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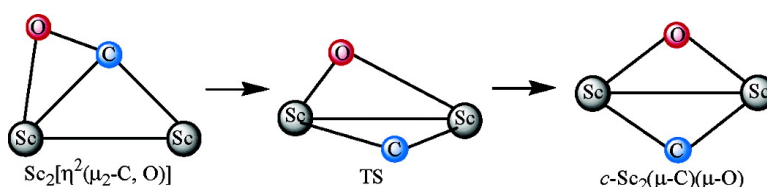
Observation of Anomalous C–O Bond Weakening on Discandium and Activation Process to CO Dissociation

Ling Jiang, and Qiang Xu

$Sc_2[\eta^2(\mu_2\text{-C, O})]$ → TS → $c\text{-}Sc_2(\mu\text{-C})(\mu\text{-O})$

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Observation of Anomalous C−O Bond Weakening on Discandium and Activation Process to CO Dissociation

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The interaction of carbon monoxide with transition metals may lead to breaking and making chemical bonds and triggering important catalyzed reactions.[1] The long-standing goal of elucidating mechanisms of the catalyzed reactions has motivated numerous experimental investigations of CO chemisorption on transition metal surfaces. Remarkably, the chemisorbed CO molecular state with unusual low C−O stretching frequencies (ν_{C-O}) (ca. 1200 cm^{-1}) has been found on some transition metal surfaces.[2] The so-called "bridging" and "semi-bridging" types of CO coordination have also been recognized and interpreted by several groups.[3] For instance, a low ν_{C-O} value (1330 cm^{-1}) was found for $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_7$.[3e] Even so, there has been no report thus far on a simple homoleptic metal carbonyl molecule with a side-on-bonded CO, and almost nothing is known about the structural configuration of CO as a precursor to dissociation. Here we report $Sc_2[\eta^2(\mu_2\text{-}C, O)]$, an unprecedented homoleptic dinuclear metal carbonyl with an asymmetrically bridging and side-on-bonded CO, and evidence that it is an intermediate to CO dissociation.

The matrix-isolated $Sc_2[\eta^2(\mu_2\text{-}C, O)]$ (**1**) molecules were produced by co-deposition of laser-ablated Sc atoms with CO in excess argon at 7 K and were investigated using FTIR spectroscopy.[4] Recent studies have shown that, with the aid of an isotopic substitution technique, matrix isolation infrared spectroscopy combined with quantum chemical calculation is very powerful in investigating the spectrum, structure, and bonding of novel species.[5,6] The IR spectra as a function of changes of CO concentrations and laser energies are of particular interest here. With high CO concentration (0.50%) and low laser energy (3 mJ/pulse), $ScCO^+$ (1924.1 cm^{-1}) and $Sc(CO)_n$ ($n = 1-4$) (1834.9; 1852.8; 1778.2; 1717.0; 1822.7; and 1865.6 cm^{-1}) are the primary products upon sample deposition (not shown here), which have been previously identified.[7] New absorptions were produced on sample depositions with lower CO concentration (0.06%) and higher laser power (12 mJ/pulse) (Table 1 and Figure 1). The 1203.1 and 1193.4 cm^{-1} bands increased on sample annealing, disappeared after broad-band irradiation, and did not recover upon further annealing, whereas new bands at 742.6, 740.3, and 614.1 cm^{-1} slightly increased on annealing, sharply increased upon broad-band irradiation at the expense of the 1203.1 and 1193.4 cm^{-1} bands, and observably decreased on further annealing. On the basis of the growth/decay characteristics as a function of changes of experimental conditions, the absorptions in the 1180−1210 cm^{-1} region can be grouped together to one species and the absorptions in the 600−750 cm^{-1} region to another one. Furthermore, the latter comes from an isomer of the former. Note that the new bands were only observed with lower CO concentration and higher laser power than those for mononuclear Sc carbonyls, indicating that the new products involve more than one Sc atom. Doping with CCl$_4$ as an electron scavenger has no effect on these bands, indicating that the products are neutral (Figure 1).

