

Carbon Dioxide Chemistry: Characterization of the Carbon Dioxide Reaction Product of a Dinuclear Titanium Complex

Jinfeng Ni,* Yuhua Qiu, Tamara M. Cox, Cynthia A. Jones, Chala Berry, and Laura Melon

Department of Chemistry and Physics, Texas Woman's University, Denton, Texas 76204

Simon Bott*

Department of Chemistry, University of North Texas, Denton, Texas 76203

Received April 11, 1996[®]

Summary: Reaction of $[\text{CpTi}(\mu\text{-H})_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)]$ with CO_2 (3 atm) leads to the formation of the bis(formato) complex $[\text{CpTi}(\mu\text{-}\eta^1\text{-}(\text{O})\text{CHO})_2(\text{C}_{10}\text{H}_8)]$ (**1**). Complex **1** contains monodentate bridging formate ligands. The difference between vibrational frequencies $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ is 455 cm^{-1} , the largest ever observed for a monodentate formate ligand.

Hydrogenation of carbon dioxide, an abundant and inexpensive source of carbon, to useful organic products has been of great interest. Methanol and/or methane are the major products from the hydrogenation of CO_2 over heterogeneous catalysts.¹ Homogeneous catalysts, on the other hand, catalyze the hydrogenation of CO_2 to formic acid, formate esters, or formamides when alcohol, alkyl halides, or secondary amines are present in the reactions.² Stoichiometric reduction of CO_2 to formaldehyde and methanol was achieved by using $[\text{Cp}_2\text{Zr}(\text{H})(\text{Cl})]$ as the reducing agent.³ Another intriguing reaction is the formation of the μ -formaldehyde compound $\text{Cp}(\text{CO})_2\text{Ru}(\text{CH}_2\text{O})\text{Zr}(\text{Cl})\text{Cp}_2$ from the reduction of $\text{Cp}(\text{CO})_2\text{Ru}(\text{CO})_2\text{Zr}(\text{Cl})\text{Cp}_2$ with $\text{Cp}_2\text{Zr}(\text{H})(\text{Cl})$.⁴ Considering that two metal centers held in proximity afford the possibility of cooperative reactivity, we investigated the reaction of CO_2 with the dinuclear titanium complex $[\text{CpTi}(\mu\text{-H})_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)]$ ($\text{C}_{10}\text{H}_8 = \text{fulvalene}$),⁵ isolated as "titanocene" in the reduction of Cp_2TiCl_2 by sodium. This fulvalene-bridged complex $[\text{CpTi}(\mu\text{-H})_2(\text{C}_{10}\text{H}_8)]$ has so far been shown to react with S_8 to form $[\text{CpTi}(\mu\text{-S})_2(\text{C}_{10}\text{H}_8)]$ and H_2S and with H_2O to form $[\text{CpTi}(\mu\text{-OH})_2(\text{C}_{10}\text{H}_8)]$ and H_2 .⁶ Although the molecular structure of the complex $[\text{CpTi}(\mu\text{-H})_2(\text{C}_{10}\text{H}_8)]$ has not been solved, the crystal structures of its analogs $[\text{CpTi}]_2(\mu\text{-H})(\mu\text{-Cl})$

(C_{10}H_8), $[\text{CpTi}]_2(\mu\text{-H})(\mu\text{-H}_2\text{AlEt}_2)(\text{C}_{10}\text{H}_8)$, and $[\text{CpTi}(\mu\text{-H}_2\text{AlEt}_2)_2(\text{C}_{10}\text{H}_8)]$ are known, in which the Ti-Ti separation ranges from 2.910 to 3.125 Å.⁷ In this communication we report the characterization of the CO_2 reaction product of the titanium dinuclear complex $[\text{CpTi}(\mu\text{-H})_2(\text{C}_{10}\text{H}_8)]$.

Reaction of the complex $[\text{CpTi}(\mu\text{-H})_2(\text{C}_{10}\text{H}_8)]$ with CO_2 (3 atm) in toluene leads to the formation of the bis(formato) complex $[\text{CpTi}(\mu\text{-}\eta^1(\text{O})\text{CHO})_2(\text{C}_{10}\text{H}_8)]$ (**1**).⁸ Insertion of CO_2 into a metal-hydride bond to produce formate is a key step in catalytic hydrogenation of CO_2 . Many formate complexes have been synthesized from CO_2 and transition-metal hydride complexes, and some have been structurally characterized.⁹ A very recent example, reported by Bergman and co-workers, is the complex $\text{Cp}_2\text{Zr}(\eta^1\text{-OCOH})(\mu\text{-N}^t\text{Bu})(\mu\text{-H})\text{IrCp}^*$, prepared by reaction of CO_2 with $\text{Cp}_2\text{Zr}(\text{H})(\mu\text{-N}^t\text{Bu})(\mu\text{-H})\text{IrCp}^*$.^{9f} An interesting finding by Bergman and co-workers is that CO_2 inserts selectively into the terminal Zr-H bond and leaves the bridging H intact. The reaction, however, was carried out in the ratio of about 1:1 for CO_2 and $\text{Cp}_2\text{Zr}(\text{H})(\mu\text{-N}^t\text{Bu})(\mu\text{-H})\text{IrCp}^*$. It remains unknown whether CO_2 would react with the bridging H, similar to our reaction, if an excess amount of CO_2 were present.

