

mA/cm<sup>2</sup>, so we can expect a small loss in efficiency if for no other reason than this as current density approaches such high values.

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## Reactivity of $[\mu-(\eta^1:\eta^5-C_5H_4)](\eta-C_5H_5)_3Ti_2$ with Dinitrogen. Structure of a Titanium Complex with a Triply-Coordinated N<sub>2</sub> Ligand

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**Abstract:** The titanium metallocene complex,  $\mu-(\eta^1:\eta^5\text{-cyclopentadienyl})\text{-tris}(\eta\text{-cyclopentadienyl})\text{dittitanium} (Ti-Ti)$ ,  $[\mu-(\eta^1:\eta^5-C_5H_4)](\eta-C_5H_5)_3Ti_2$  (**1**), displays a wide range of chemical reactivity with dinitrogen. In hydrocarbon solvents **1** reacts reversibly with N<sub>2</sub> to yield a deep blue complex of composition  $[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$ . Reaction of **1** with N<sub>2</sub> (~10 atm) in 1,2-dimethoxyethane (glyme) yields N<sub>2</sub> complex **3** characterized by  $\nu(N-N) = 1222\text{ cm}^{-1}$ , the lowest N-N vibrational frequency yet observed for any coordinated dinitrogen ligand. Reaction of **3** with tetrahydrofuran (THF) yields N<sub>2</sub>-complex **4** with  $\nu(N-N) = 1296\text{ cm}^{-1}$ . Successive treatment and workup of **3** with THF/glyme and bis(2-methoxyethyl) ether (diglyme) gave a crystalline N<sub>2</sub> complex **5** with  $\nu(N-N) = 1282\text{ cm}^{-1}$ . The composition and structure of **5** was determined by single-crystal X-ray crystallography as  $(\mu_3-N_2)[(\eta^5-\eta^5-C_{10}H_8)(\eta-C_5H_5)_2Ti_2][(\eta^1-\eta^5-C_5H_4)(\eta-C_5H_5)_3Ti_2][(\eta-C_5H_5)_2(C_6H_{14}O_3)Ti] \cdot C_6H_{14}O_3$  (**5**). In this complex, the dinitrogen ligand is coordinated simultaneously to three titanium atoms. The N<sub>2</sub> is  $\sigma$  bonded to the one formally divalent titanium atom in  $[\mu-(\eta^1:\eta^5-C_5H_4)](\eta-C_5H_5)_3Ti_2$ . It is also coordinated in what may be described as a  $\sigma,\pi$  mode to the two titanium atoms in  $(\eta^5-\eta^5-C_{10}H_8)(\eta-C_5H_5)_2Ti_2$ . As a result of the multiple coordination, the N-N length [1.301 (12) Å] in **5** is considerably longer than in free dinitrogen [1.0976 Å], and is intermediate between that for azo (>N=N<) and hydrazo (>N-N<) compounds. Treatment of solutions of **5** with H<sub>2</sub> gas, or with dry HCl, results in a loss of most of the coordinated dinitrogen (as N<sub>2</sub>). However, aqueous hydrolysis of **5** in diglyme yields mostly ammonia. The implications of this chemistry to N<sub>2</sub>-fixation systems are discussed.

Low-valent bis( $\eta$ -cyclopentadienyl)titanium complexes<sup>1b,c</sup> have been widely employed as reagents and catalysts in chemical reactions with small unsaturated molecules, e.g., hydrogen and olefins,<sup>2,3</sup> acetylene,<sup>4</sup> carbon dioxide,<sup>5</sup> carbon monoxide,<sup>6</sup> ammonia,<sup>7</sup> and nitrogen oxides.<sup>8</sup> However, their most striking property is the often extraordinarily facile reactivity with dinitrogen.

It was shown in 1964 by Vol'pin, Shur, and co-workers<sup>9</sup> that mixtures of bis( $\eta$ -cyclopentadienyl)titanium dichloride and Grignard reagents could stoichiometrically reduce dinitrogen to

ammonia. The specific organometallic titanium species responsible for this N<sub>2</sub> reduction has not been identified.<sup>10,11</sup> However, the proposed coordination of dinitrogen to titanium has since been demonstrated by the isolation of several titanium N<sub>2</sub> complexes such as  $\mu$ -dinitrogen-tetrakis( $\eta$ -pentamethylcyclopentadienyl)-dittitanium,  $[(\eta-C_5[CH_3]_5)_2Ti]_2N_2$ ,<sup>12</sup> and  $\mu$ -dinitrogen-bis(*p*-tolyl)tetrakis( $\eta$ -cyclopentadienyl)dittitanium,  $[(\eta-C_5H_5)_2(p-C_6H_4CH_3)Ti]_2N_2$ .<sup>13</sup> These have been isolated as discrete, crystalline solids and their structural and chemical properties carefully investigated. Deep blue dinitrogen complexes of stated composition  $[(C_5H_5)_2TiR]N_2$  (R = alkyl),<sup>14</sup>  $[(C_5H_5)_2Ti]_{1-2}N_2$ ,<sup>15</sup> and  $[(C_5H_5)_2Ti]_2N_2$ <sup>16</sup> have been reported and are widely referred to in the literature. Unfortunately, these complexes were not well characterized and their stated composition and structure are, at best, doubtful. Interesting titanium dinitrogen complexes, displaying unusually low  $\nu(N-N)$  vibrational stretching frequencies, have been described by Borod'ko, Shilov, and co-workers.<sup>17,18</sup> The

(1) (a) Address correspondence to this author at Air Products and Chemicals, Inc., Corporate Science Center, P.O. Box 538, Allentown, PA 18105. For recent reviews of organometallic titanium and zirconium chemistry, see: (b) Pez, G. P.; Armor, J. N. In "Advances in Organometallic Chemistry", West, R., Stone, F. G. A., Eds.; Academic Press: New York, 1981; Vol 19, p 1. (c) Labinger, J. A. *J. Organomet. Chem.* **1979**, *180*, 187 and references to prior yearly reviews cited therein.

(2) (a) Martin, H. A.; DeJongh, R. O. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 713. (b) Cannel, L. G. *J. Am. Chem. Soc.* **1972**, *94*, 6867. (c) Pez, G. P. *J. Chem. Soc., Chem. Commun.* **1977**, 560. (d) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529. (e) Bonds, W. D., Jr.; Brubaker, C. H., Jr.; Chandrasekaran, E. S.; Gibbons, C.; Grubbs, R. H.; Kroll, L. C. *Ibid.* **1975**, *97*, 2128.

(3) Pez, G. P.; Kwan, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 8079.  
(4) (a) Yokokama, K.; Azuma, K. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 859.  
(b) Hsu, S. L.; Signorelli, A. J.; Pez, G. P.; Baughman, R. H. *J. Chem. Phys.* **1978**, *69*, 106.

(5) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, J. *J. Am. Chem. Soc.* **1979**, *101*, 1767. See also reviews cited above in ref 1b.

(6) (a) Sonogoshira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1178. (b) Floriani, C.; Fachinetti, G. U.S. Patent 3 920 745, 1975.

(7) (a) Armor, J. N. *Inorg. Chem.* **1978**, *17*, 203. (b) Armor, J. N. *Ibid.* **1978**, *17*, 213.

(8) Bottomley, F.; Brintzinger, H. H. *J. Chem. Soc., Chem. Commun.* **1978**, 234.

(9) Vol'pin, M. E.; Shur, V. B. *Nature (London)* **1966**, *209*, 1236 and references cited therein.

(10) (a) Olive, G. H.; Olive, S. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 650.  
(b) Marchan, J. C.; Barbara, A. *Anal. Lett.* **1972**, *5*, 897.

(11) For reviews on Vol'pin and Shur and related N<sub>2</sub>-fixation systems, see: (a) Vol'pin, M. E. *Pure Appl. Chem.* **1972**, *30*, 607. (b) Shilov, A. E. In "A Treatise on Dinitrogen Fixation", Hardy, R. W. F., Bottomley, F., Burns, R. C., Eds.; Wiley-Interscience: New York, 1979; p 68. (c) van Tamelen, E. E. *Acc. Chem. Res.* **1970**, *3*, 362.

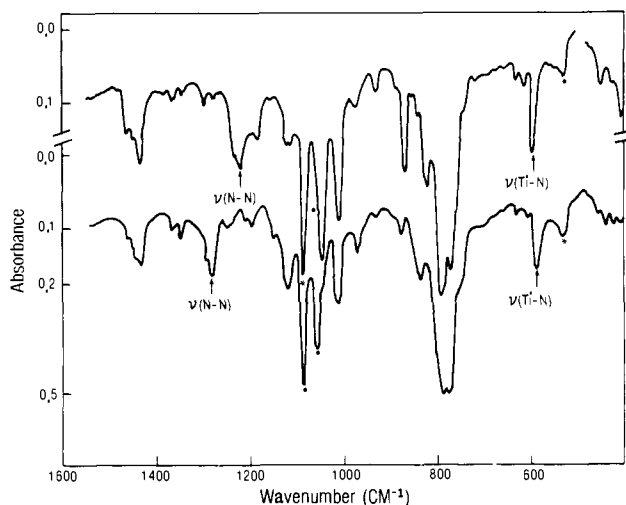
(12) (a) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087. (b) Sanner, R. D.; Duggan, D. M.; McKenzie, T. C.; Marsh, R. E.; Bercaw, J. E. *Ibid.* **1976**, *98*, 8358.

(13) (a) Zeinstra, J. D.; Teuben, J. H.; Jellinek, F. *J. Organomet. Chem.* **1979**, *170*, 39. (b) van der Weij, R. W.; Teuben, J. H. *Ibid.* **1976**, *120*, 223.

(14) Shilov, A. E.; Shilova, A. K.; Kvashina, E. F. *Kinet. Katal.* **1969**, *10*, 1402.

(15) van Tamelen, E. E.; Cretney, W.; Klaentschi, N.; Miller, J. S. *J. Chem. Soc., Chem. Commun.* **1972**, 481.

(16) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.



**Figure 1.** Infrared spectra of  $N_2$  complex **3** (upper curve) and **5** (lower curve). Absorption bands of the *n*-hexadecane- $d_{34}$  nulling agent are marked with an asterisk. [The bands labeled  $\nu(Ti-N)$  may alternatively be assigned to  $\nu(TiNN)$ , angle bending modes.]

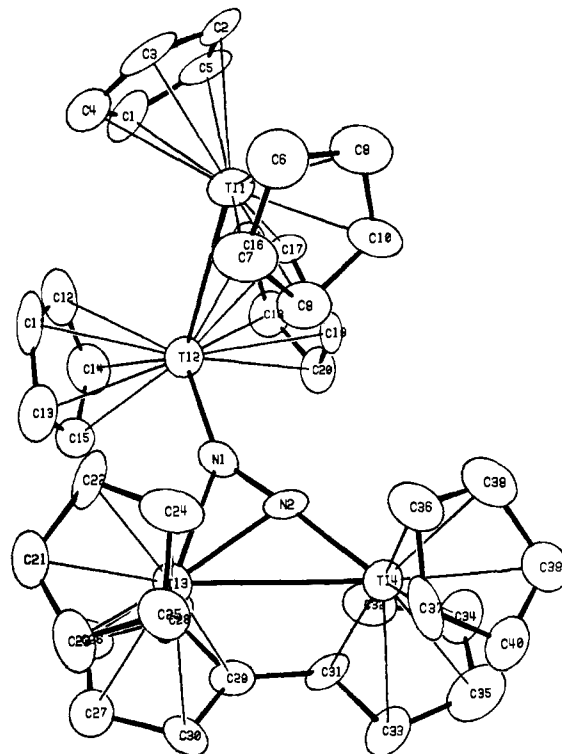
compounds were initially formulated as  $(C_5H_5)_2Ti-N=N-Ti(C_5H_5)_2$  [with  $\nu(N-N) = 1280\text{ cm}^{-1}$ ]<sup>17</sup> and  $[(C_5H_5)_2Ti]_2N_2-MgCl$  [ $\nu(N-N) = 1255\text{ cm}^{-1}$ ].<sup>18</sup> Unfortunately, these complexes apparently were not obtained as crystalline or demonstrably pure chemical compounds.<sup>17b</sup> Recently, Shilov<sup>17b</sup> has expressed doubts about the composition of the said  $(C_5H_5)_2Ti-N=N-Ti(C_5H_5)_2$ . Whatever the nature of these materials, they are nevertheless intriguing examples of complexes containing a highly reduced form of coordinated dinitrogen.

