

**Preparation of Monomeric  $(\text{Me}_5\text{C}_5)_2\text{VO}$  and  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\text{O})(\text{L})$  and Their Decomposition to  $(\text{Me}_5\text{C}_5)_4\text{M}_4(\mu\text{-O})_6$**

Milton R. Smith III, Phillip T. Matsunaga, and  
Richard A. Andersen\*

Chemistry Department and  
Chemical Sciences Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, California 94720

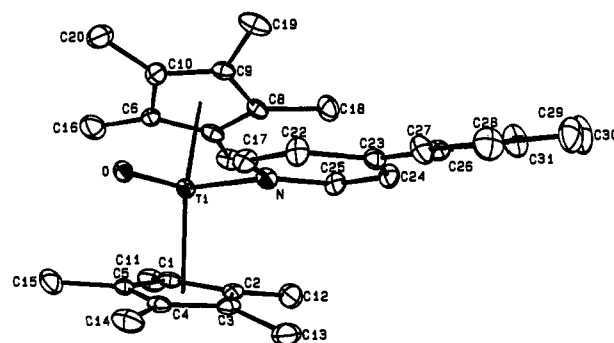
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Nitrous oxide is a convenient source of oxygen atoms for the synthesis of oxometallobenes (and the products derived therefrom) as well as for the insertion of oxygen into metal–hydrogen or –carbon bonds.<sup>1,2</sup> Reaction of nitrous oxide with either  $\text{Cp}_2\text{Ti}$  or  $\text{Cp}_2\text{V}$  gives  $(\text{Cp}_2\text{Ti})_2(\mu\text{-O})_3$  or  $\text{Cp}_2\text{V}_5(\mu\text{-O})_6$ ,<sup>4</sup> respectively. On the other hand, the pentamethylcyclopentadienyl analogues give  $(\text{Me}_5\text{C}_5)_2\text{Ti}_2(\text{CH}_2\text{C}_5\text{Me}_4)(\mu\text{-O})_2^5$  or  $(\text{Me}_5\text{C}_5)_4\text{V}_4(\mu\text{-O})_6$ ,<sup>6</sup> respectively. Monomeric oxometallobenes,  $\text{Cp}_2\text{MO}$  or  $(\text{Me}_5\text{C}_5)_2\text{MO}$  where M is Ti or V, were neither observed nor isolated, an observation we thought curious since  $(\text{RC}_5\text{H}_4)_2\text{MO}$  (M = Mo or W)<sup>7</sup> and  $(\text{Me}_5\text{C}_5)_2\text{WO}$ <sup>8</sup> have been isolated and  $(\text{Me}_5\text{C}_5)_2\text{ZrO}$  has been generated and trapped by reactions with acetylenes.<sup>9</sup> In this communication we show that  $(\text{Me}_5\text{C}_5)_2\text{VO}$  and  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\text{O})(\text{L})$ , where L is pyridine or a substituted pyridine, can be isolated in reactions between nitrous oxide and the metallocenes and that they decompose to the known tetranuclear materials  $(\text{Me}_5\text{C}_5)_4\text{V}_4(\mu\text{-O})_6$ <sup>6</sup> and  $(\text{Me}_5\text{C}_5)_4\text{Ti}_4(\mu\text{-O})_6$ .<sup>10</sup>

Exposing a red hexane solution of  $(\text{Me}_5\text{C}_5)_2\text{V}$  to nitrous oxide (4 atm) yields a green-brown solution and a black precipitate. Green-brown crystals of  $(\text{Me}_5\text{C}_5)_2\text{VO}$ <sup>11</sup> may be isolated from the

\* Address all correspondence to this author at the Chemistry Department, University of California, Berkeley.

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- (11) Anal. Calcd for  $\text{C}_{20}\text{H}_{30}\text{OV}$ : C, 71.2; H, 8.96. Found: C, 71.3; H, 8.99. EIMS: 337 (obsd *I* = 100, calcd *I* = 100) and 338 (25, 22).



