

## Novel Alkoxo- and Aryloxotitanium Carbonyls. Structural Characterization of [Ti(CO)<sub>4</sub>(μ-OPh)]<sub>2</sub><sup>2-</sup><sup>1</sup>

Paul J. Fischer, Pong Yuen, Victor G. Young, Jr., and John E. Ellis\*

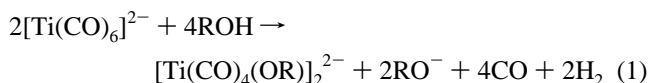
Department of Chemistry, University of Minnesota  
Minneapolis, Minnesota 55455

Received March 24, 1997

Alkoxo-, aryloxo-, and hydroxometal carbonyls and substituted versions thereof are important classes of transition metal complexes since one or more of these have been implicated as intermediates in homogeneous catalyzed hydrogenations of carbon monoxide,<sup>2</sup> aldehydes,<sup>2</sup> and carbonylations of alcohols.<sup>3</sup> They have also been proposed as models for heterogeneous catalysts derived from metal carbonyls and oxide supports.<sup>4,5</sup> Despite a substantial interest in compounds of this type, well characterized examples of the general formula [M<sub>x</sub>(CO)<sub>y</sub>(OR)<sub>z</sub>]<sup>q</sup>, where R = alkyl, aryl, or hydrogen, i.e., those for which both spectral and structural data are available, are presently known only for the group 6, 7, and 11 transition metals.<sup>5,6</sup> We now report on the synthesis and structural characterization of formally unsaturated alkoxo- and aryloxotitanium carbonyls of the general formula [Ti(CO)<sub>4</sub>(μ-OR)]<sub>2</sub><sup>2-</sup>, R = methyl (**1**) and phenyl (**2**). These are the first stable zerovalent titanium carbonyls containing oxygen donor ligands and six coordinate titanium.<sup>7</sup> Of particular interest are their spectral, chemical, and structural properties, which indicate that the doubly bridging RO ligands function as electronic equivalents of η<sup>5</sup>-cyclopentadienyl groups.

These initial examples of Ti(0) alkoxides and aryloxides were prepared by mixing [Ti(CO)<sub>6</sub>]<sup>2-</sup><sup>8</sup> with methanol or phenol in attempts to obtain the unknown hydride [Ti(CO)<sub>6</sub>H]<sup>-</sup>. In a typical synthesis of **1**, methanol (200 mL) was added to finely divided solid [K(15-crown-5)]<sub>2</sub>[Ti(CO)<sub>6</sub>] (4.10 g, 3.50 mmol) with vigorous stirring at room temperature. After 3.5 h, the resulting red solid was isolated and recrystallized from pyridine–ether. By this procedure satisfactorily pure [K(15-crown-5)]<sub>2</sub>(**1**), 1.48 g, was obtained in 63% yield as air-sensitive, dark-red microcrystals.<sup>9</sup> The analogous pure phenoxide adduct, [K(15-crown-5)]<sub>2</sub>(**2**), was prepared in 43% yield by a similar procedure, except phenol and [Ti(CO)<sub>6</sub>]<sup>2-</sup> were combined in a 4:1 molar ratio in acetonitrile at 0 °C.<sup>9</sup> Water, ethanol, 2-propanol, and 1-butanol also readily react with [Ti(CO)<sub>6</sub>]<sup>2-</sup>

to give analogous products<sup>10</sup> (eq 1).



Infrared and <sup>13</sup>C NMR spectra of **1** and **2** in the ν,δ(CO) regions<sup>9</sup> are strikingly similar to those of conventional 18 electron seven coordinate titanium tetracarbonyls. For example, solutions of **1** in DMSO exhibit IR ν(CO) bands at 1901 (m) and 1758 (s) cm<sup>-1</sup> and a <sup>13</sup>C NMR carbonyl resonance at +291 ppm. In the same solvent [Ti(CO)<sub>4</sub>C<sub>5</sub>H<sub>5</sub>]<sup>-</sup> has corresponding peaks at ν(CO) = 1921 (m) and 1777 (s) cm<sup>-1</sup> and δ(CO) = +289 ppm,<sup>11</sup> which suggests that the bridging methoxy groups in **1** are substantially stronger donors to titanium than is the η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> group in [Ti(CO)<sub>4</sub>C<sub>5</sub>H<sub>5</sub>]<sup>-</sup>!

