ (**2**), which were found to exhibit surprising affinity toward CO and CO_2 in ROH (R = Me, Et) to form the activation products $[\{(\mu\text{-H})Ru_4(CO)_{10}Se_2\}_2\{Ru_2(CO)_4(\mu\text{-}\eta^1{:}\eta^1\text{-OOCR})\}]^{3-}$ (R = Me, **3**; Et, **4**) and $[\{(\mu\text{-H})Ru_4(CO)_{10}Se_2\}_2\{Ru_2(CO)_4(\mu\text{-}\eta^1{:}\eta^1\text{-OOCOR})\}]^{3-}$ (R = Me, **5**; Et, **6**), respectively. The present study demonstrated the unprecedented selective insertion of CO and CO_2 into the C−O and O−H bonds of ROH by two protonic hydride clusters and formation of the first examples of carboxylato and alkylcarbonato Se−Ru complexes.

When K_2SeO_3 was treated with $Ru_3(CO)_{12}$ in refluxing MeOH, cluster **1** was obtained in good yield. X-ray analysis showed that cluster **1** consisted of an octahedral Ru_4Se_2 geometry with a hydride across one of the Ru−Ru bonds (see the Supporting Information (SI), Figure S1a). The resonance for the hydride of **1**, δ = −4.48 ppm, was substantially shifted downfield compared with those of the related octahedral ruthenium hydride clusters,[13] which implied the acidic character of the hydride. This acidity was also confirmed by the treatment of **1** with NaH, forming the deprotonated product $[Ru_4(CO)_{10}Se_2]^{2-}$ (**7**; see the SI, Figure S2) with the release of H_2 (4.60 ppm in the ^1H NMR spectrum). It was of great interest that when $[Et_4N][\mathbf{1}]$ was mixed with $Ru_3(CO)_{12}$ in the presence of Et_4NBr/NaBr and heated under an atmosphere of CO in MeOH/MeCN solutions at specifically 70 °C, the novel carboxylate-bridged di-HRu_4Se_2 cluster $[Et_4N]_3[\{(\mu\text{-H})Ru_4(CO)_{10}Se_2\}_2\{Ru_2(CO)_4(\mu\text{-}\eta^1{:}\eta^1\text{-OOCMe})\}]$ ($[Et_4N]_3[\mathbf{3}]$) was formed in 68% yield (Scheme 1). Complex **3** was obtained in trace amounts in the absence of a CO atmosphere, indicating the capture of CO in this reaction.

X-ray analysis showed that **3** consisted of two **1** clusters linked by a $Ru_2(CO)_4$ fragment that was further bridged by a $MeCOO^-$ group (Figure 1). The ^1H NMR spectrum of **3** gave a single hydride resonance at δ = −12.12 ppm, which was shifted upfield compared with that for cluster **1** owing to the charge effect. Its IR spectrum also showed a diagnostic band at 1551 cm^{-1}, which was attributable to the $\nu_{asym}(COO)$ mode of the carboxylato bridge, and a weaker band at 1395 cm^{-1}, which was due to $\nu_{sym}(COO)$.

To gain insight into the generation of the key fragment $MeCOO^-$ in **3**, a MeOH solution of $Ru_3(CO)_{12}$ was placed under an atmosphere of CO and refluxed under controlled reaction conditions followed by the addition of **1**. However, this

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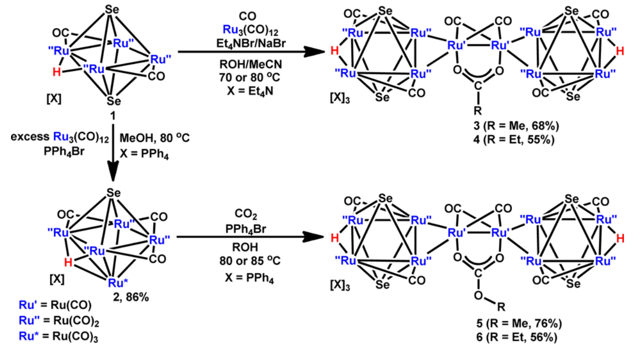
Scheme 1. Formation of CO- and CO_2-Inserted Clusters 3−6



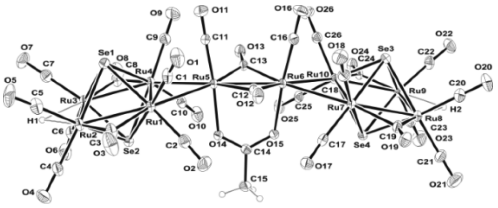


Figure 1. ORTEP of anion **3** at 30% probability.