**Figure 1.** ORTEP diagram of  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\text{O})(4\text{-phenylpyridine})$  (toluene), solvate toluene is not shown. Ti–C (av) =  $2.51 \pm 0.05$  Å (rms deviation); Ti–Cp (centroid) = 2.20 Å; Ti–O = 1.665(3) Å; Ti–N = 2.215(4) Å; Cp (centroid)–Ti–Cp (centroid) =  $135^\circ$ ; Cp (centroid)–Ti–O =  $108^\circ$ ; Cp (centroid)–Ti–N =  $103^\circ$ ; O–Ti–N =  $90.8(1)^\circ$ .

solution in 45% yield on cooling. The black precipitate was shown to be  $(\text{Me}_5\text{C}_5)_4\text{V}_4(\mu\text{-O})_6$  by infrared and mass spectroscopy.<sup>6</sup> Paramagnetic  $(\text{Me}_5\text{C}_5)_2\text{VO}$  is a monomer in the mass spectrum, and the solid-state IR shows  $\nu\text{V}=\text{O}$  at  $855\text{ cm}^{-1}$ , which shifts to  $820\text{ cm}^{-1}$  on isotopic substitution (<sup>18</sup>O). In the solid state, the compound follows Curie behavior, since a plot of  $\chi_M^{-1}$  is a linear function of temperature (5–300 K) with  $\mu_B = 1.95$  and  $\theta = -0.49$  K. The EPR spectrum at room temperature in methylcyclohexane (ca. 0.1 M) consists of an eight-line pattern with  $g_{\text{iso}} = 1.9844$  and  $A_{\text{iso}} = 25$  G. Both data are in the range expected for bent metallocenes with a  $3d^1$  electron structure.<sup>12</sup>

Similarly, exposure of  $(\text{Me}_5\text{C}_5)_2\text{Ti}$ ,<sup>13a</sup> or better,  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\text{C}_2\text{H}_4)$ ,<sup>13b</sup> to  $\text{N}_2\text{O}$  (4 atm) in pentane yields a green insoluble material whose <sup>1</sup>H NMR spectrum in  $\text{C}_6\text{D}_6$  indicates a mixture of compounds; resonances for  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\text{CH}_2\text{C}_5\text{Me}_4)(\mu\text{-O})_2$  and  $(\text{Me}_5\text{C}_5)_2\text{Ti}_4(\mu\text{-O})_6$  can be identified. Since the hypothetical  $(\text{Me}_5\text{C}_5)_2\text{TiO}$  has a vacant metal-based orbital of  $a_1$ -symmetry (half-occupied in the case of  $(\text{Me}_5\text{C}_5)_2\text{VO}$ ), we postulated that this vacancy was the source of instability of the monomeric species. If this is true, doing the reaction in presence of a two-electron donor should give  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\text{O})(\text{L})$ . Addition of nitrous oxide (1 atm) to a solution of  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\text{C}_2\text{H}_4)$  dissolved in a 1:10 solution of pyridine:tetrahydrofuran results in an instantaneous color change from green to orange and production of orange crystals of  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\text{O})(\text{py})$ <sup>14a,b</sup> on cooling the solution to  $-80^\circ\text{C}$  in 59% yield. The titanium compound is diamagnetic and  $\nu\text{Ti}=\text{O}$  is observed at  $852\text{ cm}^{-1}$ , which shifts to  $818\text{ cm}^{-1}$  in the <sup>18</sup>O-labeled isotopomer. The mass spectrum shows a monomeric  $[\text{M} - \text{py}]^+$  ion in the gas phase, see below. Using 4-phenylpyridine rather than pyridine gave orange crystals of  $(\text{Me}_5\text{C}_5)_2\text{Ti}(\text{O})(4\text{-phenylpyridine})$  upon crystallization from toluene that were suitable for an X-ray crystallographic study.<sup>14c</sup> An ORTEP diagram is shown in Figure 1 for the toluene solvate.<sup>15</sup> The geometry at the titanium center is similar to that found in  $(\text{Me}_5\text{C}_5)_2\text{TiCl}_2$ ,<sup>16</sup> the principal difference being that the averaged Ti–C distances in the titanil are longer ( $2.51 \pm 0.05$  vs  $2.44 \pm$