Despite the formally unsaturated character of **1** it has proven to be rather unreactive to thermal substitution reactions and in this respect closely resembles [Ti(CO)<sub>4</sub>C<sub>5</sub>R<sub>5</sub>]<sup>-</sup>, R = H, CH<sub>3</sub>.<sup>12</sup> For example, it failed to undergo detectable reactions with excess alkyl- and arylphosphines, trimethyl phosphite, triphenylstannyl anion, and 1,4,7-triazacyclononane at room temperature for 24 h in pyridine at 20 °C. However, unlike [Ti(CO)<sub>4</sub>C<sub>5</sub>H<sub>5</sub>]<sup>-</sup>, it did undergo complete CO exchange within an hour in pyridine at 20 °C.

Single-crystal X-ray structural analyses have been carried out for **1** and **2** and revealed nearly identical structural units for both species. Only the molecular structure of **2**, shown in Figure 1, will be discussed in detail herein.<sup>13</sup> The dimeric unit contains two Ti(CO)<sub>4</sub> groups bridged by phenoxide ligands and has an overall structure consisting of two trigonal prisms sharing an edge, defined by the bridging phenoxo oxygens. Although mononuclear complexes containing trigonal prismatic environments about a metal center are now well-established,<sup>14</sup> dinuclear species such as **2** appear to be unprecedented.

A comparison of its structure with that of the stoichiometrically related but saturated alkoxo carbonyl dimer [W(CO)<sub>4</sub>(μ-OCH<sub>2</sub>CF<sub>3</sub>)]<sub>2</sub><sup>2-</sup> (**3**)<sup>5</sup> is especially revealing. The latter has a normal structure consisting of two octahedra sharing an edge, defined by the bridging RO groups. While the bridging oxygens in **3** are pyramidal, those in **2** are trigonal planar and are of appropriate symmetry to function as π-donors. To permit effective RO π donation to empty titanium dπ orbitals, the individual M(CO)<sub>4</sub> units in **2** have been rotated by about 45° with respect to the planar M<sub>2</sub>O<sub>2</sub> core, compared to corresponding M(CO)<sub>4</sub> units in **3**. Thus, the trigonal prismatic and octahedral geometries of the metals in **2** and **3**, respectively, arise from the different electronic requirements of the d<sup>4</sup> titanium and d<sup>6</sup> tungsten atoms in six-coordinate environments.

Other structural features of **2** are consistent with the presence of an electronically saturated Ti(0) carbonyl complex. For example, the two eclipsed and symmetry equivalent Ti(CO)<sub>4</sub> units in **2** closely resemble those present in the seven-coordinate,

(10) Fischer, P. J.; Ellis, J. E. Unpublished research.

(11) Ellis, J. E.; Frerichs, S. R.; Stein, B. K. *Organometallics* **1993**, *12*, 1048.

(12) Ellis, J. E.; Stein, B. K.; Frerichs, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 4066.

(13) (a) Attempts to grow X-ray quality crystals of [K(15-crown-5)]<sub>2</sub>(**1**) or (**2**) were unsuccessful. However, [PPN]<sub>2</sub>(**1**), where PPN = N(PPh<sub>3</sub>)<sub>2</sub>, and [K(18-crown-6)]<sub>2</sub>(**2**) gave suitable crystals as pyridine solvates from ether–pyridine, (**1**) or heptane–pyridine (**2**). Spectroscopic and chemical properties of **1** and **2** were independent of the cation. (b) Crystal data for **1**: C<sub>22</sub>H<sub>76</sub>N<sub>4</sub>O<sub>10</sub>P<sub>4</sub>Ti<sub>2</sub>, M = 1617.25, triclinic, P1̄, deep red block, a = 12.4792(1) Å, b = 12.9108(1) Å, c = 13.8232(2) Å, α = 76.991(1)°, β = 71.613(1)°, γ = 78.710(1)°, Z = 1, R = 0.0421, with GOF = 1.059 on F<sup>2</sup>. Other details on **1** will be reported in a separate publication. (c) Crystal data for **2**: C<sub>54</sub>H<sub>68</sub>K<sub>2</sub>N<sub>2</sub>O<sub>22</sub>Ti<sub>2</sub>, M = 1217.10, monoclinic, P2<sub>1</sub>/n, purple block, a = 13.3462(2) Å, b = 17.2254(1) Å, c = 13.7062(2) Å, β = 102.372(1)°, Z = 4, final residual, R = 0.0432, with GOF = 1.060 on F<sup>2</sup>.

(14) Haaland, A.; Hammel, A.; Rypdal, K.; Volden, H. V. *J. Am. Chem. Soc.* **1990**, *112*, 4547.

