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 [($\mu$-H)Ru$_6$(CO)$_{10}$Se$_2$]$^-$ (1) and [($\mu$-H)Ru$_6$(CO)$_{14}$Se$_4$]$^-$ (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 alkylcarbonyl clusters [($\mu$-H)Ru$_6$(CO)$_{10}$Se$_2$]$^-$ (1) and [($\mu$-H)Ru$_6$(CO)$_{14}$Se$_4$]$^-$ (2), which were found to exhibit surprising affinity toward CO and CO$_2$ in ROH (R = Me, Et) to form the activation products [($\mu$-H)-Ru$_4$(CO)$_2$Se$_2$]$_2$[$($R$u_3$(CO)$_{12}$)$_2$($\mu$-$\eta^1$-$\eta^1$-OOCR)]$^{3-}$ (R = Me, 3; Et, 4) and [($\mu$-H)-Ru$_4$(CO)$_{10}$Se$_2$]$^-$ (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 alkylcarbonyl Se–Ru complexes.

When K$_2$SeO$_3$ 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$_6$Se$_2$ 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, $\delta = -4.48$ ppm, was substantially shifted downfield compared with those of the related octahedral ruthenium hydride clusters, 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$_2$]$^-$ (7; see the SI, Figure S2) with the release of H$_2$ (4.60 ppm in the $^1$H NMR spectrum). It was of great interest that when [Et$_4$N][1] was mixed with Ru$_3$(CO)$_{12}$ in the presence of Et,NBr/NaBr and heated under an atmosphere of CO in MeOH/MeCN solutions at specifically 70 °C, the novel carboxylato-bridged di-HRu$_4$Se$_2$ cluster [Et$_4$N]$_2$[($\mu$-H)-Ru$_4$(CO)$_{10}$Se$_2$]$^-$ (R = Me, 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$_3$(CO)$_{12}$ fragment that was further bridged by a MeCOO$^-$ group (Figure 1). The $^1$H NMR spectrum of 3 gave a single hydride resonance at $\delta = -12.12$ 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 ν$_{asym}$(CO) mode of the carboxylato bridge, and a weaker band at 1395 cm$^{-1}$, which was due to ν$_{sym}$(CO).

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 following the addition of 1. However, this
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 “MeOH2” 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. This hypothesis was also related to MeOH protonation by the acidic complex HCo(CO)₅ to form MeOH₂⁺, which was potentially followed by carbonylation. 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”⁵⁺ (from MeOH₂⁺). 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 [Et₄N]⁺[Et₃N]⁻ with Ru₄(CO)₁₂/et/NaBr under an atmosphere of CO in EtOH/MeCN solutions at 80 °C, affording the MeCOO⁻-bridged cluster [Et₄N]⁺[([μ-H]Ru₄(CO)₁₀Se₂)₂{Ru₂(CO)₄(μ-η¹:η¹-OCOEt)}][[Et₃N]⁻[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 1 toward CO in MeOH. In a preliminary study, cluster 1 with NaI was used to form an atmosphere of CO and refulxd in MeOH/CDCl₃. 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. Further studies are needed to improve the catalytic performances of 1.

On the other hand, if cluster 1 was treated with excess Ru₄(CO)₁₂ in superheated MeOH solutions under a N₂ atmosphere, a Ru₄-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 HRu₄Se₂ cluster 1, the HRu₄Se cluster 2 was inert toward CO. Surprisingly, despite the thermodynamic stability of CO₂, we found that when [PP₄H]⁺[2] in the MeOH solution was bubbled with CO₂ at 80 °C in the presence of PPh₄Br, the methylcarbonylate cluster [PP₄H]⁺,#([μ-H]Ru₄(CO)₁₀Se₂){Ru₂(CO)₄(μ-η¹:η¹-OCOEt)}][[PP₄H]⁺[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 [PP₄H]⁺ 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 (δ = −12.13 ppm for the hydrides) further confirmed that cluster 5 possessed two “HRu₄(CO)₁₀Se₂” octahedral cores linked by a MeOCOO⁻-bridged Ru₃(CO)₄ moiety. According to the Cambridge Crystallographic Data Centre, there were very few examples of polynuclear complexes coordinated with monoalkylcarbamate. Cluster 5 represents the first structurally characterized cluster equipped with a MeOCOO⁻ ligand in the μ-η¹:η¹-bonding mode. Notably, the reaction between [PP₄H]⁺[2] and CO₂ is also sensitive to the substituent of the alcohols. With EtOH, the reaction proceeded similarly to afford the analogous ethylcarbamate cluster [PP₄H]⁺,#([μ-H]Ru₄(CO)₁₀Se₂){Ru₂(CO)₄(μ-η¹:η¹-OCOEt)}][[PP₄H]⁺[6]] according to elemental analysis as well as IR and ¹H NMR spectroscopic methods.

Formation of the bridging alkylcarbonyl ROCOO⁻ groups in 5 and 6 could be considered as a result of the uptake of CO₂ by 2 accompanied by the nucleophilic attack of ROH onto the C atom of CO₂ (vide infra). These reactive alkylcarbanates, 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.

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 “Ru₄(CO)₆(μ-η¹:η¹-OCOCR)”⁻⁻ (R = Me, Et) derived from Ru₄(CO)₁₂ with CO₂, which was produced from CO insertion into the C−O bond of ROH, which was induced by the first 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 trinionic 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...
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 S6b). The space-filling model also revealed that the hydride-capped Ru plane of 2 was less hindered and therefore susceptible to the incoming CO2 (see the SI, Figure S7). Because ROH cannot be deprotonated by cluster 2, it was reasonable to postulate that the RuApicu−H bond of 2 might serve as a kind of “Lewis pair” that would polarize the incoming CO2 molecule first5–21 (see the SI, Figure S6b), and then the electrophilic C of CO2 would be attacked by ROH, resulting in the formation of a ROCO− moiety accompanied by the breakage of Ru−Ru bonds to release the Ru(CO)2 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 CO2 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 CO2 in alcohols to form novel carboxylate- and alkylcarbonate-bridged di-HRu4Se2 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 CO2 activation shown here suggests that clusters 1 and 2 may be potentially used as precursors for the catalysis of carbon monoxide 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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**REFERENCES**