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Novel transition-metal complexes in rare gas matrices

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Introduction

The interaction of metal centers with small molecules (i.e., CO, N₂, O₂, CO₂, H₂, CH₄, etc) is of considerable interest in the widely different fields of catalysis, synthesis, atmospheric chemistry, and biology. Among these small molecules, CO and N₂ are two of the most important in transition-metal chemistry from an academic or an industrial viewpoint. In the present study, reactions of laser-ablated transition-metal atoms and clusters with carbon monoxide and dinitrogen in excess rare gas have been investigated by matrix isolation infrared spectroscopy, which generate a number of novel metal and metal cluster complexes.¹⁻⁷

Methods

An experimental setup for laser ablation and matrix-isolation IR spectroscopy was used.¹⁻⁷ Briefly, metal atoms ablated with the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate) were codeposited with CO and/or N₂ in excess rare gas onto a CsI window at 4 K. IR spectra were recorded on a BIO-RAD FTS-6000e spectrometer at 0.5 cm⁻¹ resolution by using a liquid-nitrogen-cooled HgCdTe (MCT) detector for the range of 5000–400 cm⁻¹. Samples were annealed at different temperatures and subjected to broadband irradiation ($\lambda > 250$ nm) from a high-pressure mercury arc lamp (Ushio, 100 W).

Density functional theory calculations were performed to predict the structures and vibrational frequencies of the observed reaction products using the Gaussian 03 program. The B3LYP and BP86 density functional method were utilized. All geometrical parameters were fully optimized and the harmonic vibrational frequencies were calculated with analytical second derivatives.

Results and discussion

Sc₂[$\eta^2(\mu_2\text{-C,O})$],¹ the first homoleptic dinuclear metal carbonyl with an unprecedented bridging and side-on-bonded CO, generated from the reaction of laser-ablated Sc atoms with CO in a solid argon matrix, exhibits an unusually low C–O stretching frequency at 1193.4 cm⁻¹, characteristic of an anomalously weakened C–O bond (Fig. 1). This CO-activated molecule undergoes ultraviolet–visible photoinduced rearrangement to the CO-dissociated molecule, *c*-Sc₂($\mu\text{-C}$)($\mu\text{-O}$). The infrared absorptions of the new molecules are accurately predicted by quantum chemical calculations, and the activation energy for the isomerization of Sc₂[$\eta^2(\mu_2\text{-C,O})$] to *c*-Sc₂($\mu\text{-C}$)($\mu\text{-O}$) is calculated to be 15.10 kcal/mol. Our experimental and theoretical results schematically depict an activation process to CO dissociation. In the reaction

of Ti atoms with CO/Ar, a windmill-like trititanium cluster with side-on-bonded CO ligands, which may have antiaromatic character, was generated, along with other side-on-bonded mono- and polycarbonyl di- and trititanium clusters.²

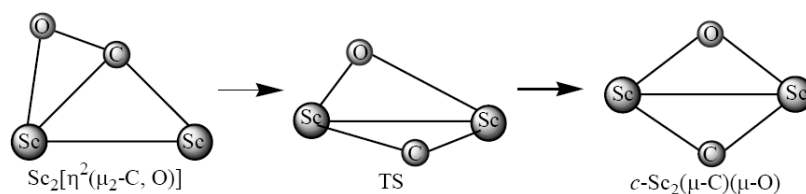


Fig. 1. C-O bond weakening on the metal clusters

Various metal dinitrogen complexes have been prepared in low-temperature matrix samples by codeposition of laser-ablated metal atoms with N₂.^{4,6} However, naked Cu(0) atoms are inert toward N₂. Interestingly, it was found that the reactivity of copper was greatly affected by the presence of CO in the N₂ matrix. New carbonylcopper dinitrogen complexes NNCuCO and (NN)₂CuCO have been prepared by the reactions of laser-ablated Cu atoms with N₂ in excess argon.⁷ DFT calculations of the geometry structures, vibrational frequencies, relative absorption intensities, and isotopic shifts strongly support the experimental infrared spectra assignments. The experimental results reveal promoted adsorption of N₂ on Cu atoms by preadsorbed CO as N₂ does not react with the Cu atoms. The theoretical results for reaction characteristics between the coadsorbed CO and N₂ agree with the experimental findings. The joint investigations provide insights regarding CO and N₂ cooperative adsorption effects and consequent reaction mechanisms. The preadsorption of one ligand (CO in our case) can effectively change the electronic structure of the metal atoms or clusters that might enable the subsequent reaction with further reactant molecules that would otherwise not be possible.

References

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