

# Observation of Carbon–Carbon Coupling Reaction in Neutral Transition-Metal Carbonyls

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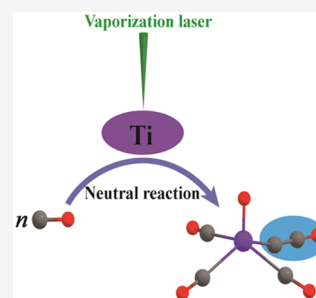


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Supporting Information

**ABSTRACT:** Neutral titanium-metal carbonyl complexes with the chemical formula  $\text{Ti}(\text{CO})_n$  ( $n = 4-7$ ) are produced in the gas phase by the reactions of titanium atoms with carbon monoxide in a pulsed laser vaporization–supersonic expansion source. Their infrared absorption spectra in the carbonyl stretching frequency region are measured by infrared plus vacuum ultraviolet (IR+VUV) two-color ionization spectroscopy based on a tunable VUV free electron laser. Infrared spectroscopy in conjunction with quantum chemical calculations confirm that all of these complexes have unexpected titanium ketylidene  $\text{OTiCCO}(\text{CO})_{n-2}$  structures. Bonding analysis indicates that the  $\text{OTiCCO}$  core structure can be described by the bonding interactions between a  $\text{TiO}^+$  cation in the doublet ground state and a doublet ground state of  $\text{CCO}^-$ . The results reveal that the C–O bond breaking and C–C bond formation proceed efficiently in the reactions between laser-vaporized titanium atoms and carbon monoxide.



Metal carbonyls play an important role in heterogeneous and homogeneous catalysis, such as in Fischer–Tropsch chemistry, hydroformylation, alcohol synthesis, and acetic acid synthesis.<sup>1–5</sup> Laser vaporization in conjunction with supersonic expansion has been proven to be a very powerful method to produce metal complexes for spectroscopic studies in the gas phase.<sup>6–9</sup> The combinations of mass spectrometric techniques and laser-based spectroscopy are among the most direct and generally applicable experimental approaches to obtain electronic and vibrational spectra of mass-selected ions in the gas phase.<sup>10–19</sup> These techniques have been successfully employed in generating and studying homoleptic metal carbonyl cations and anions in the gas phase, which serve as archetypical examples for demonstrating the metal–ligand bonding and the electron counting rules.<sup>20–24</sup>

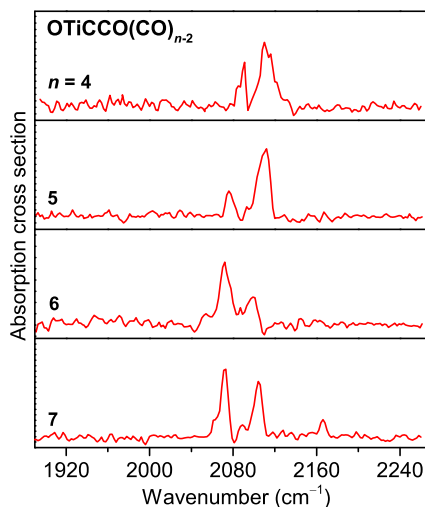
Recent highlights are reports about highly coordinated carbonyl ion complexes of the early transition metals,<sup>25–30</sup> lanthanides,<sup>31</sup> and actinides,<sup>32,33</sup> which show the limitations of the electron-counting rules. Infrared spectroscopic studies in the gas phase revealed that the heavier group 5 and group 3 cations indeed form the seven-coordinate  $\text{TM}(\text{CO})_7^+$  ( $\text{TM} = \text{Nb}, \text{Ta}$ )<sup>29</sup> and the eight-coordinate  $\text{TM}(\text{CO})_8^+$  ( $\text{TM} = \text{Y}, \text{La}$ )<sup>25,26</sup> cation complexes, which satisfy the 18-electron rule. However, the lighter ions  $\text{Sc}^+$ ,  $\text{Ti}^+$ , and  $\text{V}^+$  form primarily only seven- and six-coordinate 16- and 17-electron carbonyls.<sup>25–30</sup> More surprising results are the observations that the heavy alkaline-earth elements ( $\text{Ca}, \text{Sr}, \text{Ba}$ ),<sup>34</sup> the group 3 metal anions ( $\text{Sc}^-$ ,  $\text{Y}^-$ , and  $\text{La}^-$ ),<sup>35</sup> and the heavier group 4 metal cations ( $\text{Zr}^+$  and  $\text{Hf}^+$ )<sup>36</sup> can also bind eight CO ligands to form the eight-coordinate carbonyl complexes. The octacarbonyl

