

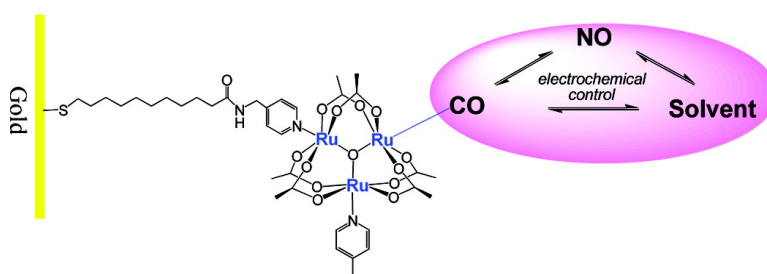
Communication

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J. Am. Chem. Soc., **2004**, 126 (24), 7434-7435 • DOI: 10.1021/ja049478j • Publication Date (Web): 29 May 2004

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Electrochemical Control of CO/NO Ligand Exchange in a Triruthenium Cluster Monolayer Assembled on a Gold Electrode Surface

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The synthesis and assembly of nanomaterials from molecular components are receiving a great deal of attention because of expectations in a wide variety of applications such as molecular devices and sensors.^{1,2} Transition-metal complexes and clusters are eminent candidates for the molecular building blocks because of their versatile physical and chemical properties. Among them, oxo-centered triruthenium complexes of the type $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6\text{L}_6]^{n+}$,³ which show reversible multistep electron transfer, have been of significant interest to explore the synthesis of ligand-bridged extended architectures,^{4,5} which is facilitated by site-selective ligand substitution in solution.^{6,7} Recently, we succeeded in constructing a self-assembled monolayer (SAM)⁸ and multilayer⁹ on a gold surface from $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{CO})(\text{L}_1)(\text{L}_2)]$, where $\text{L}_1 = \{(\text{NC}_5\text{H}_4)\text{CH}_2\text{NHC}(\text{O})(\text{CH}_2)_{10}\text{S}-\}_2$ and $\text{L}_2 = 4$ -methylpyridine (denoted as $[(\text{Ru}^{\text{II}}-\text{CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ below, in which the Roman and Arabic numerals indicate the formal oxidation states of Ru and net charge of the cluster, respectively). Because of the availability of precise ligand control in the ruthenium clusters, molecular switching properties are highly expected for the functional layers.

What we have newly established in this study is summarized in Scheme 1. First, the CO ligand can be reversibly introduced into the Ru_3 unit of the SAM under electrochemical control. Second, and most importantly, the NO molecule, which is known to form many metal–nitrosyl complexes and plays key roles in many chemical, biological, and environmental systems,^{10–12} is efficiently introduced into the SAM via a $1e^-$ electrochemical oxidation of the Ru_3 cluster. We are able to repeatedly switch the ligand among CO, NO, or solvent on the electrode surface as needed by electrochemically tuning the electronic state of the Ru site. These reactions were confirmed by both cyclic voltammetry (CV) and in situ IR measurements. These unique electrochemically controlled surface reactions are more convenient and efficient than conventional ligand exchange reactions in solution.

The synthesis of the complex was previously described.⁸ The thin gold film (ca. 50 nm) was chemically deposited on a Si prism.¹³ The SAM was prepared on the gold surface by immersing the electrode in a 50 μM ethanol solution for ca. 20 h at room temperature. The in situ IR measurement with the Kretschmann ATR configuration¹⁴ was employed to trace the reaction process. CV and IR measurements were carried out in aqueous (0.1 M HClO_4) or nonaqueous solutions (CH_3CN or 1,2-dichloroethane with 0.1M $n\text{-Bu}_4\text{NPF}_4$) in the dark to avoid possible photochemical reactions. All electrode potentials were referenced to the saturated calomel electrode (SCE). The IR spectra were obtained by integrating 15 interferograms (ca. 3 s) at a resolution of 4 cm^{-1} .

The solid line in Figure 1a shows the CV of the original SAM

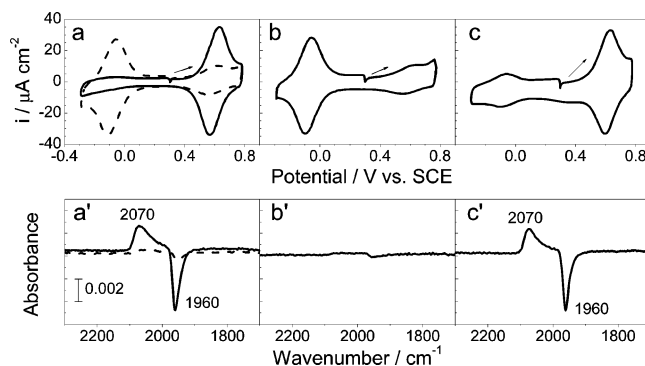
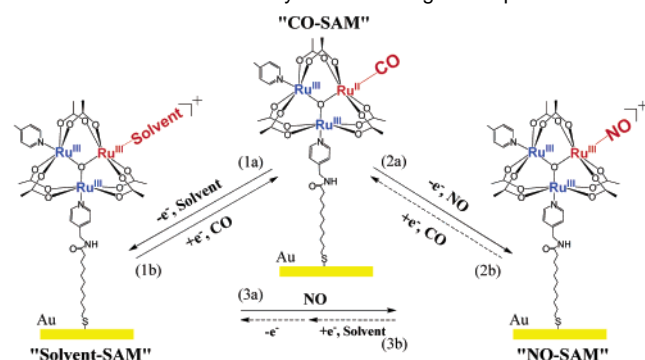


