Structure and Magnetism of μ-Dinitrogen-bis(bis(pentamethylcyclopentadienyl)-titanium(II)), $\{(\eta^5\text{-}C_5(CH_3)_5)_2Ti\}_2N_2$

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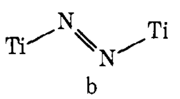
Abstract: The crystal structure of μ-dinitrogen-bis(bis(pentamethylcyclopentadienyl)titanium(II)), $\{(\eta^5\text{-}C_5(CH_3)_5)_2Ti\}_2N_2$, has been determined. The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 18.867$ (1), $b = 8.968$ (2), $c = 22.767$ (1) Å, $\alpha = 98.22$ (1), $\beta = 101.83$ (1), $\gamma = 93.86$ (1)°, and $Z = 4$. Least-squares refinement resulted in a final R index of 0.058 based on 7137 counter-collected data. The binuclear structure consists of two $(\eta^5\text{-}C_5Me_5)_2Ti$ moieties bridged by the N_2 in a linear TiN≡NTi arrangement. N-N distances are 1.165 (14) and 1.155 (14) Å for the two molecules in the asymmetric unit. The effective magnetic moment is 2.18 (1) μ_B per Ti, a value which is invariant to ca. 20 K. A qualitative molecular orbital treatment of the bonding consistent with the structure and magnetism is presented.

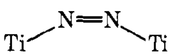
Titanocene-based N_2-fixing systems have been extensively investigated since the original report by Vol'pin and Shur that mixtures of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and ethylmagnesium bromide efficiently reduce N_2 at room temperature.[1-10] One of the species identified in such reaction mixtures, the binuclear dinitrogen complex $\{(C_5H_5)_2Ti\}_2N_2$, has been widely discussed in the literature, and at least four TiN_2Ti arrangements (a-d)

$Ti—N{\equiv}N—Ti$

a



b



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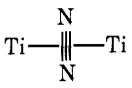

d

have been suggested. As discussed in the preceding article,[11] the instability of $(C_5H_5)_2Ti$ derivatives has precluded the x-ray crystal structure determination needed to settle the issue.

The title compound, $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ (**1**) proved sufficiently stable for crystallization, and we have solved its structure, albeit with difficulty, by single-crystal x-ray methods.

Experimental Section

$\{(C_5Me_5)_2Ti\}_2N_2$ was obtained as blue-black needles by slow diffusion of N_2 into an argon blanketed pentane solution of $(\eta^5\text{-}C_5Me_5)_2Ti$ at 0 °C. A series of Weissenberg and precession photographs (Cu Kα and Mo Kα radiation) indicated a trinclinic unit cell, which was assigned space group $P\bar{1}$. Unit cell dimensions were obtained by a least-squares fit to the observed $(\sin^2\theta)/\lambda^2$ values for 32 reflections measured on a diffractometer. Due to the extreme instability of the compound, an experimental density determination was not attempted. The calculated value of 1.19 g·cm^{-3} is, however, a reasonable value for an organometallic compound of this type. Crystal data are given in Table I.

A crystal of dimensions 0.3 × 0.8 × 0.3 mm was mounted in a glass capillary under N_2 with its needle axis (b) slightly skew to the ϕ axis of a G. E. XRD-5 quarter circle diffractometer automated by Datex. Using Mo Kα radiation monochromated with a graphite crystal, one hemisphere of data was measured between 1.5 and 45° in 2θ, using a θ–2θ scan technique at a scan rate of 1°/min; 30-s background counts were taken before and after each scan. The scan width varied linearly from 2° at $2\theta = 4°$ to 2.5° at $2\theta = 45°$. Intensities of three check reflections measured every 45 reflections showed no crystal decomposition during data collection.

Independent reflections (9711) were measured, 1001 of which were measured twice and averaged. A variance σ^2 $(F_o{}^2)$ was calculated for each reflection based on counting statistics plus a term $(0.02S)^2$, where S is the scan count. Intensities and their weights were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 4.77$ cm^{-1}). The data were then placed on an absolute scale by means of a Wilson plot,[12] with scattering factors for all atoms calculated by the method of Cromer and Mann.[13] Reflections having $F_o{}^2 < 1.5\sigma(F_o{}^2)$ were deleted, leaving 7187 reflections for the working data set.

Solution and Refinement. Reflections other than those having h, k, and l all even or all odd are systematically very weak as shown in Table II. It seemed probable, then, that the four molecules in the unit cell form an approximate face-centered array with their Ti-N-N-Ti axes closely parallel and that the contributions to the systematically weak reflections are due primarily to different orientations of the various C_5Me_5 groups; indeed, a three-dimensional Patterson map clearly indicated a single orientation for all of the Ti-N vectors. Two such arrangements were considered: (1) four independent, centrosymmetric molecules in the cell, each lying on a different center of symmetry at, e.g., 000, 0½½, ½0½, ½½0; (2) two pairs of independent, acentric molecules with their midpoints at, e.g., ±(¼0¼; ¼½¾). Arrangement 1 seemed unlikely, since it would require that the C_5Me_5 groups on the two ends of each molecule be eclipsed; accordingly, attention was concentrated on arrangement 2.