(1) Highly Reduced Organometallics. Part 41. Part 40: Fischer, P. J.; Young, V. G., Jr.; Ellis, J. E. *Chem. Commun.* In press.

(2) (a) Dombeck, B. D. *Adv. Catal.* **1983**, *32*, 326. (b) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61 and references cited therein. (c) Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259.

(3) Bryndza, H. E.; Kretschmar, S. A.; Tulip, T. H. *J. Chem. Soc., Chem. Commun.* **1985**, 977. (b) Darenbourg, D. J.; Gray, R. L.; Ovalles, C. *J. Mol. Catal.* **1987**, *41*, 329 and references cited therein.

(4) Lamb, H. H.; Gates, B. C.; Knözinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.

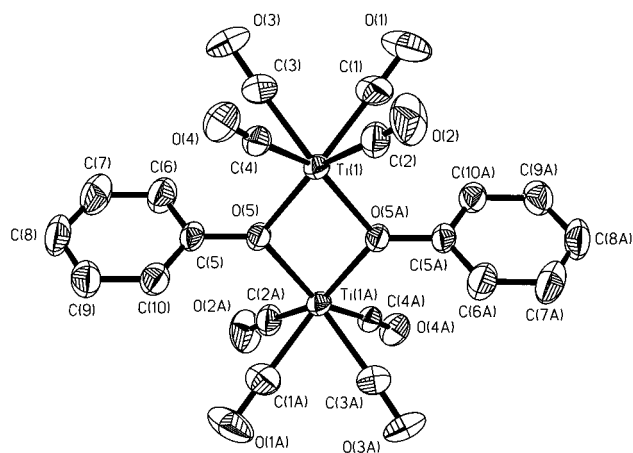
(5) Darenbourg, D. J.; Mueller, B. L.; Bischoff, C. J.; Johnson, C. J.; Sanchez, K. M.; Reibenspies, J. H. *Isr. J. Chem.* **1990**, *30*, 369.

(6) (a) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645. (b) Chisholm, M. W.; Hoffmann, D. M.; Hoffman, J. C. *Organometallics* **1985**, *4*, 986. (c) Ciani, G.; Sironi, A.; Albini, A. *Gazz. Chim. Ital.* **1979**, *109*, 615. (d) Darenbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 7094. (e) Darenbourg, D. J.; Jones, M. L. M.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 4406. (f) Geerts, R. L.; Huffman, J. C.; Foltz, K.; Lemmen, T. H.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 3503.

(7) All prior examples contain seven coordinate titanium. See: Cloke, F. G. N. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 4, p 213.

(8) Chi, K.-M.; Frerichs, S. R.; Philson, S. B.; Ellis, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 303.

(9) Correct C,H analysis for unsolvated products. See text for IR NMR data in the ν,δ(CO) regions for **1**. Corresponding selected data for [K(15-crown-5)]<sub>2</sub>(**2**): IR (CH<sub>3</sub>CN) ν(CO), 1914 (m), 1774 (s) cm<sup>-1</sup>. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>CN, 0 °C) δ(CO) +290 (s) ppm.



**Figure 1.** Molecular structure of **2** showing the labeling scheme. Selected dimensions (Å and deg): Ti–C(1) 2.004(3), Ti–C(2) 2.003(3), Ti–C(3) 2.004(3), Ti–C(4) 2.002(3), Ti–Ti 3.3782(8), Ti–O(5) 2.079(2), Ti(A)–O(5) 2.102(2), C(1)–O(1) 1.161(3), C(2)–O(2) 1.166(3), C(3)–O(3) 1.174(3), C(4)–O(4) 1.174(3), C(5)–O(5) 1.373(3), C(1)–Ti–C(2) 69.3(1), C(1)–Ti–C(3) 71.4(1), C(2)–Ti–C(4) 68.7(1), C(3)–Ti–C(4) 67.4(1), C(1)–Ti–C(4) 108.4(1), C(2)–Ti–C(3) 105.3(1), Ti–O(5)–Ti(A) 107.80(7), O(5)–Ti–O(5A) 72.20(7).