(7) (a) Perevalova, E. G.; Urazovskii, I. F.; Lemenovskii, D. A.; Slovokhotov, Y. L.; Struchkov, Y. T. *J. Organomet. Chem.* **1985**, *289*, 319. (b) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1973**, *95*, 7870.

(8) Synthesis of **1**: Samples were handled in a nitrogen-filled glovebox. A pressure reaction vessel containing a solution of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)]$ (0.160 g, 0.426 mmol) in toluene (5 mL) was connected to a system which allows the evacuation of N_2 and addition of CO_2 . After nitrogen was evacuated by vacuum, carbon dioxide (3 atm) was introduced into the vessel for 15 min while the solution was stirred. Then, the vessel was closed and the solution was stirred at room temperature. Within 1 h the solution turned brown. The solution was stirred at room temperature for 1 day and then heated to 90 °C for 1 day, and the solution became dark purple. The resulting solution was filtered to separate the very small amount of insoluble material and then concentrated under reduced pressure, followed by the addition of hexane. The resulting mixture was set at ambient glovebox temperature overnight to afford the purple solid (powder) $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-}\eta^1(\text{O})\text{CHO})_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)]$ (**1**). The product **1** was isolated, washed with hexanes, and dried under vacuum (0.156 g, 78%). Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_4\text{Ti}_2$: C, 59.48; H, 4.54. Found: C, 59.88; H, 4.84. IR (Nujol): 1664 s, 1305 w, 1205 s, 1055 m, 1012 m, 802 s, 727m, 694 w, 630 w cm^{-1} .

(9) (a) Darensbourg, D. J.; Kudarski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (b) Darensbourg, D. J.; Bauch, C. G.; Ovalles, C. *Rev. Inorg. Chem.* **1985**, *7*, 315. (c) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (d) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37. (e) Pandey, K. K.; Garg, K. H.; Tiwari, S. K. *Polyhedron* **1992**, *11*, 947. (f) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 11363.

[®] Abstract published in *Advance ACS Abstracts*, October 1, 1996.

(1) Selected reviews: (a) *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed. ACS Symposium Series No. 363; American Chemical Society: Washington, DC, 1988. (b) Sneed, R. P. A. *J. Mol. Catal.* **1982**, *17*, 349. (c) Denise, B.; Sneed, R. P. A. *CHEMTECH* **1982**, 108.

(2) (a) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259. (b) Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207. (c) Inoue, S.; Koinuma, H. *Rev. Inorg. Chem.* **1984**, *6*, 291. (d) Tsai, J.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117 and references therein. (e) Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231. (f) Pugh, J. R.; Bruce, M. R. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 86.

(3) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278.

(4) Steffey, B. D.; Vites, J. C.; Cutler, A. R. *Organometallics* **1991**, *10*, 3432.

(5) Salzmann, J. J.; Mosimann, P. *Helv. Chim. Acta* **1967**, *50*, 1831.

(6) (a) Cuenca, T.; Herrmann, W. A.; Ashworth, T. *Organometallics* **1986**, *5*, 2514. (b) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1976**, *98*, 4137.