complexes  $\text{TM}(\text{CO})_8^-$  ( $\text{TM} = \text{Sc}, \text{Y}, \text{La}$ ) and  $\text{TM}(\text{CO})_8^+$  ( $\text{TM} = \text{Zr}, \text{Hf}$ ) are formally 20- and 19-electron systems. Bonding analysis indicates that these complexes still obey the 18-electron rule, because one doubly occupied valence orbital does not mix with any of the metal valence atomic orbitals.<sup>35,36</sup> The observation of these highly coordinated carbonyl ion complexes implies that similar high coordinate neutral carbonyl complexes could also be achieved in the gas phase. However, the spectroscopic characterization of neutral species in the gas phase are significantly more challenging due to the difficulty of size selection.<sup>2,37–40</sup> Here, we report an infrared spectroscopic study on the neutral titanium carbonyl complexes in the gas phase using infrared plus vacuum ultraviolet (IR+VUV) two-color ionization spectroscopy based on a tunable vacuum ultraviolet free electron laser (VUV-FEL). Infrared spectroscopy in conjunction with quantum chemical calculations confirm that the complexes with the chemical formula of  $\text{Ti}(\text{CO})_n$  ( $n = 4-7$ ) all have unexpected titanium ketylidene  $\text{OTiCCO}(\text{CO})_{n-2}$  structures, demonstrating that the C–O bond breaking and C–C bond formation proceed in the reactions between laser-vaporized titanium atoms and carbon monoxide.

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The neutral titanium carbonyl complexes in the gas phase are prepared using a laser vaporization–supersonic expansion source and are characterized using IR+VUV spectroscopy.<sup>41</sup> The tunable IR light pulse is introduced at approximately 50 ns prior to the VUV-FEL pulse in a crossed manner. The resonant absorption of IR photons leads to an enhanced ionization efficiency for a given size of complex when its ionization potential is just above the VUV-FEL photon energy. IR spectra are recorded in the difference mode of operation (IR laser ON minus IR laser OFF). The spectra in the carbonyl stretching frequency region for the  $\text{Ti}(\text{CO})_n$  complexes with  $n = 4–7$  are shown in Figure 1. The number densities of the  $n \leq 3$  and  $n \geq$

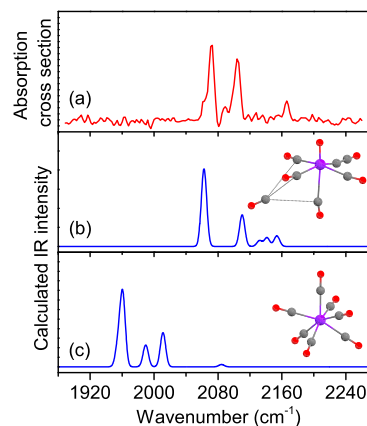


**Figure 1.** Experimental IR spectra of the neutral  $\text{OTiCCO}(\text{CO})_{n-2}$  ( $n = 4–7$ ) complexes.

8 complexes are too low to obtain well-resolved spectra. Each complex exhibits at least two bands above  $2070 \text{ cm}^{-1}$ . These band positions ( $2071–2167 \text{ cm}^{-1}$ ) are remarkably higher than the carbonyl stretching vibrational frequencies of homoleptic titanium carbonyl neutral complexes  $\text{Ti}(\text{CO})_n$  ( $n = 4–7$ ) observed in solid noble gas matrices ( $1800–1991 \text{ cm}^{-1}$ ),<sup>36,42</sup> indicating that the observed complexes are due to other structural isomers involving a more electropositive titanium metal center. The lowest band of each complex lies slightly higher than the carbonyl stretching mode of the  $\text{OTiCCO}$  molecule previously observed in solid argon matrix ( $2047.7 \text{ cm}^{-1}$ ),<sup>42</sup> suggesting that the observed species can be assigned to  $\text{OTiCCO}(\text{CO})_{n-2}$ .