Mindful of the facile  $N_2$  reduction by the Vol'pin and Shur systems, we sought to prepare specific low-valent titanium complexes that could act as possible catalysts in chemical reactions with dinitrogen. We prepared  $\mu-(\eta^1:\eta^5\text{-cyclopentadienyl})\text{-tris}(\eta\text{-cyclopentadienyl})\text{dititanium}(Ti-Ti)$ ,  $[\mu-(\eta^1:\eta^5-C_5H_4)](\eta-C_5H_5)_3Ti_2$  (**1**),<sup>19</sup> which was found to be highly reactive toward  $N_2$  and  $H_2$ ,<sup>3</sup>  $NH_3$ ,<sup>7</sup> and olefins<sup>20,3</sup> (cf. structure of the bis(tetrahydrofuran) adduct of **1**). The formation of a deep blue complex  $[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$  (**2**) from **1** and  $N_2$  has been described.<sup>3</sup> We later found that **1** can form several different dinitrogen derivatives. One of these (subsequently labeled **5**) has now been characterized by single-crystal X-ray crystallography. In this paper we report on the basic chemical reactivity of **1** with dinitrogen and on the synthesis and structure of a  $(\mu_3-N_2)$ -tetratitanium metallocene complex.

## Results and Discussion

### Reactions of $[\mu-(\eta^1:\eta^5-C_5H_4)](\eta-C_5H_5)_3Ti_2$ (**1**)<sup>19</sup> with Dinitrogen.

The title compound displays a highly varied chemistry with  $N_2$ . In relatively nonpolar solvents (e.g., hexane, toluene, and diethyl ether) **1** reacts reversibly with  $N_2$  to form  $[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$  (**2**).<sup>3</sup> Deep green solutions of **1** in toluene give the characteristic blue color of **2** upon contact with as little as 3 torr of  $N_2$  at  $-80^\circ\text{C}$ ! In relatively polar, ether solvents **1** shows a strikingly different reactivity with dinitrogen. Solutions of **1** in 1,2-dimethoxyethane (DME) turn deep blue, but only under  $N_2$  pressure ( $\sim 10\text{ atm}$ ). When **1** is stirred in DME under  $N_2$ , the blue color slowly fades leaving a green solution and a dark precipitate **3**. Filtration under  $N_2$  yields a dark (gray to almost black) material (**3**) which was found to contain nitrogen. However, despite many attempts we were not able to arrive at a reproducible and rational elemental composition for the material. Thermal decomposition of **3** under



**Figure 2.** ORTEP view of the  $(\mu_3-N_2)[(\eta^5:\eta^5-C_{10}H_8)(\eta-C_5H_5)_2Ti_2]-[(\eta^1:\eta^5-C_5H_4)(\eta-C_5H_5)_3Ti_2]$  unit in **5** with C, Ti, and N atom labels.

**Table I.** Table of Selected Interatomic Bond Distances (Å) for **5**

Ti1-Ti2	3.334 (4)	C29-C31	1.46 (2)
Ti2-Ti3	3.949 (4)	C51-O1	1.48 (2)
Ti2-Ti4	4.881 (3)	C52-C53	1.50 (3)
Ti3-Ti4	3.101 (3)	C53-O2	1.59 (2)
Ti1-(C1-C5) <sup>a</sup>	2.39 ± 0.02	Ti2-Cp4	2.035
Ti1-Cp1 <sup>b</sup>	2.056	Ti3-N1	2.181 (10)
Ti1-(C6-C10)	2.40 ± 0.02	Ti3-N2	2.097 (11)
Ti1-Cp2	2.064	Ti3-(C21-C25)	2.414 ± 0.014
Ti1-C17	2.175 (13)	Ti3-Cp5	2.080
Ti2-N1	1.953 (11)	Ti3-(C26-C30)	2.413 ± 0.013
Ti2-(C11-C15)	2.45 ± 0.02	Ti4-N2	1.857 (11)
Ti2-Cp3 <sup>b</sup>	2.128	Ti4-(C31-C35)	2.434 ± 0.014
Ti2-(C16-C20)	2.379 ± 0.013	Ti4-Cp7	2.098
Ti5-O1	2.202 (14)	Ti4-(C36-C40)	2.467 ± 0.014
Ti5-O2	2.160 (15)	Ti5-(C41-C45)	2.37 ± 0.02
N1-N2	1.301 (12)	Ti5-Cp9	2.042
Cp(C-C) <sup>c</sup>	1.44 ± 0.02	Ti5-(C46-C50)	2.36 ± 0.02
Cp(C-C) <sup>d</sup>	1.41 ± 0.03	Ti5-Cp10	2.027
C <sub>10</sub> H <sub>8</sub> (C-C) <sup>e</sup>	1.46 ± 0.02		

<sup>a</sup> Mean of Ti-C distances, i.e., from Ti1-C1 to Ti1-C5. <sup>b</sup> Denotes distance to centroid of cyclopentadienyl (Cp) ring. Cp1 denotes Cp ring with atoms C1-C5, etc. <sup>c</sup> Mean C-C distances for Cp rings on Ti1-Ti4. <sup>d</sup> Mean C-C distance for Cp rings on Ti5. <sup>e</sup> Mean C-C distance for fulvalenyl ligand.

vacuum ( $> 50^\circ\text{C}$ ) gave dinitrogen. Infrared spectra of all samples of **3** gave medium intensity absorptions at 1222 and  $592\text{ cm}^{-1}$ , in addition to the typical metallocene bands [Figure 1 (upper curve)]. When **3** was prepared using  $^{15}N_2$ , the latter absorptions were shifted to 1182 and  $581\text{ cm}^{-1}$ , respectively. Compound **3** was thus identified as a novel titanium dinitrogen complex, having a characteristic  $\nu(N-N)$  stretching frequency of  $1222\text{ cm}^{-1}$ . The absorption at  $581\text{ cm}^{-1}$  is assignable to either a  $\nu(Ti-N)$  stretching or a  $\nu(TiNN)$  angle bending mode. The  $1222\text{-cm}^{-1}$  N-N stretching frequency is the lowest yet observed for any dinitrogen metal complex.

Treatment of **3** with tetrahydrofuran (THF) gave deep red solutions (without loss of  $N_2$ ) from which a reddish-brown solid (**4**) was isolated. The latter has a clearly observed  $\nu(N-N)$  stretching mode at  $1296\text{ cm}^{-1}$  ( $1252\text{ cm}^{-1}$  with  $^{15}N_2$ ) as well as a  $\nu(Ti-N)$  [or  $\nu(TiNN)$ ] absorption at  $581\text{ cm}^{-1}$  (cf. Table III).

(17) (a) Borod'ko, Yu. G.; Ivleva, I. N.; Kachajina, L. M.; Salienco, S. I.; Shilova, A. K.; Shilov, A. E. *J. Chem. Soc., Chem. Commun.* **1972**, 1178. (b) Ivleva, I. N.; Shilova, A. K.; Salienco, S. I.; Borod'ko, Yu. G. *Dokl. Phys. Chem. (Engl. Transl.)* **1973**, *213* (1), 116.

(18) Borod'ko, Yu. G.; Ivleva, I. N.; Kachajina, L. M.; Kvashina, E. F.; Shilova, A. K.; Shilov, A. E. *J. Chem. Soc., Chem. Commun.* **1973**, 169.

(19) Pez, G. P. *J. Am. Chem. Soc.* **1976**, *98*, 8072.

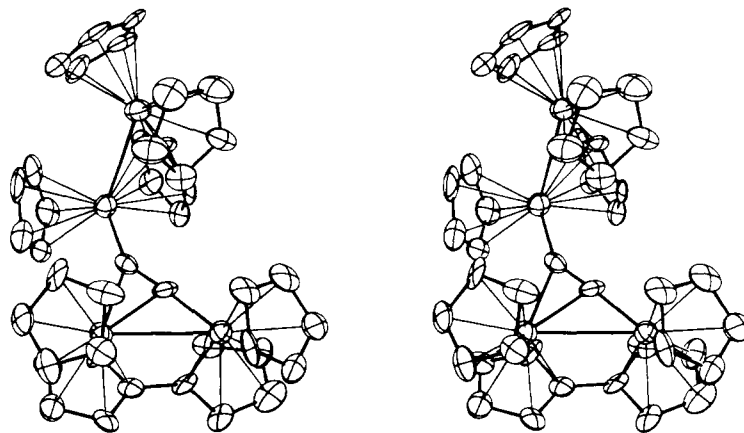


Figure 3. Stereoscopic view of the  $(\mu_3\text{-N}_2)[(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2][(\eta^1\text{-}\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2]$  unit in **5**.

Table II. Table of Selected Bond Angles for **5** in Degrees

Ti2-Ti1-Cp1 <sup>a</sup>	113.2	Ti3-N2-Ti4	103.1 (5)
Ti2-Ti1-Cp2	112.3	Ti4-N2-N1	169.4 (9)
Ti1-Ti2-Cp3	118.1	Ti4-Ti3-N1	70.7
Cp1-Ti1-Cp2	133.3	Ti4-Ti3-N2	35.7
Cp3-Ti2-Cp4	133.4	Ti3-Ti4-N2	41.2
Ti1-Ti2-N1	102.5	Ti4-Ti3-Cp5	116.5
Ti2-N1-N2	145.6 (9)	Ti4-Ti3-Cp <sup>b</sup> (C26-C30)	98.6
Ti2-N1-Ti3	145.6 (6)	Cp9-Ti5-Cp10	134.3
N1-Ti3-N2	35.3 (3)	O1-Ti5-O2	74.6 (6)
Ti3-N1-N2	68.8 (7)	O1-Ti5-Cp10	110.1
Ti3-N2-N1	75.8 (7)	O2-Ti5-Cp9	105.3

<sup>a</sup> Denotes angle to centroid of cyclopentadienyl ring. <sup>b</sup> Denotes centroid of designated fulvalenyl ligand ring.

Also, a definitive composition could not be established for this compound, but fortunately we were able to prepare a crystalline derivative from diglyme solutions. Slow diffusion of isopentane into solutions of purified samples of **4** in bis(2-methoxyethyl) ether (diglyme) gave a red-brown crystalline solid (**5**) with  $\nu(\text{N-N}) = 1282 \text{ cm}^{-1}$  [ $\nu(^{15}\text{N-}^{15}\text{N}) = 1240 \text{ cm}^{-1}$ ]. Fortunately, the crystals of **5** proved to be suitable for X-ray crystallographic studies. After the elucidation of the structure of **5** the reasons for the difficulties encountered in the attempts to characterize **3** and **4** became readily apparent. Specific details of the preparation and basic chemical properties of **3**, **4**, and **5** are given in the Experimental Section.

