

Reactions of Th Atoms with CO: The First Thorium Carbonyl Complex and an Unprecedented Bent Triplet Insertion Product

Mingfei Zhou and Lester Andrews*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Jun Li and Bruce E. Bursten*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received September 13, 1999

Transition metal carbonyl complexes, $M(\text{CO})_n$, are cornerstones of modern coordination chemistry and organometallic chemistry.¹ Carbon monoxide activation and reduction by transition metal atoms are important in a great many industrial processes.² By contrast, the coordination chemistry of CO with the actinide elements is a relatively new area of research, in part because of the experimental challenges faced in handling and characterizing actinide complexes. Some organouranium carbonyl complexes have been synthesized,^{3–6} and carbon monoxide activation by organoactinide complexes has also been studied.^{7–9} Although thorium is one of the easier-to-handle actinide elements, its chemistry with CO and the differences between thorium and uranium carbonyl chemistry have been entirely unexplored.

We have investigated reactions of laser-ablated metal atoms with small molecules such as CO and theoretical calculations have provided valuable support for spectroscopic assignments.¹⁰ A recent study has characterized uranium carbonyls, the linear singlet CUO molecule, and the photon-induced rearrangement of uranium dicarbonyl to the OUCCO and $(\eta^2\text{-C}_2)\text{UO}_2$ isomers.¹¹ Laser ablation has proven to be an effective source of thorium atoms for reaction with hydrogen and nitrogen.^{12,13} Here we report a study of reactions of laser-ablated thorium atoms with carbon monoxide in excess neon. These experiments form the first thorium carbonyl complex, ThCO, which rearranges to CThO. Although this chemistry seems parallel to that of CO with uranium atoms, we will show that it is distinctly different because of the intrinsic differences between Th and U.

The experiment for laser ablation and matrix isolation spectroscopy has been described in detail previously.¹⁰ Briefly, the Nd:YAG laser fundamental (1064 nm, 10 Hz repetition rate with 10 ns pulse width) was focused on the rotating thorium metal target (Oak Ridge National Laboratory) using 1–5 mJ/pulse, and thorium atoms were co-deposited with 0.1% CO in neon onto a 4 K CsI window. We estimate that the Th concentration is less than 0.01% in neon. Infrared spectra were recorded at 0.5 cm^{-1} resolution and 0.1 cm^{-1} accuracy.

Scalar-relativistic density functional theoretical (DFT) calculations were performed using the ADF code,¹⁴ with the inclusion of the generalized gradient approach of Perdew and Wang

(PW91).¹⁵ Slater-type-orbital (STO) basis sets of triple- ζ quality were used for Th, C, and O, with d- and f-type polarization functions for C and O. The geometries were fully optimized and the vibrational frequencies were determined numerically. Further computational details have been described elsewhere.¹⁶

The infrared spectra in the 1850–1750 and 900–600 cm^{-1} regions obtained when laser-ablated Th atoms are co-condensed with CO in excess neon are illustrated in Figure 1. The major new feature in the CO-stretching region at 1817.5 cm^{-1} doubles in intensity on annealing, disappears on photolysis at $\lambda > 470$ nm, slightly regenerates following 240–580 nm photolysis, and reappears on 10 K annealing. The weak band at 887.1 cm^{-1} is due to ThO.^{17,18} The stronger 812.2 cm^{-1} absorption is associated with a weaker 617.7 cm^{-1} band on annealing, and $\lambda > 470$ nm photolysis doubles these absorptions while full-arc 240–580 nm irradiation reduces the pair by 20%.

The 1817.5 cm^{-1} band exhibits $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ counterparts at 1777.7 and 1774.3 cm^{-1} , which yield a 12/13 frequency ratio of 1.0224 and a 16/18 ratio of 1.0243. In the mixed $^{12}\text{C}^{16}\text{O} + ^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}$ experiments, only pure isotopic counterparts are observed, which indicates a monocarbonyl complex. The 1817.5 cm^{-1} band is therefore assigned to the C–O stretching vibration of the ThCO molecule.