To validate the experimental assignment and to gain insight into the geometric and electronic structures, as well as into the bonding of the experimentally observed complexes, quantum chemical calculations are carried out at the B2PLYP-D3/def2-TZVPP level of theory (see the Supporting Information for details). Two stable structures are optimized for each complex, as shown in Figure S2. The first structure consists of a  $\text{OTiCCO}$  core and is notated with the formula of  $\text{OTiCCO}(\text{CO})_{n-2}$ . The second structure is a conventional homoleptic metal carbonyl complex  $\text{Ti}(\text{CO})_n$ . For the  $\text{OTiCCO}(\text{CO})_{n-2}$  structures, the CO ligands are coordinated to the Ti center, completing the first coordination shell at  $n = 6$ . The additional CO molecule is weakly tagged in the second coordination shell for the  $n = 7$  complex. In the  $\text{Ti}(\text{CO})_n$  structures, the Ti atom is capable of coordinating seven CO ligands, in agreement with previous reports.<sup>36,43</sup> For the small complexes with  $n = 4$  and 5,

the  $\text{OTiCCO}(\text{CO})_{n-2}$  structure is predicted to be more stable than the  $\text{Ti}(\text{CO})_n$  isomer (Figure S2). In contrast, the relative stability of these two isomers is reversed for the  $n = 6$  and 7 complexes. The calculated IR spectra of the two structures of the  $n = 7$  complex are compared with the experimental IR spectrum in Figure 2.



**Figure 2.** Experimental IR spectrum of  $\text{OTiCCO}(\text{CO})_5$  (a) and calculated IR spectra of  $\text{OTiCCO}(\text{CO})_5$  (b) and  $\text{Ti}(\text{CO})_7$  (c). The structures are embedded in the inset (Ti, violet; C, gray; O, red).

The simulated spectrum of the  $\text{OTiCCO}(\text{CO})_5$  structure provides an excellent match to the experimental spectrum, which reinforces the assumption that the observed complex has the  $\text{OTiCCO}(\text{CO})_5$  structure though this structure is predicted to be  $38.7 \text{ kcal/mol}$  higher in energy than the  $\text{Ti}(\text{CO})_7$  isomer (Figure S2). The comparisons between the simulated and the experimental spectra for the  $n = 4–6$  complexes are shown in Figures S3–S5, respectively. The results also support the assignment of the experimentally observed species of the  $n = 4–6$  complexes to the  $\text{OTiCCO}(\text{CO})_{n-2}$  structures rather than the  $\text{Ti}(\text{CO})_n$  isomers. The agreement between experiment and theory for the small complexes is not as good as for the large complexes. This might be due to the fact that the experimental spectrum is not a linear absorption spectrum. The IR spectrum is measured by enhanced ionization efficiency via the vibrational absorption of IR photons. The measured intensity depends not only on the IR photon absorption cross section but also on the VUV photon absorption cross section, the efficiency of intramolecular vibrational relaxation, the photoionization, etc. The experimental observations suggest that there is a size effect on the ionization efficiency for different vibrational modes. Table 1 provides a comparison of the calculated carbonyl stretching vibrational frequencies with the experimental values for all the  $n = 4–7$  complexes.

The  $\text{OTiCCO}$  core structure is predicted to have a closed-shell singlet ground state ( $^1A'$ ). It has a planar but nonlinear structure with a quite acute  $\text{OTiC}$  angle of  $111.8^\circ$ . The Ti–C bond length is predicted to be  $1.889 \text{ \AA}$ , very close to the sum of the covalent radii of double-bonded Ti and C atoms.<sup>44</sup> The canonical Kohn–Sham valence molecular orbitals of  $\text{OTiCCO}$  are shown in Figure S6. The highest occupied molecular orbital (HOMO) is mainly an in-plane  $\text{CCO} \pi$  orbital (the singly occupied molecular orbital (SOMO) of  $^3\Pi$  ground state  $\text{CCO}$ ), that is, C–C bonding but C–O antibonding. The HOMO–1 is an out-of-plane  $\pi$  orbital formed between the  $d_{xy}$  orbital of Ti and the  $\pi$  orbital of  $\text{CCO}$  (SOMO'). This orbital