The 1203.1 and 1193.4 cm^{-1} absorptions shifted to 1175.2 and 1165.8 cm^{-1} with $^{13}C^{16}O$ and to 1181.0 and 1171.5 cm^{-1} with

Table 1. IR Absorptions (in cm^{-1}) Observed from Co-deposition of Laser-Ablated Sc Atoms with CO in Excess Argon at 7 K

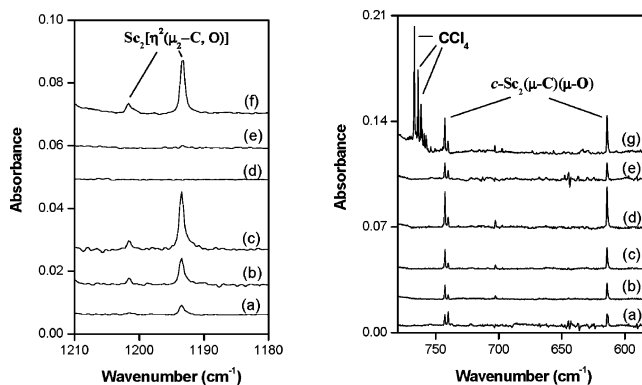| $^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{12}C/^{13}C$	$^{16}O/^{18}O$	identification
1203.1	1175.2	1181.0	1.0237	1.0187	$Sc_2[\eta^2(\mu_2\text{-}C,O)]$ site
1193.4	1165.8	1171.5	1.0237	1.0187	$Sc_2[\eta^2(\mu_2\text{-}C,O)]$
742.6	723.3	738.9	1.0267	1.0050	$c\text{-}Sc_2(\mu\text{-}C)(\mu\text{-}O)$
740.3	721.2	736.6	1.0265	1.0050	$c\text{-}Sc_2(\mu\text{-}C)(\mu\text{-}O)$ site
614.1	612.9	589.8	1.0020	1.0412	$c\text{-}Sc_2(\mu\text{-}C)(\mu\text{-}O)$

Figure 1. IR spectra in the 1210−1180 and 780−580 cm^{-1} regions for laser-ablated Sc atoms co-deposited with 0.06% CO in argon at 7 K: (a) 60 min of sample deposition, (b) after annealing to 28 K, (c) after annealing to 32 K, (d) after 20 min of broad-band irradiation, (e) after annealing to 36 K, (f) doping with 0.01% CCl$_4$, after annealing to 32 K, and (g) after 20 min of broad-band irradiation following (f).

$^{12}C^{18}O$, respectively (Table 1),[8] exhibiting isotopic frequency ratios ($^{12}C^{16}O/^{13}C^{16}O = 1.0237$ and 1.0237; $^{12}C^{16}O/^{12}C^{18}O = 1.0187$, and 1.0187) characteristic of C−O stretching vibrations. In the mixed $^{12}C^{16}O + {}^{13}C^{16}O$ and $^{12}C^{16}O + {}^{12}C^{18}O$ experiments, only pure isotopic counterparts were observed, indicating that only one CO subunit is involved. Therefore, the absorptions at 1203.1 and 1193.4 cm^{-1} are due to the C−O stretching of a species having a Sc_xCO stoichiometry with $x \geq 2$ in different matrix sites.

The 742.6 and 740.3 cm^{-1} bands showed very small shifts with $^{12}C^{18}O$ (3.7 and 3.7 cm^{-1}) but shifted to 723.3 and 721.2 cm^{-1} with $^{13}C^{16}O$. The $^{12}C^{16}O/^{13}C^{16}O$ frequency ratios of 1.0267 and 1.0265 (Table 1) imply that these bands are mainly due to a Sc−C stretching of the same species in different matrix sites.[8] The 614.1 cm^{-1} band showed a very small shift with $^{13}C^{16}O$ (1.2 cm^{-1}) but a large shift with $^{12}C^{18}O$ (24.3 cm^{-1}). The $^{12}C^{16}O/^{12}C^{18}O$ frequency ratio of 1.0412 indicates that the 614.1 cm^{-1} band is mainly due to a Sc−O stretching. The mixed isotopic spectra[8] showed that only one C and one O atom, which are separated from each other, are involved.