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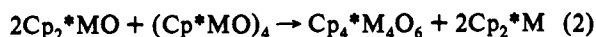
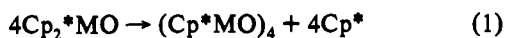
(14) (a) Anal. Calcd for  $\text{C}_{25}\text{H}_{35}\text{NOTi}$ : C, 72.6; H, 8.53; N, 3.13. Found: C, 72.6; H, 8.56; N, 3.08. The EIMS gave a parent ion for  $[\text{M} - \text{py}]^+$ , 334 (100, 100), 335 (38, 29). <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta$  8.91 (1H), 7.50 (1H), 6.74 (1H), 6.44 (2H), 1.86 (30H). The first four resonances are due to coordinated pyridine since they change to those values found for free pyridine in  $\text{C}_6\text{D}_6$  upon addition of excess pyridine-*d*<sub>5</sub>. (b)  $(\text{Me}_5\text{C}_5)_2\text{Zr}(\text{O})(\text{py})$  has been prepared by identical methodology from  $(\text{Me}_5\text{C}_5)_2\text{Zr}(\text{CO})_2$ ; Parkin, G. F. R., personal communication. (c) <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta$  9.00 (1H), 7.58 (1H), 7.18 (2H), 7.10 (3H), 6.88 (2H), 1.93 (30H). All of the resonances are complicated multiplets except the last one, a singlet due to  $\text{Me}_5\text{C}_5$ .

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0.02 Å). The spread in the individual distances is wider, presumably reflecting greater steric congestion about the titanyl center. The Ti–O bond distance of 1.665(3) Å is in the range (1.61–1.68 Å) found in six structures of titanyl groups with vastly different ligands.<sup>17</sup>

The decomposition of the monomeric oxometallocenes is not necessarily a simple event since four M=O units generate the M<sub>4</sub>O<sub>6</sub> units with loss of four Me<sub>5</sub>C<sub>5</sub> groups; the extra two oxygen atoms could arise from two additional M=O units as illustrated in eqs 1 and 2 or from adventitious water or oxygen, Cp<sub>2</sub>\*MO being replaced by O in eq 2.