**Table 1.** Comparison of the Band Positions<sup>b</sup> of the Neutral OTiCCO(CO)<sub>n-2</sub> (*n* = 4–7) Complexes Measured in the Present Work to Those Computed at the B2PLYP-D3/def2-TZVPP Level of Theory<sup>c</sup>

	exptl.	calcd	mode <sup>a</sup>
<i>n</i> = 4	2091	2072(1681)	I
	2118	2129(745)	II
		2149(24)	III
<i>n</i> = 5	2076	2064(1754)	I
	2112	2109(807)	II
		2129(182)	III
	2167	2155(253)	III
<i>n</i> = 6	2072	2064(1713)	I
	2103	2116(772)	II
		2131(47)	III
		2143(407)	III
	2166	2155(190)	III
<i>n</i> = 7	2071	2063(1726)	I
	2102	2111(706)	II
		2133(133)	III
		2142(199)	III
		2153(68)	III
		2155(183)	III
	2166	2155(183)	III

<sup>a</sup>I denotes the CO stretching mode of the CCO ligand. II denotes the antisymmetric CO stretching modes of CO ligands. III denotes the symmetric CO stretching modes of CO ligands. <sup>b</sup>In cm<sup>-1</sup>. <sup>c</sup>IR intensities are listed in parentheses in km/mol, and the calculated harmonic frequencies are scaled by a factor of 0.991.

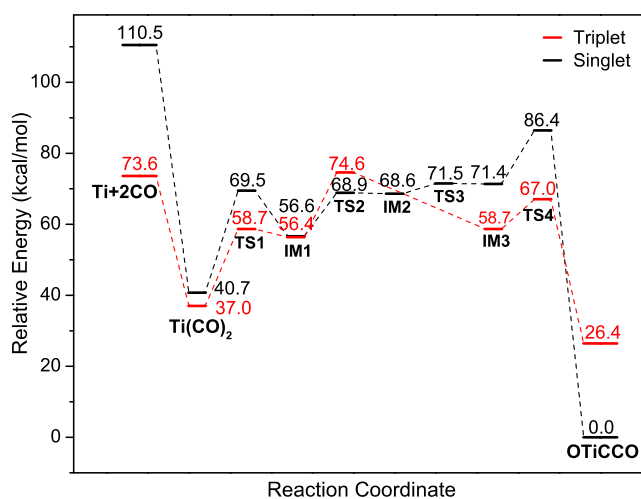
is Ti–C bonding and is the major driving force for the molecule to adopt a quite bent structure (OTiC angle of 111.8°). The HOMO–2 and HOMO–3 are in-plane and out-of-plane Ti–O π bonding orbitals, while the HOMO–4 is a Ti–O σ bonding orbital. The HOMO–5 is primarily the lone pair σ orbital of CCO that comprises a weak donation interaction with TiO. On the basis of the above bonding analysis, the electronic ground state of OTiCCO can be regarded as bonding interactions between a TiO<sup>+</sup> fragment in the doublet <sup>2</sup>Δ ground state and a CCO<sup>-</sup> fragment in the <sup>2</sup>Π ground state in forming an electron-sharing π bond.

Metal ketylidene complexes have been proposed to be important intermediates in processes such as Fischer–Tropsch catalysis.<sup>45</sup> Some transition-metal ketylidene complexes have been synthesized.<sup>46–52</sup> A few metal ketylidene complexes have also been spectroscopically detected in well-defined surfaces.<sup>53–55</sup> For example, a gold ketylidene species has been produced by partial oxidation of acetic acid on a nano-Au/TiO<sub>2</sub> catalyst, which is identified by its measured characteristic C–O stretching frequency at 2040 cm<sup>-1</sup>.<sup>56</sup>