This preliminary model contained no information for phasing the weak reflections with mixed index parities, and electron density maps reflected a composite of the orientations of all eight independent C_5Me_5 groupings. Eventually an arrangement of atoms in one pair of C_5Me_5 groups was derived and used for preliminary phasing of the weak reflections. After many subsequent cycles of structure factor and electron density calculations, tentative parameters had been assigned to all the carbon atoms; however, least-squares convergence was very slow and the R index $(\sum||F_o| - |F_c||\sum|F_o|)$ remained at about 0.44.

At this time, the program MULTAN 74[14] became available to us, and quickly led to the correct structure. The most crucial aspect of this program was undoubtedly the routine "NORMAL", which permitted the normalization of E values for each separate group of index parities (Table II) and thus led to successful phasing of the weak reflections which describe the different orientations of the C_5Me_5 groups. The resulting E map indicated the positions of the Ti and N atoms and 65 of the C atoms; the remaining 15 C atoms were positioned from geometrical considerations, yielding an R factor of 0.39.

In hindsight, the earlier model developed by electron density maps was essentially correct; six of the eight C_5 rings had been positioned within 0.1 Å of their correct locations and the atoms of the remaining two rings were misplaced by an average of about 0.3 Å. However, misplacements of a few of the methyl groups were more serious, ranging up to 2.0 Å—a value too large to be recovered by standard least-squares refinement. It is apparent that further Fourier refinement would have been needed, and that this refinement would have

Table I. Crystal Data

$C_{40}H_{60}Ti_2N_2$	Triclinic space group $P\bar{1}$
a = 18.867 (1) Å	V = 3713 Å^3
b = 8.968 (2) Å	λ(Mo Kα) = 0.71069 Å
c = 22.767 (1) Å	fw = 664.73
α = 98.22 (1)°	ρ_{calcd} = 1.19 g·cm^{-3}
β = 101.83 (1)°	Z = 4
γ = 93.86 (1)°	μ = 4.77 cm^{-1}

been expedited by emphasizing the influence of the weak reflections that serve to differentiate between the various C_5Me_5 groups.

Initial refinement was by full-matrix least-squares adjustment of the coordinates of the Ti, N, and C atoms with isotropic temperature parameters and scale factor held constant. The quantity $\sum w|F_o^2 - s^2F_c^2|^2$ was minimized, where $1/s$ is the scale factor for F_o and $w = 1/\sigma^2(F_o^2)$. A single cycle reduced the R index to 0.19 for the inner 3027 reflections. Five more cycles of least squares were run, with additional thermal parameters introduced in alternate cycles. In the fifth cycle atomic coordinates were placed in one matrix and the anisotropic thermal parameters placed in two matrices, one for each dimer. An R index of 0.087 based on 5748 reflections was obtained at this point.

Difference Fourier maps then were calculated in the 40 general planes in which the hydrogen atoms of the methyl groups were expected to lie; these maps clearly indicated the positions of all 120 hydrogen atoms. Their coordinates were not further adjusted, and their isotropic temperature factors were set at values 1.0 Å^2 larger than the isotropic values of the carbon atoms to which they are bonded.

During the course of the refinement, it became apparent that ten reflections had overrun the counter capacity and that an additional 40 reflections with large k values—hence large χ values—had systematically low values of F_o, presumably due to misalignment or slippage of the crystal. These 50 reflections were assigned weights of zero.

Final refinement was by block diagonal least squares, a 3 × 3 matrix of coordinates and a 6 × 6 matrix of anisotropic temperature parameters being collected for each of the 88 Ti, N, and C atoms. Eight cycles in this configuration gave a final R index of 0.058 and a goodness of fit, $[\sum w(F_o^2 - s^2F_c^2)/(N - P)]^{1/2}$, of 2.51 for N = 7137 reflections of nonzero weight and P = 792 parameters. In the final cycle 40 parameters shifted by more than 0.5σ, five by more than 1.0σ. All crystallographic computations were performed under the CRYM system[15] on an IBM 370-158 computer. Final parameters are given in Tables III and IV.