reaction failed to yield the activation product and resulted in the recovery of **1**. Thus, formation of the carboxylate "$MeCOO^-$" in cluster **3** was presumed to occur via protonation of MeOH by the protonic hydride of **1** to form a reactive "$MeOH_2{}^+$" species with the assistance of Br^- and a subsequent CO insertion [discussed later with density functional theory (DFT) calculations], similar to HI-promoted MeOH carbonylation.[14] This hypothesis was also related to MeOH protonation by the acidic complex $HCo(CO)_4$ to form $MeOH_2{}^+$, which was potentially followed by carbonylation.[15] The speculation concerning a halide-involved mechanism in our reaction was further supported by the fact that the yield of **3** was significantly increased by the addition of NaBr salts in the course of the reactions, which was supposed to stabilize the intermediate "Me^+" (from $MeOH_2{}^+$). It was noted that the aprotic polar solvent MeCN significantly facilitated these reactions because of the increased acidity of **1**. The same reactivity pattern was also observed in the reaction of $[Et_4N][\mathbf{1}]$ with $Ru_3(CO)_{12}/Et_4NBr/NaBr$ under an atmosphere of CO in EtOH/MeCN solutions at 80 °C, affording the $EtCOO^-$-bridged cluster $[Et_4N]_3[\{(\mu\text{-H})Ru_4(CO)_{10}Se_2\}_2\{Ru_2(CO)_4(\mu\text{-}\eta^1{:}\eta^1\text{-OOCEt})\}]$ ($[Et_4N]_3[\mathbf{4}]$) in 55% yield (Scheme 1), confirming that CO inserted into the C−O bond of ROH. Cluster **4** was isomorphous with **3** on the basis of X-ray crystallography (see the SI, Figure S3) and spectroscopic methods. These results of the formation of $RCOO^-$-bridged clusters **3** and **4** motivated us to evaluate the catalytic activity of cluster **1** toward CO in MeOH. In a preliminary study, cluster **1** with NaI was treated with an atmosphere of CO and refluxed in $MeOH/CD_3CN$. ^1H NMR analysis revealed that 6% of MeOH was converted to acetic acid with turnover number 6.44, indicating that carbonylation of MeOH did occur, although the efficiency was significantly lower than that of the known group 9 systems.[14] Further studies are needed to improve the catalytic performances of **1**.

On the other hand, if cluster **1** was treated with excess $Ru_3(CO)_{12}$ in superheated MeOH solutions under a N_2 atmosphere, a Ru_3-capped hydrido octahedral cluster **2** (see the SI, Figure S1b) was obtained (Scheme 1). The hydride of **2** could be abstracted by NaH, but contrary to the HRu_4Se_2 cluster **1**, the HRu_5Se cluster **2** was inert toward CO. Surprisingly, despite the thermodynamic stability of CO_2, we found that when $[PPh_4][\mathbf{2}]$ in the MeOH solution was bubbled with CO_2 at 80 °C in the presence of PPh_4Br, the methylcarbonate cluster $[PPh_4]_3[\{(\mu\text{-H})Ru_4(CO)_{10}Se_2\}_2\{Ru_2(CO)_4(\mu\text{-}\eta^1{:}\eta^1\text{-OOCOMe})\}]$ ($[PPh_4]_3[\mathbf{5}]$) was formed as a green solid in 76% yield (Scheme 1). This reaction was significantly influenced by the choice of the countercation, for which $[PPh_4]^+$ salt proved to be the best because of its better reactivity and solubility in MeOH. The IR spectrum showed that cluster **5** had a CO absorption pattern similar to those of **3** and **4** but with different bridging $MeOCOO^-$ stretching bands at 1580 and 1438 cm^{-1}, indicating that cluster **5** exhibited a core geometry similar to that of clusters **3** and **4**. X-ray analysis (Figure 2) and ^1H NMR ($\delta = -12.13$ ppm for the hydrides) further confirmed that cluster **5** possessed two "$HRu_4(CO)_{10}Se_2$" octahedral cores linked by a $MeOCOO^-$-bridged $Ru_2(CO)_4$ moiety. According to the Cambridge Crystallographic Data Centre, there were very few examples of polynuclear complexes coordinated with monoalkylcarbonate.[16] Cluster **5** represents the first structurally characterized cluster equipped with a $MeOCOO^-$ ligand in the $\mu\text{-}\eta^1{:}\eta^1$-bonding mode. Notably, the reaction between $[PPh_4][\mathbf{2}]$ and CO_2 is also sensitive to the substituent of the alcohols. With EtOH, the reaction proceeded similarly to afford the analogous ethylcarbonate cluster $[PPh_4]_3[\{(\mu\text{-H})Ru_4(CO)_{10}Se_2\}_2\{Ru_2(CO)_4(\mu\text{-}\eta^1{:}\eta^1\text{-OOCOEt})\}]$ ($[PPh_4]_3[\mathbf{6}]$) according to elemental analysis as well as IR and ^1H NMR spectroscopic methods.