DFT calculations at the BP86/6-311++G(d,p) and BPW91/6-311++G(d,p) levels have been performed for Sc_xCO ($x = 1-4$) for all the possible isomers.[9,10] The reliability trial calculations show that the ν_{C-O} values for the linear ScCO are 1843.3 (BP86) and 1852.6 (BPW91) cm^{-1}, respectively, in excellent agreement with
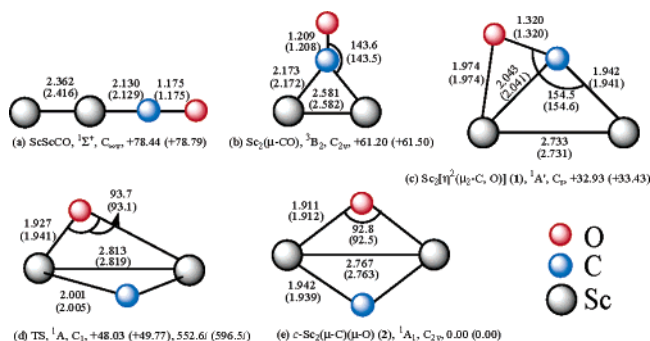
Figure 2. Optimized structures (bond lengths in Å, bond angles in degrees), electronic ground state, point group, and the relative energies (in kcal/mol) of the Sc$_2$CO isomers calculated at the BP86/6-311++G(d,p) and BPW91/6-311++G(d,p) (in parentheses) levels. For the transition state (TS, (d)), the letter "*i*" denotes the imaginary frequency (in cm^{-1}) and the dihedral angle is 65.8°.

the present experiments and previous reports.[7] The calculations show that only **1**, a unique molecule with a bridging and side-on-bonded CO, nicely matches the experimental vibrational frequencies, relative absorption intensities, and isotopic shifts in the 1180–1210 cm^{-1} region and *c*-Sc$_2$(μ-C)(μ-O) (**2**), the CO dissociated isomer of **1**, in the 600–750 cm^{-1} region. The ν_{C-O} values of **1** are 1237.6 (BP86) and 1240.4 cm^{-1} (BPW91), respectively, whereas those of Sc$_3$[η^2(μ_3-C, μ_2-O)] are predicted to be 1026.5 and 1032.4 cm^{-1} and those of Sc$_4$[η^2(μ_3-C, μ_3-O)] to be 1061.2 and 1070.9 cm^{-1}, respectively.

The excellent agreement between experimental and calculated vibrational frequencies, relative absorption intensities, and isotopic shifts points to the identification of the 1193.4 cm^{-1} absorption as the C–O stretching of **1**, and the 742.6 and 614.1 cm^{-1} absorptions as the Sc–C and Sc–O stretchings of **2**. Hereafter, mainly BP86 results are presented for discussions. The calculated ^{12}C^{16}O/^{13}C^{16}O and ^{12}C^{16}O/^{12}C^{18}O frequency ratios of **1** are 1.0252 and 1.0197,[8] respectively, in accord with the observed values (1.0237 and 1.0187). The Sc–Sc stretching is predicted to be 219.5 cm^{-1}, which is beyond the present spectral range of 5000–400 cm^{-1}. The Sc–C and Sc–O stretching frequencies of **1** are predicted to be 663.0 and 546.7 cm^{-1}, respectively, while their intensities (1 and 15 km/mol) are too small to be detected. Excellent agreement between the experimental and calculated results has also been observed for **2**. The identifications of **1** and **2** are strongly supported by the scale factors (observed to calculated frequency ratio). The scale factors are 0.964 for the C–O stretching of **1**, 0.987 for the Sc–C stretching of **2**, and 1.020 for the Sc–O stretching of **2**.[8] Additionally, the intensity ratio of the observed 1193.4, 742.6, and 614.1 cm^{-1} absorptions is 1.0:0.20:0.35, in good agreement with the corresponding calculated value, 1.0:0.19:0.40.