**Characterization and Structure of  $(\mu_3\text{-N}_2)[(\eta^2\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2][(\eta^1\text{-}\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2][(\eta\text{-C}_5\text{H}_5)_2(\text{C}_6\text{H}_{14}\text{O}_3)\text{Ti}]\cdot\text{C}_6\text{H}_{14}\text{O}_3$  (**5**).** The title compound (**5**) was crystallized from diglyme solutions as air-sensitive, dark red-brown prisms. The composition of **5** was determined primarily by single-crystal X-ray crystallography. Subsequently, a correspondence between the composition of crystalline **5** and the X-ray structure was established from a combination of elemental analyses, infrared spectra, X-ray powder diffraction work, and chemical properties. Elemental analyses obtained for carbon, hydrogen, and titanium are in excellent agreement with the calculated composition of **5**.

Analysis of diglyme (after reaction of **5** with HCl) gave ~85% recovery of  $\text{C}_6\text{H}_{14}\text{O}_3$ ; no other volatile organic solvents used in the preparation of **5** were detected. Infrared spectra of **5** (with  $^{14}\text{N}_2$  and with  $^{15}\text{N}_2$  isotopic substitution) clearly show the presence of a single, considerably reduced and/or multiply connected, dinitrogen ligand (vide infra). An X-ray powder pattern (Cu  $K\alpha$  radiation) of **5** contained, among other features relatable to the decomposition of the sample in the X-ray beam, principal reflections in agreement with the  $D$  spacings and intensities calculated from the positional atom coordinates. Analysis for total nitrogen in **5** by decomposing a sample of the complex with  $\text{I}_2$ , gave results in fair agreement with theory. However, nitrogen determinations by the Dumas technique and from quantitative chemical reactivity studies yielded somewhat higher values than expected (see Experimental Section). It may be that there is a small, nitrogen-rich impurity present in samples of **5** but, in view of the total data presented here, there is no doubt that the bulk of crystalline **5**, prepared as described above, is of the composition determined by the X-ray structural work. A description and discussion of the crystal and molecular structure of **5** follows.

Crystals of **5** are triclinic, of space group  $P\bar{1}$ , and contain two molecules of  $\text{C}_{62}\text{H}_{75}\text{O}_6\text{Ti}_5\text{N}_2$  per unit cell. Each molecule is made up of two, spatially separated titanium metallocene complexes. There is a dinitrogen complex,  $(\mu_3\text{-N}_2)[(\eta^2\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2][(\eta^1\text{-}\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2]$ , which is shown in Figures 2 and 3 and also a bis( $\eta$ -cyclopentadienyl)titanium complex which is associated with two molecules of diglyme,  $(\eta\text{-C}_5\text{H}_5)_2\text{-}(\text{C}_6\text{H}_{14}\text{O}_3)\text{Ti}\cdot\text{C}_6\text{H}_{14}\text{O}_3$  (Figure 4). The spatial relationship between the two, novel titanium metallocene complexes is clearly seen in the stereoscopic view of the full unit cell (Figure 5). Selected values of interatomic distances and angles are given in Tables I and II. The atom positional and thermal parameters are listed in Table IV.

**Structure of Dinitrogen Complex Unit in **5** (cf. Figures 2 and 3).** In the dinitrogen complex unit, the  $\text{N}_2$  ligand is simultaneously coordinated to three titanium atoms. The  $\text{N}_2$  is bonded to the one (formally divalent) titanium atom (Ti1) in a molecule of

Table III. Bond Length and Vibrational Data for Titanium Dinitrogen Complexes

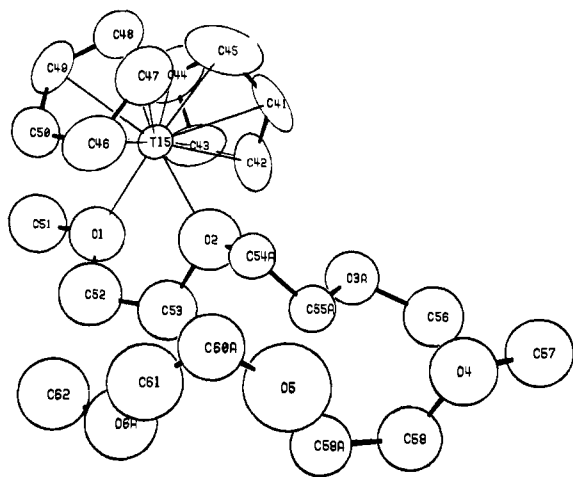
compound	$\nu(\text{Ti-N})$ ( $\nu(\text{Ti-}^{15}\text{N})$ ), <sup>a</sup> $\text{cm}^{-1}$	$D(\text{Ti-N})$ , Å	$\nu(\text{N-N})$ ( $\nu(^{15}\text{N-}^{15}\text{N})$ ), $\text{cm}^{-1}$	$D(\text{N-N})$ , Å
$\text{N}_2$ complex <b>3</b>	592 (581)		1222 (1182)	
$\text{N}_2$ complex <b>4</b>	581 (566)		1296 (1252)	
crystalline $\text{N}_2$ complex <b>5</b>	586 (573)	$1.905 \pm 0.011^b$	1282 (1240)	1.301 (12)
$[(\text{C}_5\text{H}_5)_2\text{Ti}(p\text{-tolyl})]_2\text{N}_2^{13a}$		1.962 (6)		1.162 (12)
$[(\text{C}_5\text{Me}_5)_2\text{Ti}]_2\text{N}_2^{12b}$		2.017 (10) <sup>c</sup>		1.160 (7) <sup>c</sup>
"dark precipitate, $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$ " <sup>17</sup>			1280 (1240)	
$[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2\cdot\text{MgCl}^{18}$			1255 (1215)	
$\text{N}\equiv\text{N}$ ( $\text{N}_2$ gas)			2331	1.0976
$(\text{C}_6\text{H}_5)\text{-N=N-}(\text{C}_6\text{H}_5)$			1441 (Raman) <sup>24</sup>	1.23 <sup>26</sup>
$\text{H}_2\text{N-NH}_2$			1111 (Raman) <sup>25</sup>	1.46 <sup>27</sup>

<sup>a</sup> Ti-N bond stretching or TiNN angle bending modes. <sup>b</sup> Mean of  $\sigma$ , Ti-N bond lengths. <sup>c</sup> Mean of Ti-N and N-N distances, respectively, for the two crystallographically independent molecules of  $[(\text{C}_5\text{Me}_5)_2\text{Ti}]_2\text{N}_2$ .