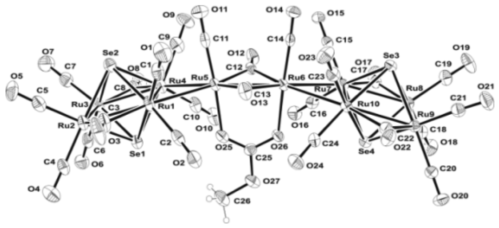


Figure 2. ORTEP of anion **5** at 30% probability.

Formation of the bridging alkylcarbonate $ROCOO^-$ groups in **5** and **6** could be considered as a result of the uptake of CO_2 by **2** accompanied by the nucleophilic attack of ROH onto the C atom of CO_2 (vide infra). These reactive alkylcarbonates, which were trapped by **5** and **6**, may serve as useful materials for the preparation of symmetrical and unsymmetrical dialkyl carbonates, which are important precursors for pharmaceuticals, agrochemicals, and lubricants.[2,17]

DFT calculations were performed in order to elucidate the carbonylation and carboxylation of alcohols by clusters **1** and **2** to form clusters **3**−**6**. Analysis showed that the lowest unoccupied molecular orbital of **1** (see the SI, Figure S4a) received a significant contribution from the d orbitals of the Ru atoms. Hence, we postulated that two molecules of **1** readily underwent a Ru−Ru edge addition of the reactive "$[Ru_2(CO)_4(\mu\text{-}\eta^1{:}\eta^1\text{-OOCR})]^-$" (R = Me, Et) derived from $Ru_3(CO)_{12}$ with $RCOO^-$,[18] which was produced from CO insertion into the C−O bond of ROH, which was induced by the five-membered intermolecular interaction of ROH with the protonic hydride of **1** (natural charge 0.32+; see the SI, Figure S5a) and the lone-pair electrons of the Se atom[19] (see the SI, Figure S6a). This led to the formation of trianionic clusters **3** and **4** (R = Me, **3**; Et, **4**). On the other hand, the highest occupied molecular orbital of **2** had a major contribution from the d orbitals of the apical Ru atom (see the SI, Figure S4b). In addition, natural population analysis[20] showed that the hydride of **2** carried a positive charge of 0.37+ and that the apical Ru atom possessed a negative charge of 0.72− (see the SI, Figure S5b). The space-filling model also revealed that the hydride-capped Ru_3 plane of **2** was less hindered and therefore susceptible to the incoming CO_2 (see the SI, Figure S7). Because ROH cannot be deprotonated by cluster **2**, it was reasonable to postulate that the Ru_{apical}−H bond of **2** might serve as a kind of "Lewis pair" that would polarize the incoming CO_2 molecule first[5d,21] (see the SI, Figure S6b), and then the electrophilic C of CO_2 would be attacked by ROH, resulting in the formation of a $ROCOO^-$ moiety accompanied by the breakage of Ru−Ru bonds to release the $Ru(CO)_x$ fragments, followed by the combination of resultant metal fragments to give rise to clusters **5** and **6** (R = Me, **5**; Et, **6**). These results indicated that the asymmetric cluster **2** plays a key role in the pronounced affinity toward CO_2, in contrast with **1**, which has a lower molecular polarizability.

In summary, we successfully synthesized two protonic hydrido Se−Ru−CO clusters, **1** and **2**, which demonstrated remarkable affinity toward CO and CO_2 in alcohols to form novel carboxylate- and alkylcarbonate-bridged di-HRu_4Se_2 clusters that were controlled by a cooperative effect of the protonic hydride, the electron-rich Ru, and the electronegative Se atom as well as the symmetry of the clusters. The facile CO and CO_2 activation shown here suggests that clusters **1** and **2** may be potentially used as precursors for the catalysis of carbonylation and carboxylation of alcohols. The related studies are currently in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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