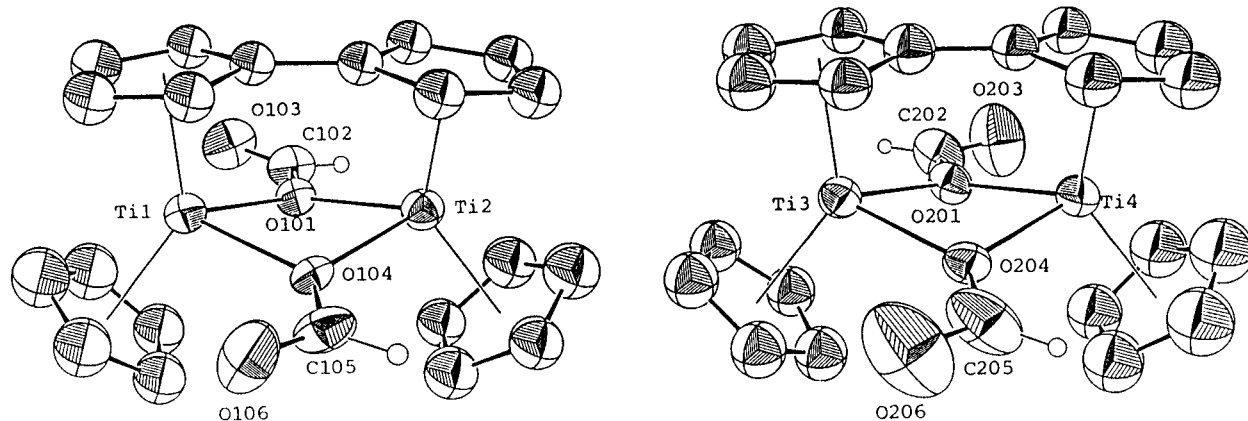


Figure 1. ORTEP diagrams of **1a** (left) and **1b** (right). Selected bond distances (Å) and angles (deg) for **1a**: Ti(1)–O(101) = 2.129(9), Ti(1)–O(104) = 2.130(7), Ti(2)–O(101) = 2.135(7), Ti(2)–O(104) = 2.142(8), O(101)–C(102) = 1.30(2), O(103)–C(102) = 1.21(1), O(104)–C(105) = 1.30(2), O(106)–C(105) = 1.22(2); O(101)–Ti(1)–O(104) = 74.6(3), O(101)–Ti(2)–O(104) = 74.2(3), Ti(1)–O(101)–Ti(2) = 102.7(4), Ti(1)–O(104)–Ti(2) = 102.4(3), O(101)–C(102)–O(103) = 125(1), O(104)–C(105)–O(106) = 124(1). Selected bond distances (Å) and angles (deg) for **1b**: Ti(3)–O(201) = 2.128(7), Ti(3)–O(204) = 2.149(8), Ti(4)–O(201) = 2.134(7), Ti(4)–O(204) = 2.142(7), O(201)–C(202) = 1.33(1), O(203)–C(202) = 1.23(1), O(204)–C(205) = 1.30(2), O(206)–C(205) = 1.22(2); O(201)–Ti(3)–O(204) = 73.6(3), O(201)–Ti(4)–O(204) = 73.6(3), Ti(3)–O(201)–Ti(4) = 103.5(3), Ti(3)–O(204)–Ti(4) = 102.6(3), O(201)–C(202)–O(203) = 121(1), O(204)–C(205)–O(206) = 121(1).

The X-ray structural analysis of **1** indicates the presence of two independent molecules (**1a** and **1b**) in one unit cell (Figure 1).¹⁰ These two molecules differ in the relative orientation of the two formate ligands. Despite the difference in their structures, **1a** and **1b** have essentially the same Ti–O bond distances (2.128(7)–2.149(8) Å), O–Ti–O bond angles (73.6(3)–74.6(3)°), and Ti–O–Ti bond angles (102.4(3)–103.5(3)°). The two titanium atoms in **1a** and **1b** are separated by 3.33 and 3.35 Å, respectively, indicative of no metal–metal bond.¹¹ The average Ti–O distance in **1a** and **1b** is 2.136(8) Å, slightly longer than the mean distance 2.08(1) Å observed for the analog [CpTi(μ -OH)]₂(C₁₀H₈).^{6b} The bridging hydroxy analog shows two quite different Ti–O–Ti bond angles (98.8(5) and 102.7(6)°). The smaller bond angle results from the effect of the formation of a hydrogen bond between the hydroxide and a THF molecule. The Ti–O–Ti bond angles in **1a** and **1b** (102.4(3)–103.5(3)°) are essentially the same as the larger bond angle in the bridging hydroxy analog. The O–Ti–O bond angles in **1a** and **1b** (73.6(3)–74.6(3)°) are also very similar to the ones in the bridging hydroxide (74.8(5)–76.0(5)°).

Complex **1** contains monodentate bridging formate ligands. Although carboxylates usually bridge metal centers in a bidentate fashion, monodentate bridging carboxylates have been observed.¹² The only known

example of a monodentate bridging formate complex is [Fe(biphme)]₂(μ - η^2 -O₂CH)₂(μ - η^1 -(O)CHO)(η^1 -(O)CHO) (biphme = bis(1-methyl-2-imidazolyl)phenylmethoxymethane), reported by Lippard and co-workers.^{12b} The formate C–O distances in **1** (1.30(2)–1.33(1) and 1.21(1)–1.23(1) Å) are consistent with the expected single bond and double bond, respectively. The monodentate bridging formate of Lippard's complex has C–O bond distances of 1.270(4) and 1.214(4) Å. It appears that the C–O bond distances are very similar for the monodentate bridging formate and the terminal formate. For example, C–O bond distances of 1.277(3) and 1.208(4) Å and of 1.276(8) and 1.208(8) Å are reported for the complexes (C₅H₅)Fe(CO)₂(CO₂H)¹³ and Cp₂Zr(O₂CH)(μ -N^tBu)(μ -H)IrCp*.^{9f}