Table IV. Positional and Thermal Parameters for  $5^b$ 

atom	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Ti1	0.3274 (2)	0.3346 (2)	0.1201 (3)	0.0048 (2)	0.0048 (2)	0.0072 (3)	-0.0010 (3)	0.0013 (4)	0.0039 (4)
Ti2	0.3199 (2)	0.1209 (2)	0.1392 (2)	0.0045 (2)	0.0043 (2)	0.0058 (2)	0.0000 (3)	0.0023 (4)	-0.0005 (4)
Ti3	0.1007 (2)	0.0612 (2)	0.2629 (2)	0.0046 (2)	0.0034 (2)	0.0062 (3)	-0.0009 (3)	-0.0004 (4)	0.0011 (3)
Ti4	0.2189 (2)	0.1151 (2)	0.4839 (2)	0.0047 (2)	0.0037 (2)	0.0053 (2)	-0.0001 (3)	0.0012 (4)	0.0006 (3)
Ti5	0.7420 (2)	0.4175 (2)	0.3856 (3)	0.0053 (2)	0.0038 (2)	0.0090 (3)	0.0009 (3)	-0.0015 (4)	0.0008 (4)
O1	0.734 (1)	0.281 (1)	0.335 (1)	10.3 (5)					
O2	0.767 (1)	0.346 (1)	0.533 (1)	12.1 (5)					
O3A	0.928 (2)	0.343 (2)	0.677 (2)	9.1 (8)					
O3B	0.933 (3)	0.340 (3)	0.759 (3)	15.4 (13)					
O4	0.828 (1)	0.366 (1)	1.000 (1)	12.0 (5)					
O5	0.670 (2)	0.300 (2)	0.851 (2)	20.7 (9)					
O6A	0.571 (3)	0.193 (3)	0.677 (3)	14.6 (13)					
O6B	0.567 (2)	0.263 (2)	0.640 (2)	9.6 (9)					
N1	0.2363 (8)	0.1073 (8)	0.2408 (9)	0.0026 (7)	0.0033 (7)	0.007 (1)	-0.001 (1)	0.001 (1)	0.001 (1)
N2	0.2256 (8)	0.1191 (8)	0.3394 (9)	0.0060 (8)	0.0031 (7)	0.005 (1)	-0.001 (1)	0.006 (1)	0.001 (1)
C1	0.381 (1)	0.2977 (14)	-0.045 (1)	0.0084 (14)	0.0115 (15)	0.004 (1)	-0.004 (2)	0.002 (2)	0.003 (2)
C2	0.402 (1)	0.4352 (13)	0.027 (1)	0.0119 (15)	0.0111 (13)	0.003 (1)	-0.013 (2)	0.000 (2)	0.007 (2)
C3	0.306 (2)	0.4326 (12)	-0.023 (1)	0.0154 (18)	0.0078 (12)	0.005 (1)	-0.003 (3)	0.004 (3)	0.009 (2)
C4	0.292 (1)	0.3465 (13)	-0.071 (1)	0.0098 (15)	0.0089 (13)	0.006 (1)	-0.008 (2)	-0.001 (3)	0.006 (2)
C5	0.443 (1)	0.3551 (12)	0.016 (1)	0.0097 (14)	0.0068 (11)	0.006 (1)	-0.003 (2)	0.006 (2)	0.007 (2)
C6	0.244 (1)	0.4577 (12)	0.176 (2)	0.0098 (15)	0.0043 (10)	0.012 (2)	0.003 (2)	0.004 (3)	0.001 (2)
C7	0.193 (1)	0.3812 (11)	0.190 (2)	0.0072 (13)	0.0046 (10)	0.013 (2)	0.001 (2)	0.005 (3)	0.003 (2)
C8	0.332 (1)	0.4529 (11)	0.249 (2)	0.0083 (14)	0.0043 (10)	0.013 (2)	-0.000 (2)	0.003 (3)	0.003 (2)
C9	0.247 (1)	0.3273 (10)	0.266 (1)	0.0038 (10)	0.0047 (10)	0.009 (1)	0.003 (2)	0.005 (2)	0.001 (2)
C10	0.334 (1)	0.3738 (10)	0.304 (1)	0.0071 (11)	0.0036 (9)	0.010 (1)	-0.003 (2)	0.011 (2)	-0.004 (2)
C11	0.242 (1)	0.1105 (14)	-0.050 (1)	0.0099 (15)	0.0115 (15)	0.004 (1)	-0.004 (3)	-0.002 (3)	-0.006 (3)
C12	0.336 (2)	0.0778 (12)	-0.049 (1)	0.0149 (19)	0.0064 (12)	0.007 (2)	-0.007 (3)	-0.000 (3)	-0.009 (2)
C13	0.194 (1)	0.0559 (14)	0.010 (1)	0.0087 (15)	0.0104 (15)	0.007 (2)	-0.004 (3)	-0.002 (3)	-0.000 (3)
C14	0.349 (1)	0.0021 (11)	0.017 (1)	0.0094 (14)	0.0048 (10)	0.008 (2)	-0.002 (2)	0.005 (2)	-0.007 (2)
C15	0.261 (1)	-0.0091 (11)	0.051 (1)	0.0094 (13)	0.0062 (11)	0.005 (1)	-0.007 (2)	0.007 (2)	-0.006 (2)
C16	0.474 (1)	0.1701 (11)	0.141 (1)	0.0022 (10)	0.0067 (11)	0.006 (1)	-0.001 (2)	-0.001 (2)	-0.000 (2)
C17	0.423 (1)	0.2342 (10)	0.197 (1)	0.0030 (9)	0.0049 (9)	0.005 (1)	-0.002 (2)	0.002 (2)	0.003 (2)
C18	0.490 (1)	0.0919 (12)	0.197 (1)	0.0027 (10)	0.0087 (13)	0.008 (2)	-0.000 (2)	-0.003 (2)	0.005 (2)
C19	0.406 (1)	0.1870 (10)	0.291 (1)	0.0036 (10)	0.0042 (9)	0.003 (1)	-0.001 (2)	-0.004 (2)	0.001 (2)
C20	0.445 (1)	0.1021 (11)	0.290 (1)	0.0038 (11)	0.0063 (11)	0.006 (1)	-0.000 (2)	-0.005 (2)	0.003 (2)
C21	-0.019 (1)	0.1007 (12)	0.113 (1)	0.0038 (11)	0.0081 (12)	0.007 (2)	0.000 (2)	-0.004 (2)	0.002 (2)
C22	0.043 (1)	0.1713 (12)	0.135 (1)	0.0054 (12)	0.0084 (12)	0.004 (1)	0.002 (2)	-0.006 (2)	0.006 (2)
C23	-0.066 (1)	0.0959 (11)	0.204 (1)	0.0033 (11)	0.0058 (11)	0.009 (2)	0.003 (2)	-0.004 (2)	-0.001 (2)
C24	0.038 (1)	0.2056 (10)	0.239 (1)	0.0030 (10)	0.0039 (9)	0.015 (2)	0.002 (2)	0.000 (2)	0.009 (2)
C25	-0.029 (1)	0.1579 (11)	0.284 (1)	0.0046 (11)	0.0042 (9)	0.010 (2)	0.001 (2)	-0.002 (2)	0.005 (2)
C26	0.104 (1)	-0.0841 (10)	0.187 (1)	0.0111 (15)	0.0014 (8)	0.010 (2)	-0.005 (2)	0.003 (3)	0.001 (2)
C27	0.021 (1)	-0.0775 (11)	0.239 (1)	0.0109 (15)	0.0033 (9)	0.007 (2)	-0.004 (2)	-0.000 (3)	0.001 (2)
C28	0.187 (1)	-0.0723 (10)	0.271 (1)	0.0117 (14)	0.0022 (8)	0.003 (1)	0.000 (2)	0.003 (2)	0.000 (2)
C29	0.157 (1)	-0.0610 (10)	0.370 (1)	0.0046 (10)	0.0030 (8)	0.007 (1)	0.000 (2)	0.001 (2)	0.005 (2)
C30	0.055 (1)	-0.0603 (9)	0.354 (1)	0.0062 (12)	0.0017 (8)	0.009 (2)	-0.003 (2)	-0.000 (2)	0.002 (2)
C31	0.217 (1)	-0.0341 (10)	0.470 (1)	0.0073 (12)	0.0029 (8)	0.005 (1)	0.002 (2)	0.002 (2)	0.006 (2)
C32	0.314 (1)	-0.0144 (11)	0.481 (1)	0.0037 (11)	0.0054 (10)	0.011 (2)	0.001 (2)	0.002 (2)	0.005 (2)
C33	0.180 (1)	-0.0162 (10)	0.568 (1)	0.0112 (15)	0.0028 (8)	0.005 (1)	0.001 (2)	-0.001 (2)	0.005 (2)
C34	0.341 (1)	0.0203 (12)	0.589 (1)	0.0075 (13)	0.0061 (11)	0.007 (2)	0.003 (2)	-0.001 (2)	0.003 (2)
C35	0.263 (1)	0.0182 (11)	0.644 (1)	0.0106 (15)	0.0047 (10)	0.009 (2)	0.007 (2)	0.003 (3)	0.006 (2)
C36	0.167 (1)	0.2662 (10)	0.481 (1)	0.0100 (13)	0.0018 (8)	0.011 (2)	-0.002 (2)	0.008 (2)	-0.005 (2)
C37	0.110 (1)	0.2209 (11)	0.540 (1)	0.0072 (13)	0.0040 (9)	0.008 (2)	-0.001 (2)	-0.000 (2)	-0.009 (2)
C38	0.262 (1)	0.2594 (10)	0.544 (1)	0.0099 (14)	0.0025 (9)	0.012 (2)	-0.003 (2)	0.009 (2)	-0.006 (2)
C39	0.257 (1)	0.2144 (11)	0.644 (1)	0.0093 (14)	0.0033 (9)	0.008 (2)	-0.002 (2)	0.005 (2)	-0.004 (2)
C40	0.164 (1)	0.1908 (11)	0.639 (1)	0.0078 (13)	0.0051 (10)	0.005 (1)	0.001 (2)	0.003 (2)	-0.001 (2)
C41	0.883 (1)	0.4887 (14)	0.452 (2)	0.0056 (14)	0.0074 (14)	0.032 (4)	-0.008 (2)	-0.007 (4)	-0.007 (4)
C42	0.910 (1)	0.4024 (15)	0.428 (2)	0.0053 (13)	0.0116 (16)	0.013 (2)	-0.006 (2)	0.003 (3)	-0.005 (3)
C43	0.884 (1)	0.3893 (14)	0.322 (2)	0.0086 (14)	0.0095 (14)	0.019 (2)	0.006 (2)	0.012 (3)	0.012 (3)
C44	0.840 (2)	0.4670 (17)	0.271 (2)	0.0122 (16)	0.0172 (20)	0.011 (2)	0.004 (3)	0.014 (3)	0.012 (3)
C45	0.841 (2)	0.5268 (16)	0.360 (2)	0.0120 (16)	0.0088 (16)	0.036 (3)	-0.001 (3)	0.028 (3)	0.007 (4)
C46	0.589 (1)	0.4331 (15)	0.430 (2)	0.0035 (11)	0.0113 (16)	0.023 (2)	0.006 (2)	0.012 (3)	0.008 (3)
C47	0.634 (1)	0.5171 (15)	0.437 (2)	0.0083 (15)	0.0112 (16)	0.014 (2)	0.004 (3)	0.010 (3)	-0.000 (3)
C48	0.646 (1)	0.5384 (14)	0.342 (2)	0.0069 (15)	0.0068 (13)	0.024 (3)	0.006 (2)	-0.005 (4)	0.001 (3)
C49	0.616 (1)	0.4712 (15)	0.261 (2)	0.0046 (13)	0.0112 (15)	0.014 (2)	0.003 (2)	-0.003 (3)	0.006 (3)
C50	0.576 (1)	0.4083 (13)	0.317 (2)	0.0041 (11)	0.0085 (13)	0.015 (2)	-0.001 (2)	0.008 (2)	0.001 (3)
atom	X	Y	Z	B(1,1)	atoms	X	Y	Z	B(1,1)
C51	0.714 (2)	0.254 (2)	0.221 (2)	12.0 (8)	C58	0.805 (2)	0.277 (2)	0.971 (2)	11.1 (8)
C52	0.704 (2)	0.227 (2)	0.395 (2)	13.0 (9)	C59A	0.701 (3)	0.256 (3)	0.915 (4)	9.8 (14)
C53	0.759 (2)	0.246 (2)	0.505 (2)	11.3 (8)	C59B	0.707 (4)	0.270 (3)	0.982 (4)	11.7 (16)
C54A <sup>a</sup>	0.755 (3)	0.363 (2)	0.635 (3)	6.2 (10)	C60A	0.568 (4)	0.331 (3)	0.795 (4)	11.2 (16)
C54B	0.804 (3)	0.414 (3)	0.629 (3)	8.2 (12)	C60B	0.573 (4)	0.221 (4)	0.826 (5)	16.4 (23)
C55A	0.835 (3)	0.321 (3)	0.704 (3)	6.5 (11)	C61	0.536 (2)	0.268 (2)	0.731 (2)	15.4 (11)
C55B	0.919 (3)	0.402 (3)	0.699 (3)	8.6 (13)	C62	0.527 (2)	0.191 (2)	0.578 (2)	14.4 (10)
C56	1.018 (2)	0.327 (2)	0.775 (2)	11.6 (8)					
C57	0.930 (2)	0.393 (2)	1.034 (2)	12.5 (9)					

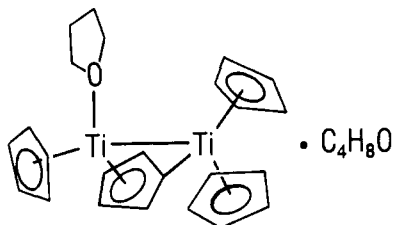
<sup>a</sup> Atoms with "A" and "B" suffixes were refined at 0.5 occupancy. <sup>b</sup> The form of the anisotropic thermal parameter is:  $\exp[-(B(1,1)*h^2 + B(2,2)*k^2 + B(3,3)*l^2 + B(1,2)*h*k + B(1,3)*h*l + B(2,3)*k*l)]$ .



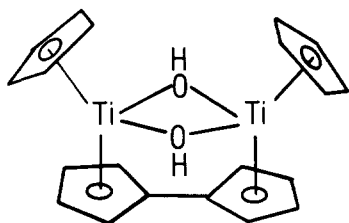
**Figure 4.** ORTEP view of the  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$  unit in **5** with C, Ti, and O atom labels.

$[\mu\text{-}(\eta^5\text{-C}_5\text{H}_4)](\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$  (**1**). It is also coordinated in a  $\sigma, \pi$  fashion<sup>20</sup> to the two (formally divalent) titanium atoms (Ti4 and Ti3, respectively) in a molecule of  $[\mu\text{-}(\eta^5\text{-C}_{10}\text{H}_8)](\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$ .

The  $[\mu\text{-}(\eta^1\text{-}\eta^2\text{-C}_5\text{H}_4)](\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$  fragment (cf. Figure 2) is recognized as the starting material **1** used for the preparation of **5**. It is isostructural with the bis(tetrahydrofuran) adduct complex of **1**,  $[\mu\text{-}(\eta^1\text{-}\eta^2\text{-C}_5\text{H}_4)](\eta\text{-C}_5\text{H}_5)_3(\text{C}_4\text{H}_8\text{O})\text{Ti}_2 \cdot \text{C}_4\text{H}_8\text{O}$  (**1a**).<sup>19</sup> In



fact, the dinitrogen ligand bound to  $[\mu\text{-}(\eta^1\text{-}\eta^2\text{-C}_5\text{H}_4)](\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$  in **5** occupies the same coordination site as the molecule of coordinated tetrahydrofuran in **1a**. The  $[\mu\text{-}(\eta^5\text{-C}_{10}\text{H}_8)](\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$  fragment shows a framework similar to that in  $(\mu\text{-OH})_2[\mu\text{-}(\eta^5\text{-C}_{10}\text{H}_8)](\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$ <sup>21</sup> less the bridging hydroxy ligands. This is also the structure proposed<sup>22</sup> (from chemical



properties and NMR studies) for  $(\mu\text{-H})_2[\mu\text{-}(\eta^5\text{-C}_{10}\text{H}_8)](\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$ , with the hydroxy ligands being replaced by bridging hydrides.

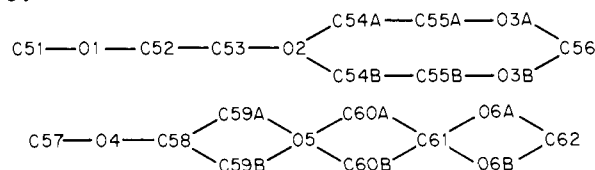
The multiple coordination to three titanium atoms has obvious and pronounced structural chemical and spectroscopic consequences on the dinitrogen ligand. The N-N bond length for dinitrogen of 1.301 (12) Å in **5** is much longer than the 1.0976 Å separation in free dinitrogen. The length is intermediate be-

(20) The  $\sigma, \pi$  description is only approximate, since in the molecule there is not a plane of symmetry perpendicular to the N-N axis.