The sharp bands at 812.2 and 617.7 cm^{-1} each with nearby matrix site-split bands double in concert on $\lambda > 470$ nm photolysis, suggesting different vibrational modes of the same molecule. The increase upon photodestruction of ThCO implies that the new product is generated from ThCO. The 812.2 cm^{-1} band shifted to 811.9 cm^{-1} with $^{13}\text{C}^{16}\text{O}$ and to 769.2 cm^{-1} with $^{12}\text{C}^{18}\text{O}$, giving a small 12/13 ratio (1.0004) and a large 16/18 ratio (1.0559). In contrast, the 617.7 cm^{-1} absorption shifted to 595.0 cm^{-1} with $^{13}\text{C}^{16}\text{O}$ and to 617.3 cm^{-1} with $^{12}\text{C}^{18}\text{O}$, which define a large 12/13 ratio (1.0382) and a small 16/18 ratio (1.0006). Isotopic substitution shows that the upper band is mostly Th–O and the lower absorption mostly Th–C in vibrational character. The mixed $^{12}\text{C}^{16}\text{O} + ^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O} + ^{12}\text{C}^{18}\text{O}$ isotopic spectra each reveal only two isotopic bands and clearly indicate that only one O and one C atom are involved in these two modes. Analogous to the CUO molecule,¹¹ these two absorptions are assigned to the Th–O and Th–C stretching vibrations of the CO-insertion product CThO.

The spectra in Figure 1 clearly demonstrate that laser-ablated thorium atoms react with CO in a neon matrix to form two one-to-one adducts: ThCO, which is the first thorium carbonyl complex, and CThO, which is the product of insertion of the Th atom into the C–O triple bond. Further CO-addition products are also formed, as will be discussed later.¹⁹ The behavior of the spectral bands for the new products leads us to propose the following reactions:



(1) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.

(2) Muettterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

(3) Brennan, J. G.; Andersen, R. A.; Robbins, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 335.

(4) Bursten, B. E.; Strittmatter, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 6606.

(5) Parry, J.; Carrona, E.; Coler, S.; Hursthouse, M. *J. Am. Chem. Soc.* **1995**, *117*, 2649.

(6) Bursten, B. E.; Strittmatter, R. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1069.

(7) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051.

(8) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

(9) Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484.

(10) Zhou, M. F.; Andrews, L. *J. Chem. Phys.* **1999**, *110*, 10370 and references therein.

(11) Zhou, M. F.; Andrews, L.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1999**, *121*, 9712.

(12) Souter, P. F.; Kushto, G. P.; Andrews, L.; Neurock, M. *J. Phys. Chem. A* **1997**, *101*, 287.

(13) Kushto, G. P.; Souter, P. F.; Andrews, L. *J. Chem. Phys.* **1998**, *108*, 7121.

(14) ADF 2.3, Theoretical Chemistry, Vrije Universiteit, Amsterdam; G. te Velde, E. J. Baerends, *J. Comput. Phys.* **1992**, *99*, 94.

(15) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(16) Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 11456.

(17) The Th + O₂ reaction in a neon matrix gave ThO at 887.1 cm^{-1} and ThO₂ at 756.8 and 808.4 cm^{-1} .