Complex **1** has a very intriguing IR spectrum in the CO₂ moiety region. The IR spectrum of **1** isolated as a powder reveals strong bands at 1664 cm⁻¹ (ν_{as}) and 1205 cm⁻¹ (ν_s). On the other hand, the IR spectrum of **1** isolated as crystals reveals two overlapped bands at 1672 and 1660 cm⁻¹ (ν_{as}) and two overlapped bands at 1224 and 1205 cm⁻¹ (ν_s). The crystal structure analysis illustrates the existence of two structures for **1** in the crystal state. The discovery of **1a** and **1b** explains the observation of overlapped bands in the IR spectrum of crystalline **1**. It also infers that **1**, precipitated out promptly as a powder, exists in one of the two structures, although we cannot identify which one.

The position of $\nu_{as}(\text{CO}_2)$ and the $\Delta\nu$ value between $\nu_{as}(\text{CO}_2)$ and $\nu_s(\text{CO}_2)$ have been employed as indicators for the coordination mode of a formate ligand. A monodentate formate ligand has $\nu_{as}(\text{CO}_2)$ above 1600 cm⁻¹ and $\Delta\nu$ ranging from 289 to 383 cm⁻¹.^{2d,14} For **1**, the $\nu_{as}(\text{CO}_2)$ value we obtained is as expected when compared with the literature value. However, $\Delta\nu$ for **1** is 455 cm⁻¹, which is significantly larger than the literature results. To our knowledge, the $\Delta\nu$ value for **1** is the largest ever observed for a monodentate formate

(10) Crystal data for **1**: The crystals of **1** suitable for crystal structure analysis were obtained by slowly evaporating a toluene solution at ambient glovebox temperature. C₂₂H₂₀O₄Ti₂C_{1.75}H₂, triclinic, space group *P1*, *a* = 12.508(1) Å, *b* = 13.505(2) Å, *c* = 14.693(2) Å, α = 78.38(1)°, β = 68.147(9)°, γ = 63.56(1)°, *V* = 2060.7(5) Å³, *Z* = 4, *D_c* = 1.506 g cm⁻³. Data were collected on an Enraf-Nonius CAD-4F diffractometer at ambient temperature using graphite monochromated Mo K α radiation (λ = 0.710 73 Å) and $\theta/2\theta$ scan technique. A total of 3822 reflections were measured in the range of 2° < 2 θ < 40°. Data were corrected for Lorentz and polarization effects, but not for absorption, to give 3822 unique reflections, of which 2080 had *F* > 6 σ (*F*). The structure was solved by direct methods (SHELX-81). Final *R* = 0.0583 and *R_w* = 0.0630.

(11) Gambarotta, S.; Chiang, M. Y. *Organometallics* **1987**, *6*, 897 and references therein.

(12) (a) Rardin, R. L.; Tolman, W. B.; Lippard, S. J. *New J. Chem.* **1991**, *15*, 417. (b) Tolman, W.; Liu, S.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 152. (c) Wages, H. E.; Taft, K. L.; Lippard, S. J. *Inorg. Chem.* **1993**, *32*, 4985. (d) Baldwin, M. J.; Kampf, J. W.; Pecoraro, V. *J. Chem. Soc., Chem. Commun.* **1993**, 1741.

(13) Darensbourg, D. J.; Day, C. S.; Fischer, M. B. *Inorg. Chem.* **1981**, *20*, 3577.

(14) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986. (b) Tso, C. C.; Cutler, A. R. *Inorg. Chem.* **1990**, *29*, 471.

ligand. The unusually large Δv for **1** can be attributed to the fact that the C–O single bond and C=O double bond in **1** are relatively discrete, or in other words, the delocalization within the CO₂ moiety is less extensive in **1**, compared to the monodentate formate ligand in the compounds reported in the literature.

Complex **1** results from the reaction of the dinuclear titanium complex [CpTi(μ -H)]₂(C₁₀H₈) with CO₂ at 3 atm. Further investigation is directed toward the characterization of reaction products of the dinuclear titanium complex with CO₂ at low pressure.

Acknowledgment. We wish to thank the Research Corp. (Grant No. C-3665), the TWU Research Enhancement Program, and the Robert A. Welch Foundation for financial support.

Supporting Information Available: Tables of crystal data, crystal data collection parameters, positional parameters, general displacement parameter expressions, bond distances, and bond angles for **1** (26 pages). Ordering information is given on any current masthead page.

OM960280K