The standard deviations listed in Table III were obtained directly from the inverse matrices, and are undoubtedly underestimated for two reasons. First, the refinement was stopped somewhat short of complete convergence. More important, the block-diagonal configuration of the matrices ignored the correlations between different atoms; some of these correlations, particularly those relating the Ti and N atoms of different N-Ti groupings, would be expected to be quite large because of the pseudo-face-centered symmetry of the structure. We believe, then, that the esd's in Table III should be approximately doubled for the C atoms and perhaps tripled for the N and Ti atoms, leading to uncertainties of about 0.01 Å in the positions of the C and N atoms and 0.003 Å in the Ti positions. These revised esd's are in good agreement with the root mean square variations in equivalent bond lengths.

Magnetic Measurements. Magnetic susceptibility measurements were made on a Princeton Applied Research Model 150 A vibrating sample magnetometer, run at 14.8 kG and standardized with $CuSO_4·5H_2O$ using the procedure outlined previously.[16] EPR spectra were recorded using Varian equipment, including the E-12 console, E101 bridge, and FR2503 power supply for fields to 14 kG. An Air Products Helitran system was used to obtain sample temperatures to ~12 K.

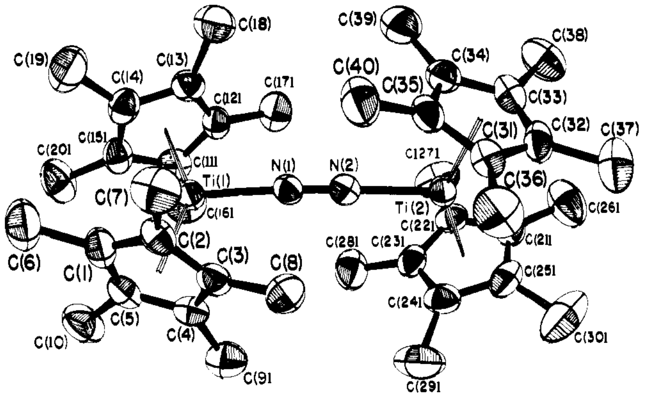

Figure 1. The molecular configuration of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ (Ti(1)–Ti(2) dimer). In this and subsequent figures, thermal ellipsoids are drawn at the 50% probability level.

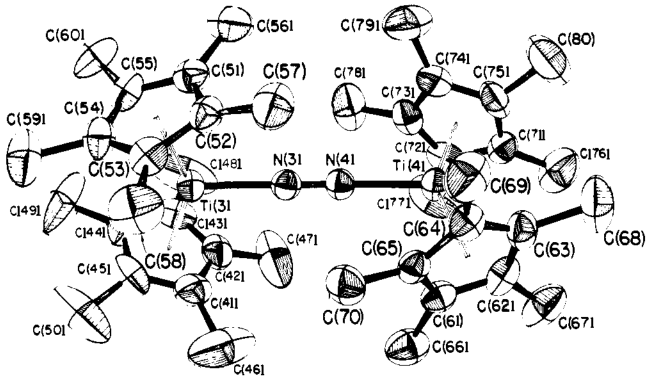

Figure 2. The molecular configuration of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ (Ti(3)–Ti(4) dimer).

Results and Discussion

The molecular structures of the two independent molecules are shown in Figures 1 and 2, a stereoscopic view is shown in Figure 3, and the packing of the molecules in the unit cell is shown in Figure 4. The binuclear structure consists of two $(\eta^5\text{-}C_5Me_5)_2Ti$ moieties bridged by the N_2 in an essentially *linear* TiN≡NTi arrangement. The skeletal views in Figure 5 illustrate the roughly trigonal disposition of $(\eta^5\text{-}C_5Me_5)$ rings and N_2 about Ti. This appears to be the only known example of a trigonal bis(cyclopentadienyl)titanium derivative; for all other titanocene derivatives one finds, in addition to the cyclopentadienyl rings, at least *two* ligand atoms occupying additional coordination sites about Ti.[17]

The centroid-Ti-centroid angles (R-Ti-R; Table V) average 145.7 (3)°,[18] significantly larger than those for $(\eta^5\text{-}C_5H_5)_2TiL_2$ (L = Cl, Ph, S, $\eta^1\text{-}C_5H_5$, CO): 131° for $(\eta^5\text{-}C_5H_5)_2TiCl_2$,[19] 136° for $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$,[20] 134° for $(\eta^5\text{-}C_5H_5)_2TiS_5$,[21] 130° for $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$,[22] and 139° for $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$,[23] and also significantly larger than that for $(\eta^5\text{-}C_5Me_5)_2TiCl_2$, 137°.[24] The R-Ti-R expansion for **1** may be attributed to reduced ligand crowding in the trigonal, rather than tetrahedral geometry about Ti. The R-Ti-N angles average 107.2 (4)°.