Figure 1. CVs and IR spectra at +0.8 V for (a, a'): CO-SAM (solid) and solvent-SAM (dotted) in 0.1 M HClO_4 . (b, b'): Solvent-SAM after contact with CO at +0.3 V for 1 h. (c, c'): Solvent-SAM after contact with CO at -0.3 V for 30 min. Each IR background was recorded at +0.3 V. Scan rate: 500 mV/s.

Scheme 1. Electrochemically Controlled Ligand Replacement



(denoted as "CO-SAM") in 0.1 M HClO_4 with a nearly full coverage of 6.0×10^{13} molecule/ cm^2 .⁸ A single redox peak is observed around +0.6 V, corresponding to the $1e^-$ electron transfer between $[(\text{Ru}^{\text{II}}-\text{CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ and $[(\text{Ru}^{\text{III}}-\text{CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+1$.¹⁵ The potential difference IR spectrum taken at +0.8 V (background: +0.3 V) (Figure 1a', solid line) shows a downward peak at 1960 cm^{-1} and an upward peak at 2070 cm^{-1} , corresponding to the stretching vibrations of the CO ligand in the $[(\text{Ru}^{\text{II}}-\text{CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ and $[(\text{Ru}^{\text{III}}-\text{CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+1$, respectively, during the redox reaction. The blue-shift in the CO peak position reveals a decrease in the electron density on the Ru ion by the oxidation reaction, which weakens the π -electron backdonation from the Ru to CO and hence strengthens the C–O bond.¹⁵

As shown by the dotted line in Figure 1a, the redox peak at +0.6 V significantly decreased and a new peak appeared at -0.1 V after keeping the potential at +0.8 V for 20 min. The in situ IR spectrum showed that the CO peak disappeared (Figure 1a', dotted line), indicating that the CO is dissociated from $[(\text{Ru}^{\text{III}}-\text{CO})\text{Ru}^{\text{III}}-\text{Ru}^{\text{III}}]^+1$ and could be replaced by other ligands available (possibly

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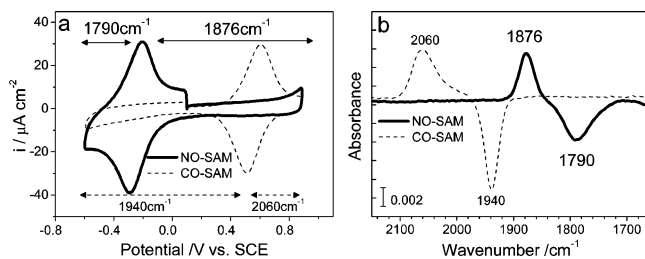


Figure 2. (a) CVs and (b) IR spectra of CO-SAM before (dotted) and after (solid) contact with NO at +0.8 V for 1 h in 1,2-dichloroethane. IR spectra were recorded at +0.8 V (dotted) and +0.1 V (solid) with respect to that at +0.3 V and -0.5 V, respectively. Scan rate: 500 mV/s.

by solvent molecules,^{6,7} as denoted by “solvent-SAM” here; Scheme 1, reaction 1a). It is noted that the rest potential of the solvent-SAM is ca. +0.3 V and is almost identical to that of CO-SAM but with a different oxidation state, i.e., $[(\text{Ru}^{\text{III}}-\text{solvent})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$.

It is interesting to see whether CO can be reintroduced into the solvent-SAM. As shown in Figure 1b,b', no change was observed in either the CV or IR spectrum of the solvent-SAM after contact with the CO-saturated solution for 1 h at the rest potential (ca. +0.3 V). However, when the potential was changed to -0.3 V, where the solvent-SAM was reduced to $[(\text{Ru}^{\text{II}}-\text{solvent})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$, dramatic changes were observed after 30 min. Both the CV (Figure 1c) and IR spectrum (Figure 1c') became similar to those of the original CO-SAM (solid line in Figure 1a,a'), indicating that CO replaces the solvent ligand and rebinds to the central Ru ion under potential control (Scheme 1, reaction 1b). This result is reasonable if one considers the higher stability of $\text{Ru}^{\text{II}}-\text{CO}$ than that of $\text{Ru}^{\text{III}}-\text{CO}$.^{6,7} It is noteworthy that this is an advantage over the conventional syntheses in bulk solution where the chemical reduction of $[(\text{Ru}^{\text{III}}-\text{solvent})]^+$ by hydrazine is necessary to form the $[(\text{Ru}^{\text{II}}-\text{CO})]^0$ cluster, while such a surface reaction can be quantitatively controlled by the electrochemical potential.