(21) Guggenberger, L. J.; Tebbe, F. N. *J. Am. Chem. Soc.* **1976**, *98*, 4137. Note that in the  $[\mu\text{-}(\eta^5\text{-C}_{10}\text{H}_8)](\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$  fragment [as in  $(\mu\text{-OH})_2[\mu\text{-}(\eta^5\text{-C}_{10}\text{H}_8)](\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$ ] the fulvalenyl ligand as a whole is not planar; the dihedral angle between the two fulvalenyl ligand rings is 15.1° (see Supplementary Material).

(22) (a) Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182. (b) Davison, A.; Wreford, S. S. *J. Am. Chem. Soc.* **1974**, *96*, 3017.

**Scheme I.** A Possible Disorder Scheme for the Diglyme Molecules<sup>a</sup>



<sup>a</sup> Atoms with "A" and "B" suffixes were refined at 0.5 occupancy. Atoms without suffixes were refined at 1.0 occupancy. Atoms with "A" suffixes are probably not present at the same time as atoms with "B" suffixes, within each diglyme molecule.

tween that of a typical N=N double bond (1.24 ± 0.01 Å) and an >N-N< single bond (1.44 ± 0.04 Å).<sup>23</sup> This dramatic lowering in the N-N bond order from the dinitrogen molecule is also reflected in the corresponding vibrational  $\nu(\text{N-N})$  bond stretching frequencies of 1282  $\text{cm}^{-1}$  for complex **5** and 2331  $\text{cm}^{-1}$  for free dinitrogen. A listing of relevant N-N and Ti-N distances and bond stretching frequencies is given in Table III.

A comparison of  $\nu(\text{N-N})$  and  $\nu(\text{Ti-N})$  stretching frequencies for **3**, **4**, and **5** clearly shows that the Ti-N bond strength [as reflected in  $\nu(\text{Ti-N})$ ] progressively increases with a lowering of the  $\nu(\text{N-N})$  vibrational frequency. We do not know the structure of **3** and **4** but, from the infrared data (Figure 1, Table III), it is reasonable to conclude that these complexes also contain a multiply-coordinated dinitrogen ligand. It also seems very likely that such a multiply-bridged  $\text{N}_2$  ligand may be present in the "dark precipitate",  $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$  [ $\nu(\text{N-N}) = 1280 \text{ cm}^{-1}$ ]<sup>17</sup> and  $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2\text{MgCl}$  [ $\nu(\text{N-N}) = 1255 \text{ cm}^{-1}$ ]<sup>18</sup> compounds referred to earlier.

The  $\mu_3$ -dinitrogen bonding in **5** is unique; it is the only metal complex yet reported wherein  $\text{N}_2$  is connected to three or more transition-metal atoms. A multiple binding of  $\text{N}_2$  to a combination of two nickel and several alkali metal atoms is seen in  $[(\text{C}_6\text{H}_5\text{-Li})_6\text{Ni}_2\text{N}_2 \cdot (\text{C}_6\text{H}_5)_2\text{O}]_2$ <sup>28</sup> and  $[\text{C}_6\text{H}_5(\text{Na-O}[\text{C}_2\text{H}_5])_2\text{N}_2\text{Na-Li}_6(\text{OC}_2\text{H}_5)_4 \cdot \text{O}(\text{C}_2\text{H}_5)_2]_2$ .<sup>29</sup> The N-N distances here are 1.35 Å and 1.359 (18) Å, respectively. These distances, and the N-N distance of 1.301 (12) Å in **5**, are considerably longer than those for most metal dinitrogen complexes, wherein the N-N length usually ranges from 1.12 Å (as in  $[(\text{NH}_3)_5\text{Ru}]_2\text{N}_2[\text{BF}_4]_4$ )<sup>30</sup> to about 1.182 (5) Å (as in  $[(\text{Me}_5\text{C}_5)_2\text{ZrN}_2]_2$ ).<sup>12b</sup> An unusually long N-N bond of 1.28 (5) Å is seen in *trans*- $[\text{MoCl}_4(\text{N}_2)\text{-ReCl}(\text{PMe}_2\text{Ph})_4]_2$ .<sup>31a</sup> The very recently described<sup>31b</sup> tantalum dinitrogen complex  $(\mu\text{-N}_2)[\text{Ta}(\text{CHCMe}_3)(\text{PMe}_3)_2(\text{CH}_2\text{CMe}_3)]_2$  shows an N-N distance of 1.298 (12) Å.

Instances of multiple metal coordination are known for other triply-bonded molecules. A coordination of diphenylacetylene to three iron atoms is seen in  $\text{Fe}_3(\text{PhC}\equiv\text{CPh})(\text{CO})_9$ .<sup>32</sup> In the recently reported  $\text{Fe}_3[\mu_3\text{-}(\text{N}\equiv\text{C-}n\text{-Pr})](\text{CO})_9$  cluster the nitrile ligand is coordinated in a  $(\sigma + 2\pi)$  fashion to the three iron atoms. The C-N bond distance of 1.260 (3) Å in this complex is significantly longer than that of a nitrile triple bond (1.16 Å), but does not reach the 1.29 Å length for a C=N double bond.

(23) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. 3, p 270.

(24) Schroetter, H. W. *Naturwissenschaften* **1967**, *54*, 513.

(25) Durig, J. R.; Bush, S. F.; Mercer, E. E. *J. Chem. Phys.* **1966**, *44*, 4238.

(26) Monteath Robertson, J. *J. Chem. Soc.* **1939**, 232.

(27) "Interatomic Distances"; Chemical Society: London, 1958.

(28) (a) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 997. (b) Kruger, C.; Tsay, Y.-H. *Ibid.* **1973**, *12*, 998.

(29) Jonas, K.; Brauer, D. J.; Kruger, C.; Roberts, P. J.; Tsay, Y.-H. *J. Am. Chem. Soc.* **1976**, *98*, 74.

(30) Treitel, I. M.; Flood, M. T.; Marsh, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1969**, *91*, 6512.

(31) (a) Cradwick, P. D.; Chatt, J.; Crabtree, R. H.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 351. (b) Turner, H. W.; Fellmann, J. D.; Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1980**, *102*, 7809-7811.

(32) Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hubel, W. *J. Am. Chem. Soc.* **1966**, *88*, 292.

(33) Andrews, M. A.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7260.

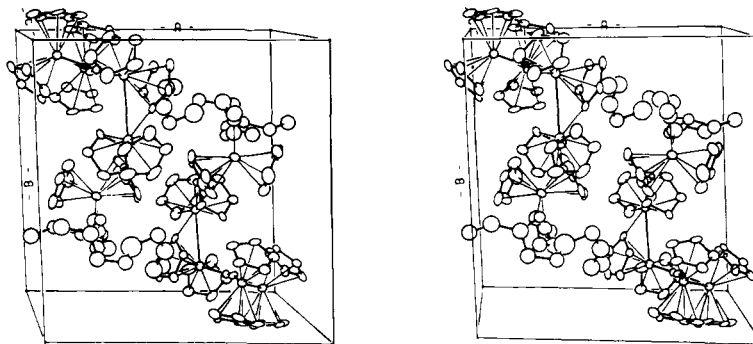


Figure 5. Stereoscopic view of the full unit cell of **5**.

**Structure of the Titanocene Diglyme Unit (Figure 4).** In this structure, one molecule of diglyme<sup>34</sup> is coordinated via two adjacent oxygen atoms to a "bent" bis( $\eta$ -cyclopentadienyl)titanium unit. There is a second diglyme molecule in the vicinity of, but not coordinated to, Ti5. Some of the atoms of the diglyme ligands are disordered (cf. Scheme 1). The two cyclopentadienyl ligands and the two oxygen ligands of the coordinating diglyme are arranged in a distorted tetrahedral arrangement around titanium (Ti5). The angle subtended by Ti5 and the centroids of the ( $\eta$ -C<sub>5</sub>H<sub>5</sub>) rings is 134.3° (Table II). This value is intermediate between that found for ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub> (131.0°) and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(CO)<sub>2</sub> (138.6°)<sup>35</sup> and is similar to the corresponding angle of 133.5° in  $[(\eta-C_5H_5)_2Ti(CH_3OCH_2CH_2OCH_3)]-Zn_2Cl_6 \cdot C_6H_6$ .<sup>36</sup> The ( $\eta$ -C<sub>5</sub>H<sub>5</sub>) rings in **5** are eclipsed as they are in ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(CO)<sub>2</sub>, in contrast to ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub> where the rings are staggered. The mean Ti-C (cyclopentadienyl) distance of  $2.36 \pm 0.020$  Å in **5** is comparable to that in ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(CO)<sub>2</sub> [2.347 (9) Å] and to the average Ti-C separation of 2.379 Å for ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti<sup>IV</sup>X<sub>2</sub> complexes.<sup>35</sup>

We have thus far described the structure of the two titanium metallocene complex units in **5**. These units may conceivably be separate molecules that have cocrystallized in the unit cell or else parts of an ionic complex salt, i.e.  $[(C_5H_5)_2Ti(C_6H_{14}O_3) \cdot C_6H_{14}O_3]^+ [(C_{10}H_8)(C_5H_5)_5(C_5H_4)Ti_4N_2]^-$ . For the titanocene diglyme unit in **5** the coordination geometry is similar to that seen in the  $[(\eta-C_5H_5)_2Ti(CH_3OCH_2CH_2OCH_3)]^+$  cation.<sup>36</sup> However, from the juxtaposition of the two complex units in **5** (see Figure 5) there is no evidence of a preferred spatial orientation, or of short intermolecular contacts (C...O and C...O distances <3.2 Å) as might be expected for a close ion-pair model. As a criterion for the possible ionic character of **5** we measured the electrical conductivity of solutions of the complex in diglyme. Unfortunately, because of difficulties associated with the possible presence of traces of (partly ionized) cyclopentadiene in the very dilute solutions, the results were inconclusive. A determination of the relationship between the two complex units in **5** will require further studies.

With so little available structural data on "titanocene" systems,<sup>1b,c</sup> it is remarkable to be able to view the structures of three different titanium metallocenes in the unit cell of **5**. The rearrangement of a  $\mu-(\eta^1:\eta^5-C_5H_4)$  metallocene structure, as in the starting material **1**, to a ( $\eta^5:\eta^5-C_{10}H_8$ ) fulvalenyl structure, as found in **5**, has also been observed with ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>H<sub>2</sub> $[\mu-(\eta^1:\eta^5-C_5H_4)]_2$  and related molybdenum complexes.<sup>37</sup> There appears

to be no precedent for the transformation of dimeric metallocene systems to yield monomer units such as ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(diglyme). This diversified, "chameleon-like behavior"<sup>38</sup> seems to be quite unique to the low-valent titanium metallocenes.

**Chemical Properties of Dinitrogen Complexes.** Compounds **4** and **5** readily dissolve in tetrahydrofuran (THF) giving deep red solutions. The crystalline complex **5** is only sparingly soluble in diglyme. Solutions of **4** and **5** in THF are stable for several hours at room temperature, but over longer periods they decompose with some loss of N<sub>2</sub>. Under dinitrogen pressure (10 atm), the deep red color of **4** in THF persists for several days at ca. 23 °C. Labeling experiments (using <sup>15</sup>N<sub>2</sub>-labeled **4**) show that under these conditions there is an exchange of N<sub>2</sub> in the complex with dinitrogen in the gas phase.