In order to address this question we isolated the <sup>18</sup>O-labeled compounds (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>V(<sup>18</sup>O) or (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Ti(<sup>18</sup>O)(py) and allowed them to decompose to (Me<sub>5</sub>C<sub>5</sub>)<sub>4</sub>V<sub>4</sub>(<sup>18</sup>O)<sub>x</sub>(<sup>16</sup>O)<sub>6-x</sub> at room temperature or (Me<sub>5</sub>C<sub>5</sub>)<sub>4</sub>Ti<sub>4</sub>(<sup>18</sup>O)<sub>x</sub>(<sup>16</sup>O)<sub>6-x</sub> at higher temperature. The tetranuclear compounds were analyzed by electron-ionization mass spectroscopy, as the unlabeled compounds yield molecular ions. Figure 2a shows the mass spectrum of unlabeled (Me<sub>5</sub>C<sub>5</sub>)<sub>4</sub>Ti<sub>4</sub>(O)<sub>6</sub>. The bar graphs represent the experimental intensities (shaded) and the calculated intensities (unshaded). Inspection shows that the calculated spectrum matches the experimental spectrum closely. The mass spectrum of (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Ti(<sup>18</sup>O)<sub>x</sub>(<sup>16</sup>O)<sub>1-x</sub>(py) shows a molecular ion for [(Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Ti(<sup>18</sup>O)<sub>x</sub>(<sup>16</sup>O)<sub>1-x</sub>]<sup>+</sup> from which the isotopic ratio of <sup>18</sup>O:<sup>16</sup>O was determined to be 0.60:0.40, *i.e.*, *x* = 0.60. The decomposition of this mixed isotopomer gives the tetranuclear species whose experimental and calculated mass spectra are illustrated in Figure 2b. The calculated spectrum was derived by assuming that all of the oxygen atoms are exclusively derived from the monomer of isotopic composition <sup>18</sup>O:<sup>16</sup>O = 0.60:0.40 rather than from some other source of <sup>16</sup>O atoms.<sup>18</sup> Inspection shows that, under this assumption, the experimental and calculated mass spectra match very well. This is consistent with, but does not prove, our assumption that the assembly of the (Me<sub>5</sub>C<sub>5</sub>)<sub>4</sub>Ti<sub>4</sub>(O)<sub>6</sub> occurs predominantly from (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>TiO. A similar conclusion can be reached for the decomposition of (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>V(<sup>18</sup>O<sub>0.76</sub>)(<sup>16</sup>O<sub>0.24</sub>) to (Me<sub>5</sub>C<sub>5</sub>)<sub>4</sub>V<sub>4</sub>[(<sup>18</sup>O<sub>0.76</sub>)(<sup>16</sup>O<sub>0.24</sub>)]<sub>6</sub>.<sup>18</sup> We conclude that the pro-

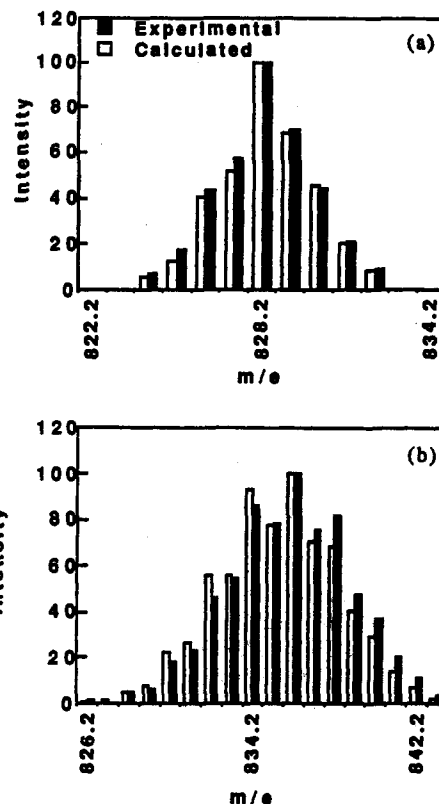


Figure 2. (a) Spectrum for (Me<sub>5</sub>C<sub>5</sub>)<sub>4</sub>Ti<sub>4</sub>(O). (b) Spectrum for (Me<sub>5</sub>C<sub>5</sub>)<sub>4</sub>Ti<sub>4</sub>(<sup>18</sup>O:<sup>16</sup>O = 0.60:0.40)<sub>6</sub>.

longed incubation times used by Bottomley<sup>6</sup> preclude isolation of monomeric (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>VO and that the titanyl analogue can be stabilized by use of a two-electron  $\sigma$ -donor Lewis base.

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**Supplementary Material Available:** Tables of positional parameters, thermal parameters, bond lengths and bond angles, and crystal data; details for the mass spectral simulation of the molecular ions derived from (Me<sub>5</sub>C<sub>5</sub>)<sub>4</sub>V<sub>4</sub>(<sup>18</sup>O:<sup>16</sup>O)<sub>6</sub> and (Me<sub>5</sub>C<sub>5</sub>)<sub>4</sub>Ti<sub>4</sub>(<sup>18</sup>O:<sup>16</sup>O)<sub>6</sub> (18 pages). Ordering information is given on any current masthead page.

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