Our BP86 calculations predict that **1** has a ^{1}A′ ground state with a Sc–O bond of 1.974 Å and two unequivalent Sc–C bonds of 1.942 and 2.043 Å in the same plane (Figure 2). CO leans toward the two Sc atoms with ∠Sc–C–O of 154.5°. The anomalous R_{C-O} in **1** is 1.320 Å, much longer than that in OSc(η^2-CO) (1.211 Å).[11] In contrast, the η^2(μ_3-C, μ_2-O) ligand in (η^5-C$_5$H$_5$)$_3$Nb$_3$(CO)$_7$ leans toward the Nb(1)–Nb(2) vector, with ∠Nb(3)–C-O of 169.6° and R_{C-O} of 1.303 Å.[3e] An analogous Mn–C–N unit with ∠Mn–C–N of 168° is observed in (μ-*p*-CH$_3$C$_6$H$_4$NC)Mn$_2$(Ph$_2$PCH$_2$PPh$_2$)$_2$(CO)$_4$.[3f]

1 lies 32.93 kcal/mol above its most stable isomer, **2**, whereas the terminal-bonded ScScCO and bridge-bonded Sc$_2$(μ-CO) isomers are 78.44 and 61.20 kcal/mol higher than **2** (Figure 2). The markedly elongated C–O bond (1.320 Å) in **1** is inclined to dissociation. The C–O bond is dissociated in the TS, in which the dihedral angle

is 65.8°. The barrier height for the **1** to **2** isomerization is 15.10 kcal/mol,[8] which can be attained by ultraviolet visible irradiation. The snapshots of isomerism have fortunately been captured by the matrix-isolation technique.

Our BP86 calculations show that the side-on-bonded mononuclear Sc(η^2-CO) (^{4}A″, C_s, R_{C-O} = 1.233 Å, ν_{C-O} = 1510.9 cm^{-1}) lies 14.09 kcal/mol above the most stable, linear ScCO ($^4\Sigma^-$, $C_{\infty v}$, 1.181 Å, 1843.3 cm^{-1}), indicating a drastic C–O bond weakening by the side-on-bonding coordination. Larger R_{C-O} and smaller ν_{C-O} values are predicted for dinuclear **1** (^{1}A′, C_s, 1.320 Å, 1237.6 cm^{-1}), trinuclear Sc$_3$[η^2(μ_3-C, μ_2-O)] (^{2}A″, C_s, 1.405 Å, 1026.5 cm^{-1}), and tetranuclear Sc$_4$[η^2(μ_3-C, μ_3-O)] (^{1}A′, C_s, 1.387 Å, 1061.2 cm^{-1}), suggesting that R_{C-O} increases and ν_{C-O} decreases with increasing the extent of side-on-bonding. Such C–O bond weakening has been reported for chemisorbed CO in side-on-bonded modes on transition metal surfaces as model catalysts, for which the ν_{C-O} values were observed around 1100–1400 cm^{-1}.[2] Interestingly, the structures of Sc$_2$CO isomers in Figure 2 represent almost all the main modes of metal–CO coordination to date. The present observation schematically depicts the whole process starting with the interaction of CO with metal to CO dissociation. We must conclude that the present finding is a key for explaining the unusual low ν_{C-O} values (1100–1400 cm^{-1}) of the chemisorbed CO molecules on transition metal surfaces[2] and for understanding the activation process to CO dissociation on metal catalysts.

Supporting Information Available: Isotopic IR data; calculated potential energy surface for the isomerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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