Solutions of **4** and **5** in THF (or diglyme) slowly turn from red to a light green upon contact with hydrogen (~1 atm). The same effect is observed with H<sub>2</sub>/N<sub>2</sub> mixtures, under pressure, although in this case the reaction proceeds more slowly. Most of the ligating dinitrogen is lost as N<sub>2</sub>; however, small amounts of nitrogen can be recovered as ammonium chloride by treatment of the resulting complex with HCl. In contrast to the behavior of the blue N<sub>2</sub> derivative of **1** (compound **2**), with H<sub>2</sub>, the displacement of N<sub>2</sub> by hydrogen from **5** is irreversible. A green, organometallic product is obtained which has been shown (from its infrared spectrum and reactivity with HCl) to contain, as a major component, the hydride complex  $\mu(H)_2[\mu-(\eta^5:\eta^5-C_{10}H_8)](\eta-C_5H_5)_2Ti_2$ .<sup>22</sup> The latter does not react with N<sub>2</sub> (at least under mild conditions: 23 °C, 10 atm of N<sub>2</sub>). It is striking that even such a multiply-ligated, tightly-bound, dinitrogen ligand as in **5** should be so easily displaced by H<sub>2</sub>. Clearly, with the titanium metallocene systems, thermodynamic factors seem to favor the formation of hydrides rather than dinitrogen complexes.

Solutions of **5** in THF are oxidized by excess iodine with attendant loss of N<sub>2</sub>. Treatment of solutions of **5** in diglyme with HCl results in loss of most of the bound nitrogen as N<sub>2</sub>. In reactions of **4** in THF, with HCl, traces of NH<sub>3</sub> (as NH<sub>4</sub>Cl) and hydrazine have been observed; however, the major product of reaction of both **4** and **5** with HCl is N<sub>2</sub>. This is in marked contrast to the reaction of  $(\mu-N_2)[(\eta-C_5Me_5)_2Zr(N_2)]_2$  with HCl which yields 1 mol of N<sub>2</sub>H<sub>4</sub> per Zr<sub>2</sub> unit. Bercaw and co-workers believe that the terminal dinitrogen ligands in this complex facilitate the protonation and subsequent reduction of dinitrogen.<sup>39</sup>

While **4** or **5** yield mainly N<sub>2</sub> upon reaction with HCl, surprisingly, reaction of the complexes with water (in ether solvents) yields mostly ammonia. Thus treatment of solutions of **5** in THF with water at 23 °C results in the conversion of at least 90% of the bound N<sub>2</sub> into N<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub>, the ammonia being the major product. This result was carefully checked using <sup>15</sup>N<sub>2</sub>-labeled **5**. It has been shown<sup>40</sup> that the protonation of dinitrogen in molybdenum and tungsten complexes, e.g., *cis*-[W(N<sub>2</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>4</sub>]

(34) We are aware of only one other structural study of a diglyme-coordinated complex, K<sub>2</sub>(C<sub>8</sub>H<sub>8</sub>)(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>O, see: Noordik, J. H.; van den Hark, Th. E. M.; Mooij, J. J.; Klaassen, A. A. K. *Acta Crystallogr., Sect. B* **1974**, *B30*, 833.

(35) Atwood, J. L.; Stone, K. E.; Alt, H. G.; Hrcncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1975**, *96*, C4.

(36) Sekutowski, D. G.; Stucky, G. D. *Inorg. Chem.* **1975**, *14*, 2192. For the [Cp<sub>2</sub>Ti(DME)]<sup>+</sup> cation  $\angle Cp-Ti-Cp = 133.5^\circ$ ,  $\angle O-Ti-O = 76.6(2)^\circ$  and Ti-O distances are 2.121 (4) Å and 2.109 (4) Å. The corresponding parameters in the Cp<sub>2</sub>Ti(diglyme) unit in **5** are 134.3°, 74.6 (6)°, 2.160 (15) Å, and 2.202 (14) Å [Cp = ( $\eta$ -C<sub>5</sub>H<sub>5</sub>); DME = 1,2-dimethoxyethane].

(37) (a) Cooper, N. J.; Green, M. L. H.; Cauldwell, C.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1977**, 145. (b) Berry, M.; Davies, S. G.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1978**, 99.

(38) The phrase is due to Professor H. Brintzinger, University of Konstanz, Germany.

(39) Manriquez, J. M.; Sanner, R. D.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 3042.

(40) (a) Chatt, J. A.; Pearman, A. J.; Richards, R. L. *J. Organomet. Chem.* **1975**, *101*, C45. (b) Chatt, J. A. *Ibid.* **1975**, *100*, 17.

to yield  $\text{NH}_3$ , proceeds most readily with  $\text{H}_2\text{SO}_4/\text{CH}_3\text{OH}$  systems where there is a potentially strongly coordinating (nucleophilic) counterion species (i.e.,  $\text{HSO}_4^-$ ). In a similar manner, in reaction of **5** with  $\text{H}_2\text{O}/\text{THF}$ , dinitrogen reduction could be facilitated by the formation of intermediate hydroxo-titanium- $\text{N}_2$  complexes.

Reaction of **4** in THF with ethylene ( $\sim 1$  atm) gave a mixture of 1-butene and 1,3-butadiene; a similar reaction is observed with **1** with  $\text{C}_2\text{H}_4$  but at higher pressures.<sup>2c</sup> Treatment of **4** with diglyme (to yield **5**) and subsequently with carbon monoxide (1 atm) yields a new titanium dinitrogen carbonyl complex of approximate composition  $\text{C}_{20}\text{H}_{20}\text{Ti}_2\text{N}_2(\text{CO})_2$  (**6**). The latter contains an apparently  $\mu_2$ -bridging dinitrogen [ $\nu(^{14}\text{N}-^{14}\text{N}) = 1502\text{ cm}^{-1}$ ,  $\nu(^{15}\text{N}-^{15}\text{N}) = 1453\text{ cm}^{-1}$ ] as well as bridging and terminal carbonyls. In this reaction, it is remarkable that the  $\text{N}_2$  ligand is largely retained even in the presence of excess carbon monoxide.<sup>41</sup>

### Relevance to $\text{N}_2$ -Fixation Systems

The present work may help to provide some insight into the nature of the various  $\text{N}_2$ -fixation systems. As noted earlier, Vol'pin et al.<sup>9</sup> and others<sup>10,11</sup> found that mixtures of  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  and Grignard reagents (or sodium naphthalene) are very effective, stoichiometric, reducing agents for dinitrogen, much more so than the metal halide, e.g.,  $\text{TiCl}_4$ ,  $\text{VCl}_3/\text{RMgX}$  systems. The unique reactivity of the  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2/\text{RMgX}$  [or  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2/\text{Na}^+\text{C}_{10}\text{H}_8^-$ ] reagents toward dinitrogen may now be ascribed to the peculiar capacity of intermediate  $[(\text{C}_5\text{H}_5)_2\text{Ti}^{\text{II}}]$  and related species to multiply-coordinate and in this way significantly activate  $\text{N}_2$  for reduction. In the above systems, nitrogen is recovered as an ammonium salt after hydrolysis. Although various cyclical, ammonia-producing systems have been devised,<sup>11</sup> a truly catalytic dinitrogen fixation process using  $\text{N}_2$  complexes, wherein the reducing agent is hydrogen gas, has never been achieved. One basic problem is that hydrogen displaces coordinated dinitrogen. This has been observed with, for example,  $\text{RuH}_2(\text{Ph}_3\text{P})_3\text{N}_2$ ,<sup>43</sup> molybdenum dinitrogen complexes,<sup>42a</sup>  $[(\text{C}_5\text{Me}_5)_2\text{Ti}]_2\text{N}_2$ ,<sup>12a</sup> and  $[(\text{C}_5\text{-H}_4)(\text{C}_5\text{H}_5)_3\text{Ti}]_2\text{N}_2$ .<sup>3</sup> Even the tightly-held  $\text{N}_2$  in complex **5** is readily displaced by hydrogen. Such a displacement might, however, be avoidable by the use of separate hydrogen activation or hydrogen transfer cocatalysts (vide infra). Yet another problem in designing a molecular catalytic  $\text{N}_2$  reduction system is the possible inhibiting effect of the product (i.e., ammonia) on the organometallic systems. Armor<sup>7</sup> has shown that  $\text{NH}_3$  reacts with  $(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_5)_3\text{Ti}_2$  (**1**) to yield a titanium imine complex and hydrogen. In contrast, solutions of **5** appear to be inert toward ammonia; no hydrogen is produced.<sup>44</sup> It is interesting that **5**, a dinitrogen derivative of  $(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_5)_3\text{Ti}_2$  (**1**), should be stable to  $\text{NH}_3$ . Ammonia usually displaces metal-coordinated dinitrogen.<sup>42a</sup> Compound **5** may be considered as possessing at least some of the necessary properties (i.e., extensive dinitrogen activation,  $\text{NH}_3$  resistance) that may be envisaged for a hypothetical  $\text{N}_2$ -hydrogenation catalyst.

In biological  $\text{N}_2$ -fixation systems, the nitrogenase enzyme converts  $\text{N}_2$  to ammonia, under mild conditions, using reducing agents that have essentially the reduction potential of hydrogen.<sup>42b</sup> In common with the metal complex systems, gaseous hydrogen is a competitive inhibitor of  $\text{N}_2$  fixation by nitrogenase. However, in the presence of hydrogenase (a cocatalyst), hydrogen can serve as a reductant for  $\text{N}_2$  in certain organisms.<sup>42c</sup> Many mechanisms have been proposed<sup>42b-d</sup> for the nitrogenase-catalyzed reduction of  $\text{N}_2$  and other triply-bonded substrates. Most such mechanisms have been speculative since little information has been available about the composition and structure of the active site. However,

(41) Treatment of  $[(\eta\text{-C}_5\text{Me}_5)_2\text{ZrN}_2]_2\text{N}_2$  with CO successively yields  $[(\eta\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})]_2\text{N}_2$  and  $2[(\eta\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2]$ , see: Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. Other carbonyl, dinitrogen complexes are known, e.g.,  $[\text{ReCl}(\text{Ph}_3\text{P})_2(\text{CO})_2\text{N}_2]$ , see: Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Organomet. Chem.* **1970**, *21*, 49.

(42) (a) Bottomley, F. In "A Treatise on Dinitrogen Fixation", Hardy, R. W. F., Bottomley, F., Burns, R. C., Eds.; Wiley-Interscience: New York, 1979; Chapter 3. (b) Hardy, R. W. F. *ibid.*, Chapter 4. (c) Burris, R. H. *ibid.*, Chapter 5. (d) Burns, C. B. *ibid.*, Chapter 3.

(43) Knoth, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 7172.

(44) Armor, J. N. (Allied Corp.), private communication.

recent X-ray absorption spectroscopy studies on the molybdenum iron protein,<sup>45</sup> and on the Mo-Fe cofactor of nitrogenase,<sup>46</sup> have shown that the molybdenum atom site is closely associated with two or three iron atoms at a distance of  $2.72 \pm 0.05\text{ \AA}$ . A multiple coordination<sup>47</sup> of dinitrogen to the molybdenum and iron atoms thus seems likely. A  $(\mu_3\text{-N}_2)$  (or  $(\mu_4\text{-N}_2)$ ) coordination is at least structurally possible. Also, with a relatively electron-rich, elongated, dinitrogen ligand as in a  $(\mu_3\text{-N}_2)$  structure, stepwise protonation to ammonia should be easily realizable. In compound **5** we have a firm example of a triply-metal-coordinated dinitrogen ligand which can undergo facile aqueous hydrolysis to yield ammonia.

### Conclusions

The complex  $[\mu\text{-}(\eta^1\text{-}\eta^5\text{-C}_5\text{H}_4)](\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$  (**1**) displays a wide range of chemical reactivity with dinitrogen. Depending on reaction conditions, several different dinitrogen derivatives of **1** can be prepared. One of these (compound **5**) has been characterized by single-crystal X-ray crystallography as  $(\mu_3\text{-N}_2)[(\eta^5\text{-C}_{10}\text{H}_8)(\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2][(\eta^1\text{-}\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2] \cdot [(\eta\text{-C}_5\text{H}_5)_2\text{-}(\text{C}_6\text{H}_{14}\text{O}_3)\text{Ti}] \cdot \text{C}_6\text{H}_{14}\text{O}_3$ . The key feature in **5** is the presence of a dinitrogen ligand  $(\mu_3\text{-N}_2)$  that is simultaneously coordinated to three titanium atoms. One dinitrogen atom is connected to the formally divalent titanium in a molecule of **1**. The same  $\text{N}_2$  ligand is also bound to the two titanium atoms of the fulvalene-bridged metallocene complex,  $(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$  (Figure 2).