18-electron species  $\text{Ti}(\text{CO})_4(\text{Me}_3\text{tacn})^{15}$  (**4**). For compound **4**, the average Ti–C and C–O distances are 1.996(6) and 1.17(1) Å, respectively,<sup>15</sup> while corresponding values in **2** are essentially identical, i.e., 2.003(3) and 1.169(6) Å. Also the average *cis* and *trans* C–Ti–C angles in the  $\text{Ti}(\text{CO})_4$  units in **4** (*cis*, 68–(2)°; *trans*, 104.6(3)°) and **2** (*cis*, 69(2)°; *trans*, 106(2)°) are experimentally indistinguishable (and differ greatly from corresponding values in the tungsten dimer, **3**<sup>5</sup>). Similarly, acute *cis* C–M–C angles of 72° and 74.3° have been observed in  $\text{Mo}(\text{CO})_2(\eta^1\text{-pyridine})_2(\text{O-tBu})_2$ <sup>16</sup> and  $\text{Mo}(\text{CO})_2(\text{S}_2\text{CN-iPr}_2)_2$ ,<sup>17</sup> respectively, which are also formally unsaturated 6-coordinate low-spin  $d^4$  metal carbonyls, containing potential  $\pi$ -donor ligands. The unusual structures adopted by the latter species, and undoubtedly also those of **1** and **2**, are necessary to optimize both ligand  $\pi$ -donation and metal  $d\pi\text{-}\pi^*$  (CO) back-donation,<sup>17,18</sup> and serve to emphasize the cooperative  $\pi$ -donor (OR)–

(15) Ellis, J. E.; DiMaio, A. J.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 10676.  $\text{Me}_3\text{tacn}$  = 1,4,7-trimethyl-1,4,7-triazacyclononane.

(16) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7615.

(17) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6568.

(18) The dithiocarbamate complex (ref 17) appears to be the only previously known trigonal prismatic metal carbonyl complex.

$\pi$ -acceptor (CO) interactions present in these species. The Ti–Ti distances in **1** and **2** of 3.340(6) and 3.378(1) Å, respectively, are similar to that in the paramagnetic dimer  $[\text{Ti}(\text{C}_5\text{H}_5)_2(\mu\text{-OMe})_2]_2$ , 3.358(2) Å,<sup>19</sup> in which direct Ti–Ti bonding is believed to play a minor role at best.<sup>20</sup> The average Ti–O distance in **2** of 2.09(1) Å is only slightly longer than those in **1**, 2.07(1) Å, and the aforementioned Ti(III) dimer, 2.065(2) Å.<sup>20</sup> While all of our other data strongly suggest that the Ti–O bonds in **1** and **2** have some degree of multiple bonding, the Ti–O distances are rather uninformative in this regard since there exist no other Ti(0)–oxygen bond data for comparison. Anions are well-separated from the  $[\text{K}(18\text{-crown-6-pyridine})]^+$  cation in the crystalline lattice.<sup>21</sup>

Compounds **1** and **2** represent two new examples of a growing number of compounds in which “ $\pi$ -stabilized unsaturation” plays a key role in defining their chemical, spectroscopic, and structural properties.<sup>22</sup> In the past, alkoxides, aryloxides, and similar “hard” donors bound to early transition metals in high oxidation states provided the best examples of this phenomenon.<sup>23,24</sup> But this work and related reports on formally unsaturated group 6 and 7  $\eta^2$ -catecholato metal carbonyls<sup>25</sup> emphasize that RO ligands bound to low-valent metal centers bearing good acceptor ligands can also function as effective  $\pi$ -donors in stable compounds.

**Acknowledgment.** We thank the National Science Foundation and donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research. We are grateful to Ms. Christine Lundby for expert assistance in the preparation of this manuscript.

**Supporting Information Available:** Complete crystallographic data for **2**, including structural details of the counterion (8 pages). See any current masthead for ordering and Internet access instructions.

JA970926F

(19) Samuel, E.; Harrod, J. F.; Gourier, D.; Dromzec, Y.; Robert, F.; Jeannin, Y.; *Inorg. Chem.* **1992**, *31*, 3252.

(20) The possibility of Ti–Ti bonding in **1** or **2** cannot be ruled out but it is probably of minor importance, since both of these species contain  $\text{Ti}(\text{CO})_4$  units that are spectrally and structurally almost identical with those present in the monomeric **4**.

(21) Details on the cation structure are available as Supporting Information.

(22) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25 and references cited therein.

(23) Buhro, W. E.; Chisholm, M. H. *Adv. Organomet. Chem.* **1987**, *27*, 311.

(24) (a) Chisholm, M. H. *Chemtracts–Inorg. Chem.* **1992**, *4*, 273. (b) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(25) (a) Hartl, F.; Vlcek, A., Jr.; deLearie, L. A.; Pierpont, L. G. *Inorg. Chem.* **1990**, *29*, 1073. (b) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331. (c) Darensbourg, D. J.; Klausmeyer, K. K.; Mueller, B. L.; Reibenspies, J. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1503. (d) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 1529 and references cited therein.