Table II. Mean Values of E^2 According to (hkl) Parity Group

(hkl) parity group	*EEE*	*OEE*	*EOE*	*OOE*	*EEO*	*OEO*	*EOO*	*OOO*
Mean E^2 (before normalization)	2.20	0.61	0.54	0.29	0.28	0.57	0.62	2.12
No. in group	1104	893	895	761	779	901	898	1127
Normalization factor	0.674	1.280	1.361	1.857	1.890	1.324	1.270	0.687

Table III. Final Nonhydrogen Atom Parameters (coordinates × 10^5, U_{ij} × 10^4)[a,b,c]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti1	15 393 (4)	86 362 (9)	15 287 (3)	438 (5)	338 (5)	348 (4)	46 (4)	29 (4)	35 (4)
Ti2	34 256 (4)	115 462 (9)	33 908 (3)	382 (5)	457 (6)	369 (4)	5 (4)	60 (4)	−3 (4)
Ti3	33 269 (4)	64 639 (9)	84 493 (3)	386 (5)	479 (6)	386 (4)	41 (4)	51 (4)	26 (4)
Ti4	16 398 (4)	35 278 (9)	64 669 (3)	465 (5)	361 (5)	411 (5)	59 (4)	−10 (4)	22 (4)
N1	22 497 (17)	98 516 (37)	22 405 (14)	448 (22)	349 (23)	425 (20)	41 (18)	84 (17)	36 (18)
N2	26 792 (17)	104 962 (39)	26 575 (14)	444 (23)	421 (24)	462 (21)	52 (18)	96 (18)	39 (18)
N3	26 318 (17)	53 812 (39)	76 793 (14)	450 (23)	434 (24)	443 (21)	42 (19)	100 (18)	66 (18)
N4	22 618 (17)	47 300 (39)	72 360 (14)	448 (22)	408 (24)	426 (20)	62 (19)	54 (17)	64 (18)
C1	10 591 (24)	60 291 (51)	12 968 (19)	590 (31)	429 (31)	506 (28)	−39 (25)	−20 (24)	17 (24)
C2	12 947 (23)	64 084 (48)	19 353 (18)	568 (30)	343 (28)	479 (26)	0 (23)	140 (23)	44 (23)
C3	20 528 (23)	67 121 (47)	20 676 (18)	580 (30)	310 (27)	456 (26)	97 (23)	81 (23)	58 (22)
C4	22 932 (23)	66 063 (49)	15 166 (19)	519 (29)	368 (28)	546 (28)	120 (24)	157 (23)	72 (23)
C5	16 760 (24)	61 764 (49)	10 425 (19)	682 (33)	383 (33)	467 (27)	71 (25)	125 (24)	−29 (23)
C6	3 165 (27)	52 945 (60)	9 733 (23)	753 (38)	578 (38)	825 (38)	−141 (31)	−85 (31)	34 (32)
C7	8 271 (26)	62 871 (59)	23 881 (22)	723 (37)	647 (38)	766 (36)	28 (30)	311 (30)	186 (31)
C8	25 379 (25)	69 229 (55)	26 898 (20)	646 (33)	579 (35)	543 (29)	156 (28)	15 (25)	150 (27)
C9	30 551 (26)	66 695 (60)	14 402 (22)	670 (35)	690 (39)	764 (36)	159 (30)	247 (29)	96 (31)
C10	17 129 (30)	56 404 (62)	3 950 (21)	1090 (46)	708 (41)	539 (32)	242 (36)	131 (31)	−83 (30)
C11	14 414 (24)	102 414 (52)	7 782 (19)	621 (31)	523 (32)	479 (27)	116 (26)	147 (24)	229 (25)
C12	14 072 (22)	111 704 (47)	13 239 (18)	521 (29)	338 (28)	490 (26)	28 (23)	−4 (22)	80 (23)
C13	7 796 (23)	106 570 (50)	15 060 (19)	528 (29)	422 (30)	506 (27)	137 (24)	84 (23)	118 (24)
C14	4 126 (22)	94 295 (52)	10 648 (19)	461 (28)	531 (33)	509 (27)	48 (25)	6 (23)	137 (25)
C15	8 218 (23)	91 956 (52)	6 106 (18)	585 (31)	511 (32)	407 (26)	19 (26)	−7 (23)	97 (24)
C16	20 122 (29)	104 633 (67)	4 234 (23)	924 (43)	964 (48)	706 (36)	122 (37)	353 (33)	298 (35)
C17	19 046 (26)	125 649 (54)	16 250 (22)	758 (37)	410 (33)	821 (37)	10 (28)	−33 (30)	180 (29)
C18	4 790 (28)	113 894 (63)	20 236 (22)	778 (39)	800 (43)	697 (35)	266 (34)	154 (30)	22 (32)
C19	−3 403 (26)	87 307 (65)	10 393 (25)	543 (34)	824 (45)	935 (41)	−7 (31)	12 (30)	150 (36)
C20	5 647 (30)	82 186 (63)	62 (20)	1105 (46)	705 (41)	437 (29)	81 (35)	−102 (29)	30 (29)
C21	45 972 (22)	128 834 (55)	35 117 (20)	415 (28)	625 (35)	575 (29)	−56 (25)	137 (23)	−21 (27)
C22	42 178 (22)	128 764 (52)	29 111 (20)	393 (27)	516 (32)	629 (30)	57 (24)	140 (23)	115 (26)
C23	41 239 (21)	113 706 (56)	26 161 (18)	352 (26)	742 (37)	463 (26)	54 (25)	85 (22)	56 (26)
C24	44 085 (23)	104 379 (54)	30 259 (21)	425 (29)	529 (33)	762 (33)	78 (25)	192 (25)	58 (28)
C25	47 092 (22)	113 788 (58)	35 835 (20)	371 (28)	799 (40)	580 (30)	70 (27)	34 (23)	176 (29)
C26	49 574 (29)	142 420 (70)	39 524 (25)	759 (41)	1020 (52)	901 (42)	−320 (37)	295 (34)	−258 (38)
C27	40 293 (28)	142 096 (65)	26 090 (26)	674 (37)	837 (46)	1155 (47)	137 (34)	339 (35)	484 (39)
C28	38 382 (27)	109 134 (71)	19 404 (21)	609 (35)	1227 (54)	553 (31)	30 (35)	179 (27)	−93 (35)
C29	45 178 (29)	87 847 (64)	28 992 (29)	719 (40)	625 (42)	1532 (59)	220 (34)	322 (40)	43 (41)