While the structures of bis( $\eta$ -pentamethylcyclopentadienyl)-titanium(II)<sup>12</sup> and of bis( $\eta$ -cyclopentadienyl)(aryl)titanium(III)<sup>13</sup> dinitrogen derivatives have been determined, this work describes for the first time the structure of a bis( $\eta$ -cyclopentadienyl)titanium(II)-based dinitrogen complex. Traditionally, it has been the  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ -related systems (as exemplified by the work of Vol'pin and Shur<sup>9</sup> and others<sup>10,11</sup>) that have proved to be extremely effective for dinitrogen reduction. In the  $\text{N}_2$  complexes cited above there is an essentially linear  $\text{Ti}-\text{N}=\text{N}-\text{Ti}$  arrangement, with an N-N distance of  $1.16\text{ \AA}$  (cf. Table III). In compound **5**, we have a simultaneously end-bonded and sideways-bonded<sup>48</sup> dinitrogen ligand.

This unique  $(\mu_3\text{-N}_2)$  coordination results in a considerably elongated N-N bond [ $1.301(12)\text{ \AA}$  vs.  $1.0976\text{ \AA}$  in  $\text{N}_2$  gas] and an exceptionally low  $\nu(\text{N}-\text{N})$  vibrational frequency ( $1282\text{ cm}^{-1}$ ). The N-N bond order of the coordinated dinitrogen is intermediate between that of azo ( $-\text{N}=\text{N}-$ ) and hydrazo ( $>\text{N}-\text{N}<$ ) compounds.

Despite this multiple coordination, the  $\text{N}_2$  ligand in **5** is irreversibly displaced by gaseous hydrogen. Reaction of **4** and **5** with HCl yields mostly  $\text{N}_2$ , although traces of ammonia and hydrazine are formed. However, reaction of **5** in THF with water results in the conversion of most of the ligated dinitrogen to ammonia.

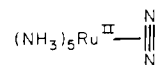
In view of the present work the effectiveness of the Vol'pin and Shur and related  $\text{N}_2$ -reduction systems<sup>11</sup> may be ascribed to the

(45) Cramer, S. P.; Hodgson, K. O.; Gillum, W. O.; Mortenson, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 3398.

(46) Cramer, S. P.; Gillum, W. O.; Hodgson, K. O.; Mortenson, L. E.; Steifel, E. I.; Chisnell, J. R.; Brill, W. J.; Shah, V. K. *J. Am. Chem. Soc.* **1978**, *100*, 3814.

(47) Boon-Keng, T.; Averill, B. A. *Biochem. Biophys. Res. Commun.* **1979**, *88*, 1454.

(48) The nickel complexes described in ref 28 and 29 contain sideways-bonded  $\text{N}_2$ ; here, however, alkali metal atoms are also associated with the dinitrogen ligand. We are not aware of any simple, definitively characterized, transition metal,  $\pi$ -bonded  $\text{N}_2$  complexes. The intermediacy of a



species has been demonstrated, see: Armor, J. A.; Taube, H. *J. Am. Chem. Soc.* **1970**, *92*, 2560. A report of a sideways-bound  $\text{N}_2$  complex of permethyltitanocene has since been disclaimed, see: Bercaw, J. E.; Rosenberg, E.; Roberts, J. D., *J. Am. Chem. Soc.* **1974**, *96*, 612 and ref 12b. There are some indications for the presence of a sideways-bonded  $\text{N}_2$  in the complex  $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\text{Cl})(\text{N}_2)[(\text{Me}_3\text{Si})_2\text{CH}]$ , see: Jeffrey, J.; Lappert, M. F.; Riley, P. I. *J. Organomet. Chem.* **1979**, *181*, 25. Gynane, M. J. S.; Jeffrey, J.; Lappert, M. F. *J. Chem. Commun.* **1978**, *34*.

peculiar ability of low-valent titanocene-based systems to simultaneously coordinate a  $N_2$  ligand onto several metal atom sites. Recent studies have shown that in the nitrogenase enzyme, the  $N_2$ -reduction site is associated with one molybdenum and two or three iron atoms.<sup>45,46</sup> An activation of dinitrogen via a multiple metal coordination<sup>47</sup> at this site is structurally possible. Compound **5** provides a firm example of such a multiple coordination of dinitrogen.

### Experimental Section

All the titanium metallocenes described herein are highly air sensitive and were handled under rigorously anaerobic conditions. Solids and involatile liquids were transferred in a Vacuum Atmospheres drybox containing <5 ppm of  $O_2$  or moisture. Transfers of volatile solvents and other operations were done on high-vacuum lines. Solvents were purified by prolonged treatment with Na/K alloy (hydrocarbons) or by treatment with  $LiAlH_4$  and then Na/K alloy-anthracene, radical anion solutions (ethers). Further details of our general experimental procedures are given in ref 19.

**Preparation of  $N_2$  Complex 3.** A heavy-wall glass reactor tube of ~70-mL capacity, sealed to an 8 mm Kontes Teflon stopcock valve, was loaded with  $(C_5H_4)(C_5H_5)_3Ti_2$  (**1**) (3 g) and 1,2-dimethoxyethane (DME) (35 mL). For **1**, the gray-black solid, as obtained directly from the low-temperature reduction of  $(\eta-C_5H_5)_2TiCl_2$ ,<sup>19</sup> was used. The reactor tube was attached to a high-vacuum metal manifold, cooled to 16 °C, and pressured with  $N_2$  (11 atm). The solution of **1** in DME turned from green to bright blue upon contact with the  $N_2$ . It was stirred for ~23 h at 16 °C. The blue color gradually faded during this time, giving a green solution and a black precipitate. This mixture was filtered under a positive pressure of  $N_2$  (2 atm), washed carefully with small amounts of DME, and dried briefly in vacuo. In this manner a dark, almost black solid (**3**) (1.6 g) was isolated. The synthesis was repeated using  $^{15}N_2$ . A comparison of the infrared spectra of **3**, prepared with  $^{14}N_2$  and  $^{15}N_2$ , indicated it to be a dinitrogen complex with  $\nu(^{14}N-^{14}N) = 1222\text{ cm}^{-1}$  and  $\nu(^{15}N-^{15}N) = 1182\text{ cm}^{-1}$  (cf. Table III). The complex can be handled (under anaerobic conditions) at ambient temperatures, but it is unstable over long periods and was stored at -80 °C. It is practically insoluble in DME and in hydrocarbon solvents. Because of this insolubility and the lack of any applicable purification methods, we were not able to arrive at a rational elemental composition. The nitrogen content of **3** (obtained by decomposing the complex with HCl and measuring  $N_2 + N_2H_4 + NH_3$ ) was variable (~3% N). The complex has a very characteristic infrared spectrum, shown in Figure 1 (upper curve).

**Preparation of  $N_2$  Complex 4.** Addition of tetrahydrofuran (THF) to **3** gave a deep red solution. The solution was evaporated, and after treatment with *n*-octane a red-brown solid (**4**) was obtained. An  $^{15}N_2$ -labeled material was also prepared. Infrared spectra indicated **4** to be a dinitrogen complex with  $\nu(^{14}N-^{14}N) = 1296\text{ cm}^{-1}$  and  $\nu(^{15}N-^{15}N) = 1252\text{ cm}^{-1}$ . Again, because of a lack of available purification techniques on this extremely air-sensitive and reactive compound, we were not able to arrive at a rational elemental composition. A red-brown complex, which displays a similar infrared spectrum to **4**, was prepared by direct reaction of **1** in THF with  $N_2$  (11 atm, 16 h, 23 °C).

**Preparation of Crystalline  $N_2$  Complex 5.** An apparatus consisting of three vertical tubes (A, B, and C) sealed onto 8 mm Kontes stopcocks and connected by porous glass filter disks was used. Volumes: A and C, 72 mL; B, 250 mL. Tube A was loaded with  $N_2$  complex **3** (1.2 g), bis(2-methoxyethyl) ether (diglyme) (15 mL), and THF (60 mL). The mixture was stirred until a deep red solution was obtained. This was pumped to dryness under a vacuum and the remaining solid washed with added diglyme (25 mL). 1,2-Dimethoxyethane (DME) (35 mL) was added to A, and the mixture was stirred at ~23 °C for 20 min. After the mixture was allowed to settle, a reddish-green DME solution was filtered into B and thence transferred quantitatively into C (B was left clean). The DME in C was then removed under vacuum. To the dark solid remaining in A was added diglyme (110 mL), and the mixture was stirred for ~1 h at 23 °C until a red solution was obtained. This was filtered into B with assistance from a back pressure of argon. Isopentane (total ~220 mL) was added to A and C. The middle tube B was placed in a constant-temperature bath at -14 °C; tubes A and C were immersed in an ice/salt mixture at -20 °C. With slow warming of the ice/salt bath, a very gradual transfer of the isopentane, to cover the diglyme solution in B, was achieved. Tube B was kept at -14 °C for 25 days, during which time a very slow interdiffusion of the diglyme and isopentane layers occurred. (In some cases it was found advantageous to use less isopentane, ~150 mL in A only.) Crystals were formed on the sides of B, as well as on the glass rods in B. The remaining solution in B was filtered into A and the crystals (**5**) were washed with a little isopentane. The Yield of **5** was 220 mg. In a similar synthesis starting

with **3** (400 mg) that had been prepared with  $^{15}N_2$ , 60 mg of  $^{15}N_2$ -labeled, crystalline **5** were obtained.

Infrared spectra of **5** in an *n*-hexadecane-*d*<sub>34</sub> (Merck & Co., Inc., Rahway, NJ) mull gave  $\nu(^{14}N-^{14}N) = 1282\text{ cm}^{-1}$ ,  $\nu(^{15}N-^{15}N) = 1240\text{ cm}^{-1}$ ,  $\nu(Ti-^{14}N) = 586\text{ cm}^{-1}$ , and  $\nu(Ti-^{15}N) = 573\text{ cm}^{-1}$  (cf. Table III). Titanium was determined gravimetrically as  $TiO_2$ . Carbon and hydrogen were determined using a Hereaus combustion tube at 1000 °C in order to prevent the possible formation of carbides. Analyses for **5** were done by decomposing **5** with  $I_2$  and measuring  $N_2$  and  $NH_3$  (see section on Reactivity of **5** with  $I_2$ ). Anal. Calcd for  $(C_{62}H_{75}O_6Ti_5N_2)$ : C, 62.91; H, 6.38; Ti, 20.23; N, 2.37. Found: C, 63.28; H, 6.33; Ti, 21.06; N, 2.60 (by  $I_2$  decomposition), 3.54 (Dumas N determination, Schwartzkopf Microanalytical Lab.). The diglyme content in **5** was determined as follows. A solution of **5** in toluene was treated with excess HCl gas at -80 °C (0.5 h), then at 0 °C (4 h). The volatile organic products were collected by distillation in vacuo and analyzed by gas chromatography (Tween 80 column, temperature program, 75-180 °C). Calcd for **5** 22.6% w/w diglyme, found 19.2% w/w diglyme. No THF, DME, or other organic solvents used in the preparation of **5** were detected.