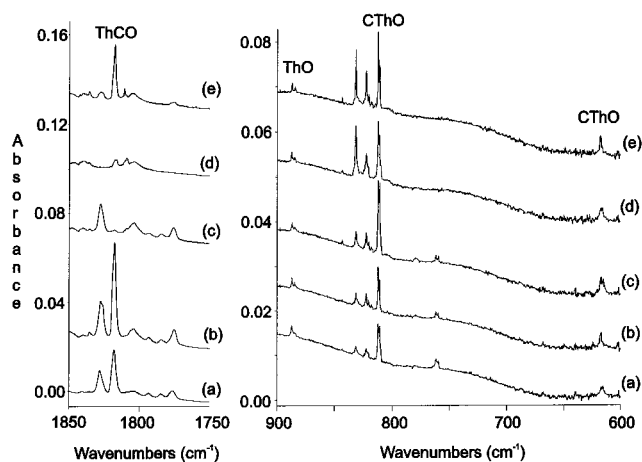


Figure 1. Infrared spectra in the 1850–1750 and 900–600 cm^{-1} regions for laser-ablated thorium co-deposited with 0.1% $^{12}\text{C}^{16}\text{O}$ in neon at 4 K. Spectrum after (a) 30 min sample deposition, (b) annealing to 8 K, (c) 15 min $\lambda > 470$ nm photolysis, (d) 15 min full arc photolysis, and (e) annealing to 10 K.

Table 1. Calculated Ground States, Geometries, Vibrational Frequencies (cm^{-1}), and IR Intensities (km/mol , in parentheses) of ThCO and CThO

	ThCO	CThO
ground state	$^3\Sigma^-$	$^3A'$
Th–C (\AA)	2.261	2.124
Th–O/C–O (\AA)	1.181	1.889
bond angle (deg)	180	108.9
calcd freq (int)	292 (16), 345 (0.22), 1790 (839)	160 (12), 621 (57), 811 (174)
	$\delta(\text{Th–C–O}), \nu(\text{Th–C}),$ $\nu(\text{C–O})$	$\delta(\text{C–Th–O}), \nu(\text{Th–C}),$ $\nu(\text{Th–O})$
exptl freq ^a	1817.5	617.7 (1.0), 812.2 (3.8)

^a For CThO, the experimental relative intensities are given.

The ThCO absorption increases on annealing, suggesting that reaction 1 is exothermic and requires negligible activation energy. The formation of the insertion product CThO requires greater activation energy as indicated by the sharpening upon annealing and growth upon photolysis of its infrared absorption bands. CThO might be formed by the direct reaction of energetic Th atoms with CO, as indicated in reaction 2. It is clear that CThO can also be formed from ThCO; the ThCO band disappears upon irradiation with $\lambda > 470$ nm light, while the CThO absorptions double in intensity. As summarized in reaction 3, this conversion of ThCO to CThO is reversed upon UV irradiation.

To provide insight into the structure and bonding in ThCO and CThO, we turn to relativistic DFT calculations, which provide very reliable predictions of the state energies, structures, and vibrational frequencies of actinide-containing molecules.^{11,16} The calculated ground states, geometries, and vibrational frequencies of ThCO and CThO are presented in Table 1.

The CO-stretching frequency in ThCO, 1817.5 cm^{-1} , is the lowest of any neutral binary terminal metal carbonyl complex, which implies extensive metal-to-carbonyl back-bonding in this molecule. According to our calculations, the ground state of ThCO reflects the Th $7s^26d^2$ ground electron configuration of the Th atom. The molecule is predicted to have a $^3\Sigma^-$ ground state, with two metal-based electrons occupying the nonbonding 6σ molecular orbital (MO), which is largely Th $7s$ in character, and the remaining two occupying the doubly degenerate 3π MO, which comprises significant Th $6d \rightarrow \text{CO } 2\pi$ back-bonding. In fact, because Th is so electropositive, the 3π MO of ThCO contains

nearly 40% CO 2π character, which explains the remarkably low CO-stretching frequency. Greater back-bonding could be achieved by placing all four electrons in the 3π MO of ThCO, but doing so requires the promotion of the Th $7s$ electrons, which is unfavorable: We find that the $^1\Sigma^+$ (3π)⁴ state is 35.6 kcal/mol higher in energy than the $^3\Sigma^-$ (6σ)²(3π)² ground state.