C30	51 887 (29)	108 611 (84)	41 194 (26)	649 (39)	1729 (72)	931 (44)	342 (43)	36 (34)	582 (48)
C31	30 183 (23)	107 874 (51)	42 433 (18)	545 (30)	478 (31)	409 (25)	−5 (25)	115 (22)	27 (23)
C32	34 474 (23)	121 760 (55)	44 568 (17)	527 (29)	724 (37)	290 (23)	−22 (27)	42 (21)	13 (24)
C33	31 122 (24)	133 100 (52)	41 616 (18)	623 (32)	492 (32)	422 (26)	−19 (26)	131 (23)	−39 (24)
C34	24 526 (24)	126 231 (52)	37 657 (18)	584 (31)	547 (33)	431 (26)	185 (26)	137 (23)	62 (24)
C35	23 949 (22)	110 890 (53)	38 260 (18)	458 (28)	595 (33)	411 (25)	−43 (25)	162 (22)	−76 (24)
C36	31 639 (29)	93 269 (60)	44 597 (22)	1034 (45)	634 (39)	672 (34)	98 (34)	190 (32)	226 (31)
C37	40 807 (27)	124 455 (66)	49 934 (20)	786 (39)	1007 (48)	450 (29)	−151 (35)	26 (27)	67 (31)
C38	33 217 (30)	149 831 (59)	42 997 (23)	1013 (44)	530 (37)	807 (38)	−27 (33)	360 (34)	−37 (31)
C39	18 892 (28)	134 220 (67)	34 103 (22)	795 (39)	1008 (48)	604 (33)	298 (36)	216 (29)	53 (33)
C40	17 282 (25)	100 000 (65)	35 672 (21)	580 (33)	944 (46)	624 (32)	−164 (32)	219 (27)	−137 (32)
C41	25 972 (28)	54 064 (58)	90 584 (20)	998 (42)	608 (37)	500 (29)	−55 (32)	349 (29)	15 (28)
C42	21 947 (24)	64 139 (63)	87 672 (19)	526 (31)	1038 (47)	425 (27)	−41 (31)	173 (24)	66 (30)
C43	25 472 (26)	78 520 (57)	89 655 (21)	741 (35)	709 (39)	716 (33)	364 (31)	411 (29)	308 (30)
C44	31 782 (24)	77 477 (58)	94 051 (20)	532 (31)	689 (38)	585 (30)	−17 (28)	193 (25)	−159 (28)
C45	32 095 (26)	61 901 (60)	94 524 (19)	767 (36)	852 (42)	398 (27)	360 (33)	133 (25)	112 (28)
C46	23 794 (50)	37 660 (76)	90 355 (32)	3232 (111)	731 (51)	1321 (61)	−420 (63)	1557 (72)	−198 (46)
C47	14 448 (29)	60 217 (85)	83 684 (25)	538 (30)	3013 (110)	648 (39)	−80 (53)	173 (32)	7 (55)
C48	22 609 (44)	92 699 (84)	87 838 (32)	2272 (84)	1377 (68)	1480 (64)	1251 (65)	1283 (64)	836 (56)
C49	36 379 (34)	90 492 (87)	98 181 (31)	1020 (52)	1533 (71)	1460 (61)	−527 (49)	592 (47)	−1013 (55)
C50	37 235 (37)	55 164 (95)	99 048 (26)	1432 (61)	2165 (88)	716 (41)	965 (62)	392 (42)	654 (51)
C51	40 559 (22)	74 015 (53)	78 154 (20)	391 (27)	591 (35)	651 (31)	70 (25)	120 (24)	186 (27)
C52	41 573 (22)	58 698 (52)	78 090 (19)	414 (27)	518 (32)	537 (28)	−15 (24)	163 (22)	−31 (25)
C53	44 878 (22)	56 328 (52)	83 922 (20)	435 (28)	500 (32)	630 (30)	124 (24)	159 (24)	68 (26)
C54	46 196 (22)	70 634 (56)	87 701 (20)	376 (27)	657 (36)	588 (30)	104 (26)	25 (23)	13 (27)
C55	43 462 (23)	81 388 (51)	84 208 (21)	421 (28)	422 (30)	725 (32)	−3 (24)	91 (24)	−43 (26)
C56	38 097 (27)	81 749 (70)	72 869 (25)	630 (36)	1156 (53)	928 (41)	114 (36)	200 (32)	556 (40)
C57	40 077 (26)	47 086 (64)	72 402 (22)	609 (34)	867 (44)	753 (36)	−49 (32)	294 (29)	−126 (33)
C58	47 498 (29)	41 816 (62)	85 767 (25)	813 (40)	652 (40)	1045 (44)	280 (33)	246 (35)	235 (35)
C59	51 212 (27)	73 784 (72)	93 831 (24)	553 (35)	1174 (55)	790 (38)	59 (36)	−80 (30)	−115 (38)
C60	44 321 (29)	98 232 (61)	86 025 (27)	782 (40)	521 (38)	1272 (50)	−54 (32)	320 (37)	−40 (36)
C61	14 296 (22)	14 690 (49)	69 830 (19)	501 (29)	394 (29)	599 (29)	59 (24)	170 (24)	94 (24)
C62	10 470 (23)	10 492 (52)	63 748 (21)	462 (29)	422 (31)	742 (33)	−11 (25)	34 (25)	−10 (27)
C63	15 683 (24)	9 436 (50)	60 091 (19)	676 (33)	399 (30)	457 (27)	93 (26)	29 (24)	−22 (23)
C64	22 641 (23)	12 846 (50)	63 832 (19)	515 (29)	403 (30)	559 (28)	102 (24)	145 (24)	35 (24)
C65	21 811 (22)	15 868 (47)	69 921 (18)	478 (27)	314 (27)	500 (26)	52 (22)	81 (22)	56 (22)
C66	10 938 (28)	15 088 (61)	75 203 (24)	811 (39)	675 (40)	911 (40)	50 (32)	431 (33)	149 (33)
C67	2 553 (28)	4 948 (63)	61 982 (27)	630 (37)	641 (41)	1262 (51)	−83 (31)	−97 (35)	196 (38)
C68	14 179 (31)	2 155 (63)	53 427 (23)	1161 (49)	704 (43)	618 (34)	154 (38)	−71 (33)	−198 (32)
C69	29 580 (27)	11 602 (62)	61 779 (23)	729 (37)	705 (41)	867 (39)	17 (32)	348 (32)	−122 (33)