**Collection of X-ray Data and Structure Determination.**<sup>49</sup> For the X-ray work, crystals of **5** were mounted in quartz capillaries under argon (traces of Apiezon grease were used to prevent crystal movement). Data were collected<sup>49</sup> on an Enraf-Nonius CAD4 diffractometer, using Mo  $K\alpha$  radiation from a graphite-crystal incident-beam monochromator ( $\lambda$  0.71073). Cell constants were obtained by computer centering of 25 reflections. Least-squares refinement of the setting angles gave the following values for the cell parameters:  $a = 14.516$  (6) Å,  $b = 15.509$  (6) Å,  $c = 12.695$  (4) Å,  $\alpha = 91.07$  (3)°,  $\beta = 101.27$  (3)°,  $\gamma = 88.62$  (3)°, and  $V = 2801.8$  (10) Å<sup>3</sup>. The space group was initially taken to be  $P1$ . For the data collection, a prismatic crystal of approximate dimensions  $0.3 \times 0.3 \times 0.5$  mm was mounted on the diffractometer. Data were taken in the range of  $0^\circ < 2\theta(\text{Mo } K\alpha) < 45^\circ$  with a scan range from  $2\theta(\text{Mo } K\alpha_1) - 0.9^\circ$  to  $2\theta(\text{Mo } K\alpha_2) + 0.9^\circ$  (the crystal was at  $23 \pm 1^\circ$  C). A scan rate of 4-20°/min was used. A total of 6061 independent reflections were collected. Three representative reflections were measured periodically as a check on crystal and electronic stability. There was no significant change. Lorentz and polarization corrections were applied to the data. Extinction and absorption corrections were not necessary.

The structure was solved using the Patterson method. Initially, ten titanium atoms were readily located in the unit cell. The location of the cyclopentadienyl rings, dinitrogen molecules, and finally the diglyme ligands was determined from the synthesis of successive three-dimensional Fourier maps. The structure was refined (in sections) using a unit weighting scheme and assuming a  $P1$  space group. Subsequently, examination of the resultant atom coordinates showed the space group to be  $P\bar{1}$ . The structure was then refined<sup>49</sup> (in  $P\bar{1}$ ) using full-matrix, least-squares techniques minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure-factor amplitudes, and the weight,  $w$ , is  $4F_o^2/\sigma^2(F_o^2)$ . The agreement indices are defined as  $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$  and  $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ . Scattering factors were taken from Cromer and Waber,<sup>50</sup> and the anomalous dispersion terms were those of Cramer and Liberman.<sup>51</sup> Only the 2201 reflections having  $F_o^2 > 3\sigma(F_o^2)$  were used. Hydrogen atoms were not included. Anisotropic temperature factors were included for all atoms except those of the diglyme ligands. In the final cycle of least-squares refinement, the agreement factors were  $R_1 = 0.072$  and  $R_2 = 0.080$ . The final difference Fourier map showed peaks that were considerably smaller than any of the refined atoms. Of these, the largest peaks were in the vicinity of the disordered diglyme molecules and indicative of anisotropic vibrations and/or further disorder in this region.

**$^{14}N/^{15}N$  Exchange with **4**.** Dinitrogen complex **3** (70 mg), prepared using  $^{15}N_2$  (>99%  $^{15}N_2$ ), contained in a heavy-wall glass tube, was treated with THF (5 mL) and stirred until a deep red solution of **4** was obtained. This was stirred under  $^{14}N_2$  (11 atm) for 3 days at 21-23 °C. Evaporation of the solution in vacuo afforded a dark solid having infrared absorptions characteristic of both ligated  $^{15}N_2$  and  $^{14}N_2$  (cf. Table III). Decomposition of this solid with HCl in THF gave dinitrogen, which was shown by mass spectral analysis to consist of approximately 50%  $^{14}N_2$ , 49.5%  $^{15}N_2$ , and 0.5%  $^{14}N^{15}N$ .

**Reactivity of **5** with  $H_2$ .** A solution of **5** (128.63 mg, 0.1087 mmol) in diglyme (12 mL) was cooled to 0 °C and  $H_2$  (~0.9 atm) added. The

(49) Data were collected by J. Troup of Molecular Structure Corp. (College Station, TX). The final refinement of the structure was done by M. Eckstein, also of Molecular Structure Corp.

(50) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, in preparation; Vol. IV.

(51) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.



solution was stirred under  $H_2$  at 0 °C (1 h), then at 23 °C (1.5 h). While at the higher temperature the solution turned from a red to a stable green color, with accompanying evolution of  $N_2$  (0.1195 mmol). Reaction of the product with HCl (1 mmol), -60 °C to 0 °C, gave  $H_2$  (0.4312 mmol) as the only noncondensable gas. The ratio  $5:H_2 = 1:3.97$ . The residue was analyzed (as detailed below) for hydrazine and ammonia. Found:  $NH_3$ , 0.006 mmol;  $N_2H_4$ , none detected (<0.001 mmol).

**Reactivity of 5 with  $I_2$ .** In a glass reactor tube was made up a solution of **5** (49.18 mg, 0.0415 mmol) in THF (5 mL). Iodine (300 mg) was added to the solution from an evacuated side arm.  $N_2$  gas evolved (0.044 mmol) was collected with the aid of a Töpler pump. Subsequently, 3 M aqueous HCl (5 mL) was added to the residue. This was analyzed for total N (Kjeldahl technique) with an appropriate blank made up of all the reagents employed. Found: 0.06 mg N (0.002 mmol). The ratio  $5:N_2 = 1:1.1$ .

**Reactivity of 5 with HCl and with Water.** A deep red solution of **5** (96.45 mg, 0.0815 mmol) in diglyme (10 mL) was cooled to -196 °C and HCl gas (~1 mmol) was added, in vacuo. The mixture was then warmed and stirred at -60 °C (30 min) and 0 °C (30 min). A deep purple solution was obtained. Noncondensable gases were measured with the aid of a Töpler pump. Collected:  $H_2$  (0.1224 mmol) and  $N_2$  (0.0841 mmol). The ratio  $5:H_2 = 1:1.50$  and  $5:N_2 = 1:1.03$ .

In another experiment, a glass reactor tube equipped with an evacuable side arm was loaded with a mixture of **5** (42.41 mg, 0.0358 mmol) and **5** prepared from  $^{15}N_2$  (14.82 mg, 0.0125 mmol). The crystals were dissolved in added THF to yield a deep red solution. Water (400 mg) was distilled onto the solution which was cooled to -196 °C. The mixture was warmed and stirred at 23 °C for 3 h. During this time, the solution turned from an initial purple to a light blue color, with the formation of a white precipitate. Collected noncondensable gases:  $H_2$  (0.0372 mmol) and  $N_2$  (0.0028 mmol). The ratio  $5:H_2 = 1:0.77$  and  $5:N_2 = 1:0.06$ . The residue was then analyzed for hydrazine. From the side arm of the reaction tube, 10 mL of a scrupulously outgassed mixture of 0.015 M  $KIO_3$  in 5 M  $H_2SO_4$  was added. The dinitrogen formed (from  $N_2H_4$  oxidation) was collected with the aid of a Töpler pump. Collected: dinitrogen (0.0057 mmol). The ratio  $5:N_2H_4 = 1:0.12$ . Mass spectral analysis of this gas showed it to be a mixture of  $^{14}N_2$  and  $^{15}N_2$ . Finally, Kjeldahl N analyses gave  $NH_3$  (1.82 mg, 0.1037 mmol). The ratio  $5:NH_3 = 1:2.15$ . (For the Kjeldahl analyses a blank titre, using THF,  $KIO_3/H_2O/H_2SO_4$  solutions, was determined.) The Kjeldahl titration

residue was then evaporated to near-dryness and heated with an excess of KOH to recover the  $NH_3$ , which was measured volumetrically (0.109 mmol). This  $NH_3$  was heated in the presence of Pt black in a quartz tube at 500 °C. The dinitrogen formed was shown by mass spectral analysis to consist of a mixture of  $^{14}N_2$ ,  $^{14}N^{15}N$ , and  $^{15}N_2$ .

**Reactivity of 4 (and 5) with Carbon Monoxide.** An H-shaped apparatus, equipped with a filter disk in the horizontal arm, was loaded with  $N_2$  complex **3** (800 mg) and THF (10 mL). The mixture was stirred giving a deep red solution of **4**. The solvent was then replaced with diglyme and after being stirred at room temperature the diglyme was removed in vacuo and THF once again added. Exposure of the resulting deep red (red-purple) solution to carbon monoxide (0.7 atm) gave an immediate, deep blue coloration. After being stirred (under CO) for ~2.5 h at 23 °C, the solution slowly turned to a deep green and carbon monoxide uptake ceased. The resulting solution was filtered, pumped to dryness, and extracted to exhaustion with octane. A dark, octane-insoluble material **6** was obtained.  $^{15}N_2$ - and  $^{13}CO$ -labeled materials were also prepared. Infrared spectral data:  $\nu(^{14}N-^{14}N) = 1502\text{ cm}^{-1}$ ,  $\nu(^{15}N-^{15}N) = 1453\text{ cm}^{-1}$ ,  $\nu(\text{bridging})(>^{12}C-O) = 1710\text{ cm}^{-1}$ ,  $\nu(\text{bridging})(>^{13}C-O) = 1669\text{ cm}^{-1}$ , and  $\nu(\text{terminal})(C-O) = 1875, 1965\text{ cm}^{-1}$ . Atomic ratios from elemental analyses and the above spectral data suggest **6** to have the approximate composition  $C_{20}H_{20}Ti_2N_2(CO)_2$ . We were not able to prepare the compound in a crystalline form, which precluded any more definitive identification of its composition and structure.

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**Supplementary Material Available:** A listing of structure factor amplitudes, general temperature factor expressions, intermolecular contacts to 3.75 Å, and a table of weighted least-squares planes and dihedral angles between planes (37 pages). Ordering information is given on any current masthead page.

## Electron Paramagnetic Resonance Spectra and Molecular Structure of Vanadium Hexacarbonyl

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**Abstract:** Electron paramagnetic resonance spectra of vanadium hexacarbonyl have been measured in frozen cyclohexane (X- and Q-band frequencies) and in chromium hexacarbonyl (X band) hosts. The spectrum in cyclohexane is sensitive to alkene impurities.  $V(CO)_6$  gives a nonaxial spectrum in both media. The EPR parameters in cyclohexane are  $g_x = 2.066$ ,  $g_y = 2.055$ , and  $g_z = 1.984$  and  $A_x = 52.6$ ,  $A_y = 49.1$ , and  $A_z = 15.7$  G. Measurements on  $^{13}CO$ -enriched  $V(CO)_6$  yield estimates for  $A_C$ . The highest symmetry distortion which is consistent with the  $g$  values,  $A$  values, and the Jahn-Teller modes is a  $D_{2h}$  angle bending distortion. Analysis of the hyperfine structure suggests considerable delocalization of spin density onto the ligands.

Vanadium hexacarbonyl is uniquely stable among binary paramagnetic metal carbonyls. Although much studied, the nature of the distortions from octahedral symmetry of this low-spin  $d^5$  complex is far from understood. There are several lines of evidence which suggest a distortion. (i) The electron diffraction pattern

of the vapor is consistent with an octahedral geometry with high amplitudes of vibration.<sup>2</sup> (ii) A recent single-crystal X-ray diffraction study<sup>3</sup> at 245 K indicates a marginally significant tetragonal distortion ( $r_{V-C}(\text{eq}) - r_{V-C}(\text{ax}) = 0.012$  (3) Å). A vibrational analysis suggests that any dynamic distortions over

(1) (a) University of Leicester. (b) University of Edinburgh. (c) University of Oxford. This work was initiated while R.N.P. was at the University of Edinburgh.

(2) Schmidling, D. G. *J. Mol. Struct.* 1975, 24, 1.  
(3) Bellard, S.; Robinson, K. A.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* 1979, B35, 271.