The observation of the neutral titanium ketylidene OTiCCO(CO)<sub>n-2</sub> structures is quite surprising as only the homoleptic metal carbonyl structures have been identified in previous spectroscopic studies on the charged metal carbonyl complexes M(CO)<sub>n</sub><sup>±</sup> formed via laser vaporization–supersonic expansion source in the gas phase.<sup>20–36</sup> The results imply that the C–O bond breaking and C–C bond formation proceed in the reactions between laser-vaporized titanium atoms and carbon monoxide. The reaction processes taking place in the high-pressure plasma conditions in the source are quite complicated and are very difficult to be clearly characterized. The non-observation of any homoleptic carbonyl structures Ti(CO)<sub>n</sub> in the present experiments indicates that the C–O

bond breaking and C–C bond formation reactions are quite efficient in the gas phase. Previous matrix isolation experiments show that the ground state metal atoms react with carbon monoxide to form the homoleptic metal carbonyls spontaneously on annealing.<sup>36,42,49–52</sup> Only the dicarbonyl complexes were found to be able to isomerize to the OMCCO isomer under UV light excitation.<sup>42,49–52</sup>

The B2PLYP-D3/def2-TZVPP calculations indicate that the Ti + CO → TiCO reaction is slightly endothermic by 2.6 kcal/mol, while the TiCO + CO → Ti(CO)<sub>2</sub> reaction is highly exothermic by 39.2 kcal/mol (Table S1). The potential energy profiles of the Ti + 2CO → OTiCCO reaction calculated at the B2PLYP-D3/def2-TZVPP level of theory are shown in Figure 3. The results show that the overall reaction is highly



**Figure 3.** Potential energy profiles of the Ti + 2CO → OTiCCO reaction calculated at the B2PLYP-D3/def2-TZVPP level of theory. Energies are given in kcal/mol after zero-point energy correction. The abbreviation “TS” stands for transition state and “IM” for intermediate. The corresponding structures are shown in Figure S7 in the Supporting Information.

exothermic with a barrier of only about 1.0 kcal/mol above the ground state reactants. The triplet state Ti(CO)<sub>2</sub> isomer is predicted to be 37.0 kcal/mol less stable than the OTiCCO isomer. The potential energy profiles clearly demonstrate that the Ti + 2CO → OTiCCO reaction is both thermodynamically exothermic and kinetically facile in the gas phase. The TiCO and Ti(CO)<sub>2</sub> intermediates cannot be stabilized via collisional cooling, and the isomerization reaction from Ti(CO)<sub>2</sub> to OTiCCO proceeds quite efficiently at the experimental conditions. The larger OTiCCO(CO)<sub>n-2</sub> complexes are formed via CO addition to the smaller ones, which are predicted to be exothermic by 21.4, 18.8, 14.8, 3.6, and 1.5 kcal/mol (Table S1), respectively, for *n* = 3–7. Although the Ti(CO)<sub>n</sub> (*n* = 6 and 7) complexes are predicted to be more stable than the OTiCCO(CO)<sub>n-2</sub> isomers, these structures are not formed due to the lack of small Ti(CO)<sub>n</sub> precursors in the gas phase.

In summary, the neutral titanium metal carbonyl complexes with a chemical formula of Ti(CO)<sub>n</sub> (*n* = 4–7) are produced in the gas phase via laser vaporization technique. Infrared plus vacuum ultraviolet (IR+VUV) two-color ionization spectroscopy based on a tunable VUV free electron laser in conjunction with quantum chemical calculations confirm that all of these complexes have unexpected titanium ketylidene

OTiCCO(CO)<sub>n-2</sub> structures. Bonding analysis indicates that the OTiCCO core structure can be described by the bonding interactions between a TiO<sup>+</sup> cation in the doublet ground state and a doublet ground state of CCO<sup>-</sup>. The results reveal that the C–O bond breaking and C–C bond formation proceed efficiently in the reactions between laser-vaporized titanium atoms and carbon monoxide. Theoretical calculations predict that the Ti + nCO → OTiCCO(CO)<sub>n-2</sub> reactions are both thermodynamically exothermic and kinetically facile in the gas phase. The observed C–O bond cleavage and C–C bond formation is a viable strategy for CO insertion for carbon-chain growth and higher alcohol synthesis.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c03766>.

Experimental and theoretical methods, Figures S1–S7, Table S1, and references (PDF)

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### Notes

The authors declare no competing financial interest.

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