Table III (*Continued*)

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C70	27 814 (25)	17 658 (55)	75 476 (20)	643 (33)	584 (36)	579 (30)	144 (28)	39 (25)	174 (27)
C71	6 924 (22)	41 059 (52)	56 894 (19)	448 (28)	518 (32)	547 (28)	3 (24)	−90 (23)	168 (25)
C72	7 187 (24)	51 788 (59)	62 319 (21)	525 (30)	821 (40)	647 (31)	324 (29)	225 (25)	337 (30)
C73	13 850 (25)	60 580 (52)	63 472 (19)	742 (35)	471 (32)	478 (27)	209 (28)	18 (25)	112 (25)
C74	17 766 (27)	55 577 (61)	59 215 (21)	800 (38)	753 (41)	541 (30)	−37 (32)	111 (28)	243 (29)
C75	13 484 (26)	43 859 (59)	55 206 (18)	781 (36)	747 (39)	333 (25)	82 (31)	41 (24)	66 (26)
C76	354 (31)	31 685 (71)	53 177 (27)	909 (44)	904 (51)	1107 (49)	−120 (38)	−393 (38)	312 (42)
C77	1 284 (33)	54 082 (87)	65 630 (29)	993 (50)	1715 (76)	1192 (53)	655 (52)	521 (44)	525 (54)
C78	16 110 (32)	74 649 (65)	68 165 (25)	1550 (59)	463 (38)	827 (41)	230 (39)	−166 (41)	44 (33)
C79	24 961 (34)	62 782 (90)	58 542 (29)	1024 (52)	1867 (80)	1072 (52)	−577 (52)	251 (43)	498 (54)
C80	15 355 (38)	37 285 (83)	49 234 (24)	1686 (67)	1390 (67)	524 (35)	205 (55)	341 (40)	87 (41)

[a] The final value of the scale factor is 0.8828. [b] The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}u_{11} + \ldots + 2klb^*c^*u_{23})]$. [c] The esd's quoted for C atoms should be doubled, while those for Ti and N atoms should be tripled. See text for explanation.