Further investigation of the reaction of SAM toward the NO molecule revealed a significantly different behavior from CO, which provides us with the selective coordination of two molecules under controlled potentials. Figure 2a,b shows the CVs and IR spectra of CO-SAM, respectively, before (dotted line) and after (solid line) contacting with NO at +0.8 V for 1 h in a 1,2-dichloroethane solution. A redox peak was newly observed at -0.25 V (Figure 2a, solid line) while the one due to CO-SAM at +0.6 V (Figure 2a, dotted line) completely disappeared. The peak position of the new redox peak is near that of the solvent-SAM in the CV (Figure 1b), but the in situ IR spectrum (Figure 2b, solid line) recorded at +0.1 V (background: -0.5V) shows a pair of new IR peaks at 1876 cm^{-1} (upward) and 1790 cm^{-1} (downward) and is totally different from that of the original CO-SAM (Figure 2b, dotted line), indicating that a new ligand was introduced instead of the solvent. The CV and IR spectrum of the newly formed species resemble those of $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{NO})(\text{py})_2]\text{PF}_6$ in solution.^{16,17} These results demonstrate well that NO replaces the CO ligand to form $[(\text{Ru}^{\text{III}}-\text{NO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ (Scheme 1, reaction 2a). The redox peak at -0.25 V (Figure 2a, solid line) can be attributed to the $1e^-$ transfer between $[(\text{Ru}^{\text{III}}-\text{NO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ and $[(\text{Ru}^{\text{II}}-\text{NO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$, whose IR absorption was observed at 1876 and 1790 cm^{-1} , respectively. The blue-shift in the $\nu(\text{NO})$ upon oxidation can be explained by a similar back-donation mechanism like that for CO-SAM. It should be mentioned here that $[(\text{Ru}^{\text{II}}-\text{NO}^+)\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ is another possible state due to the strong π -electron acceptance ability of NO^+ . As recently pointed out by Toma et al., $[(\text{Ru}^{\text{III}}-\text{NO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ seems to be a more possible species between the two equilibrium structures.¹⁶ The NO-SAM could also be created from the solvent-SAM if the SAM was electrochemically kept as

$[(\text{Ru}^{\text{III}}-\text{solvent})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ (Scheme 1, reaction 3a) but could not be formed from $[(\text{Ru}^{\text{II}}-\text{solvent})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ after contact with the NO-saturated solution.

Finally, NO-SAM $[(\text{Ru}^{\text{II}}-\text{NO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$ can be switched to solvent-SAM (Scheme 1, reaction 3b) or CO-SAM (Scheme 1, reaction 2b) if CO is present in solution. In this case, however, the reversibility of this process is relatively low (as denoted by dotted arrows) compared to the reintroduction of CO into the solvent-SAM, which may be related to the lower stability of NO-SAM compared to that of CO-SAM.

On the other hand, as shown in Figure 2b, the IR bandwidth of the CO ligand in $[(\text{Ru}^{\text{III}}-\text{CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ is much wider than that in $[(\text{Ru}^{\text{II}}-\text{CO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$, while the bandwidth of the NO ligand in $[(\text{Ru}^{\text{III}}-\text{NO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^+$ is much narrower than that in $[(\text{Ru}^{\text{II}}-\text{NO})\text{Ru}^{\text{III}}\text{Ru}^{\text{III}}]^0$. The ligand exchange only takes place when the CO or NO ligand has a wider IR bandwidth (Figures 1 and 2). The wider IR peak would indicate a broader diversity of the $\text{Ru}^{\text{III}}-\text{CO}$ and $\text{Ru}^{\text{II}}-\text{NO}$ oscillators in the mixed valence states⁴ and may be attributed to one of the possible origins for the reactivity of the ligand exchange in the Ru_3 cluster monolayer.

It should be emphasized here that the solvent also plays an important role in the transformation of the CO-SAM to the NO-SAM. The NO-SAM can be formed in 1,2-dichloroethane or aqueous solution but not in CH_3CN solution. Such solvent effects were not observed for the CO reintroduction process, implying that the interaction between NO and Ru is heavily influenced by the coordination ability of the solvent used. A current study is still in progress.

In summary, as shown in Scheme 1, we have developed a very unique electrochemically controlled ligand-switching ability among CO, NO, and solvent in the Ru_3 cluster monolayer for the first time. The present results demonstrate that precise control of the electronic environment of the central Ru ion is crucial to the ligand exchange ability of the SAM.

Acknowledgment. This work was supported by JST (PRESTO and CREST) and MEXT (Basic Research No. 14205121 and Priority Areas 417). M.A. acknowledges the support from a Sasakawa Scientific Research Grant from the Japan Science Society.

Supporting Information Available: IR spectra of Ru-CO cluster in KBr matrix and Ru-CO SAM on the gold surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA049478J