The ThCO ground state is predicted to be linear with Th–C and C–O bond lengths of 2.26 and 1.18 \AA , respectively. The linear geometry is preferred to maximize the Th-to-CO back-bonding. The calculated CO-stretching frequency in the ground-state molecule, 1790 cm^{-1} , is in quite good agreement with the experimental value.

The Th–O stretching frequency of the CThO molecule is 74.9 cm^{-1} lower than that for ThO, which is observed at 887.1 cm^{-1} in neon.^{17,18} There is no Th–CO frequency available for comparison. The Th–C stretching frequency in CThO (617.7 cm^{-1}) is significantly lower than the U–C stretching frequency in CUO (1047.3 cm^{-1}),¹¹ thus indicating a significantly weaker Th–C bond as compared to the U–C bond. On the basis of available oxidation states, the bonding in CThO is expected to be very different from that in CUO; the latter, which is isoelectronic with the common UO_2^{2+} ion, is considered an f^0 U(VI) complex whereas the maximum positive oxidation state of Th is Th(IV). Thus, relative to CUO, CThO is electron deficient and the spectroscopic results indicate that the Th–O bonding is given preference over the Th–C bonding.

Our DFT calculations on CThO predict that the molecule should be bent (108.9°) and have a triplet ground state ($^3A'$ under C_s symmetry). The triplet ground state is 6.5 kcal/mol lower than the lowest singlet state of CThO and is 2.4 kcal/mol lower than the triplet ground state of ThCO. The correctness of this predicted ground state for CThO is evident in the calculated frequencies and intensities: the calculated stretching frequencies, 811 and 621 cm^{-1} , agree within 1 and 3 cm^{-1} with the experimental neon matrix values! Equally important, the calculated 811 and 621 cm^{-1} bands are predominantly Th–O and Th–C stretches, respectively, which is in complete accord with the isotopic substitution experiments. Additionally, the observed relative integrated band intensity, 3.8, is in excellent agreement with the calculated intensity ratio, 3.1. We believe that these excellent agreements provide compelling evidence for the identification of this unprecedented triplet thorium carbide-oxide.

The fact that CThO has a bent triplet ground state whereas CUO is a linear singlet is a direct consequence of the change in the electron count from U to Th. First, because Th has four valence electrons, one can draw a convenient Lewis structure that satisfies the valence of Th ($:\text{C}=\text{Th}=\ddot{\text{O}}:$). This structure suggests that CThO should be an unsaturated metallocarbene complex, analogous to ketylidene ($:\text{C}=\text{C}=\ddot{\text{O}}:$), which has a triplet linear ground state.²⁰

The bent structure of CThO is reminiscent of the bent structure of ThO_2 ($\angle\text{O–Th–O} = 122 \pm 2^\circ$),¹⁸ a molecule that is isoelectronic with linear $[\text{OUO}]^{2+}$. The reasons for linear vs bent structures in the f^0 actinyls have been the subject of theoretical studies concerning the role of the $5f$ orbitals in the bonding of actinide metals.²¹ The CThO molecule can be viewed as OThO with two nonbonding electrons (and two protons) removed.

The reaction of laser-ablated Th atoms with CO has produced two remarkable one-to-one adducts in ThCO and CThO. The spectroscopic studies of these molecules in conjunction with relativistic DFT calculations underscore the differences between thorium and uranium chemistry.

Acknowledgment. We acknowledge support for this research from the NSF (CHE 97-00116 to L.A.), U.S. DOE (DE-FG02-86ER13529 to B.E.B.), and Los Alamos National Laboratory.

JA993300T

(18) Gablenick, S. D.; Reedy, G. T.; Chasanov, M. G. *J. Chem. Phys.* **1974**, *60*, 1167.

(19) The 1827.7 and 1775.6 cm^{-1} bands in Figure 1 are due to Th(CO)₂, which photochemically rearranges to OThCCO absorbing at 822.5 cm^{-1} .

(20) Devilliers, C.; Ramsay, D. A. *Can. J. Phys.* **1971**, *49*, 2839.

(21) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719 and references therein.