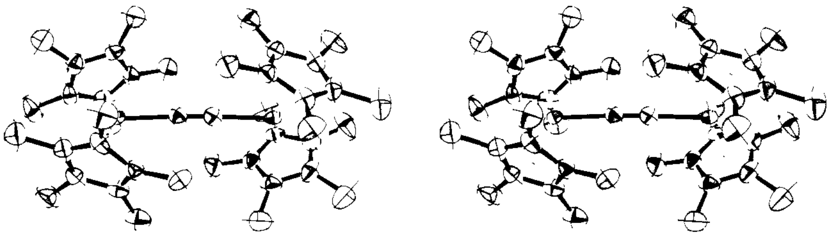

Figure 3. Stereoscopic view of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ (Ti(1)-Ti(2) dimer).

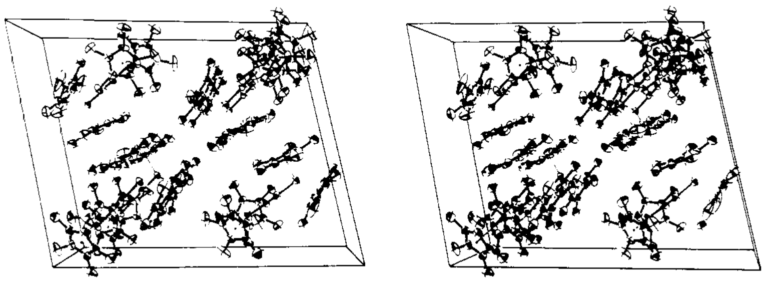

Figure 4. Stereoscopic view of the packing of molecules in the unit cell. Positive *a* runs from bottom to top, positive *b* from back to front, and positive *c* from left to right.

The cyclopentadienyl rings are closely planar (Table VII), and although $(C\text{-}C)_{ring}$ bond lengths vary from 1.378 to 1.443 Å (av = 1.404 (14) Å) (Table VI), this variation is probably not significant. Ti-ring C distances fall in the narrow range 2.363-2.416 Å, averaging 2.387 (11) Å, so that all $C_5(CH_3)_5$ rings may be considered bonded to Ti in a true pentahapto fashion. It should be noted that the average Ti-ring C distance for **1** (2.387 (11) Å) is significantly shorter than that for $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ (2.442 (25) Å). This reduction in Ti-C bond distances is consistent with the suggestion by Atwood[23] that the two additional electrons in bis(cyclopentadienyl)titanium(II) derivatives occupy a molecular orbital with some metal-ring bonding character; however, it may simply reflect the reduced ligand crowding in the trigonal geometry about Ti for **1** as compared to the pseudotetrahedral $(\eta^5\text{-}C_5Me_5)_2TiCl_2$.

As shown in Table VII, all methyl groups are bent out of their respective cyclopentadienyl planes away from titanium. Again, as observed previously for $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ and $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, methyl-methyl contacts between rings may be cited to explain the variations of these deviations. Thus short inter-ring C⋯C nonbonded distances are observed for C6-C19 (3.39 Å), C10-C20 (3.36 Å), C26-C37 (3.65 Å), C26-C38 (3.42 Å), C30-C37 (3.41 Å), C49-C59 (3.51 Å), C49-C60 (3.54 Å), C50-C59 (3.52 Å), C67-C76 (3.33 Å), and C68-C80 (3.43 Å), and accordingly these methyl carbons exhibit the greatest deviations from their ring planes. All other inter-ring methyl C⋯C contacts exceed 3.7 Å. No two rings bonded to a single Ti are strictly staggered, as indicated by the inequality of the contacts (e.g., C6-C19 (3.39 Å), C6-C20 (3.73 Å), C10-C20 (3.36 Å)).

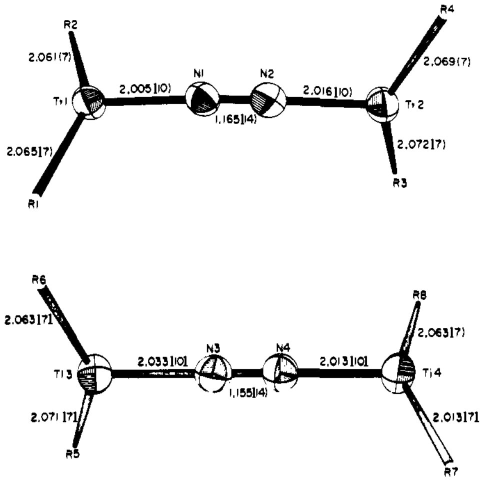

Figure 5. Skeletal views of the two independent molecules of $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$.

Metal Dinitrogen Bonding. The only other authentic bis(cyclopentadienyl)titanium(II) compound which has been

Table IV. Final Hydrogen Atom Parameters (coordinates × 10^4)[a]

Atom	*X*	*Y*	*Z*	*B*	Atom	*X*	*Y*	*Z*	*B*
H6A	300	4 154	964	6.36	H46A	2785	3 162	9 056	11.10
H6B	190	5 467	586	6.36	H46B	2037	3 313	8 645	11.10
H6C	–52	5 593	1 201	6.36	H46C	2139	3 524	9 348	11.10
H7A	1018	6 999	2 760	6.30	H47A	1290	6 891	8 181	9.44
H7B	788	5 308	2 490	6.30	H47B	1097	5 710	8 576	9.44
H7C	347	6 548	2 234	6.30	H47C	1452	5 202	8 034	9.44
H8A	2814	6 065	2 744	5.54	H48A	2597	10 152	8 956	10.38
H8B	2262	7 062	3 000	5.54	H48B	1809	9 476	8 909	10.38
H8C	2881	7 798	2 750	5.54	H48C	2157	9 255	8 347	10.38
H9A	3135	7 211	1 133	6.24	H49A	4043	8 732	10 064	10.82
H9B	3210	5 675	1 345	6.24	H49B	3356	9 566	10 074	10.82
H9C	3385	7 153	1 817	6.24	H49C	3796	9 763	9 578	10.82
H10A	1965	6 466	244	6.39	H50A	3894	4 627	9 722	10.08
H10B	1259	5 373	134	6.39	H50B	3493	5 215	10 220	10.08
H10C	2012	4 823	366	6.39	H50C	4146	6 221	10 102	10.08
H16A	2487	10 829	676	7.33	H56A	4170	8 830	7 212	7.23
H16B	1896	11 163	142	7.33	H56B	3385	8 695	7 324	7.23
H16C	2076	9 522	175	7.33	H56C	3640	7 405	6 910	7.23
H17A	2045	12 592	2 038	6.84	H57A	4315	4 968	6 969	6.29
H17B	1687	13 447	1 536	6.84	H57B	3518	4 614	7 038	6.29
H17C	2345	12 542	1 454	6.84	H57C	4133	3 730	7 339	6.29
H18A	478	10 724	2 322	6.78	H58A	5233	4 076	8 546	7.40
H18B	7	11 651	1 902	6.78	H58B	4440	3 301	8 312	7.40
H18C	782	12 311	2 238	6.78	H58C	4700	4 109	8 980	7.40
H19A	–502	7 960	701	7.29	H59A	5597	7 158	9 375	7.45
H19B	–687	9 488	1 026	7.29	H59B	4945	6 691	9 658	7.45
H19C	–362	8 310	1 409	7.29	H59C	5118	8 367	9 591	7.45
H20A	948	7 917	–169	6.61	H60A	4766	10 125	8 999	7.16
H20B	243	8 729	–264	6.61	H60B	3980	10 220	8 654	7.16
H20C	284	7 300	48	6.61	H60C	4622	10 356	8 320	7.16
H26A	5417	14 555	3 920	8.16	H66A	1376	2 266	7 858	6.28
H26B	4902	14 212	4 347	8.16	H66B	1086	569	7 659	6.28
H26C	4670	15 167	3 841	8.16	H66C	610	1 787	7 442	6.28
H27A	4363	14 460	2 367	7.41	H67A	68	440	5 773	7.29
H27B	4010	15 085	2 893	7.41	H67B	–34	1 143	6 408	7.29
H27C	3551	14 019	2 330	7.41	H67C	170	–508	6 297	7.29
H28A	4191	11 069	1 716	6.98	H68A	1776	638	5 159	7.55
H28B	3417	11 440	1 801	6.98	H68B	950	395	5 146	7.55
H28C	3654	9 840	1 847	6.98	H68C	1443	–847	5 318	7.55
H29A	4984	8 658	2 844	7.95	H69A	3373	1 459	6 508	6.92
H29B	4167	8 309	2 526	7.95	H69B	2999	1 890	5 892	6.92
H29C	4415	8 298	3 221	7.95	H69C	3003	191	5 980	6.92
H30A	5598	10 430	4 027	8.65	H70A	3241	1 740	7 435	6.14
H30B	4916	10 074	4 277	8.65	H70B	2726	990	7 781	6.14
H30C	5348	11 671	4 461	8.65	H70C	2789	2 747	7 796	6.14
H36A	3664	9 302	4 634	7.32	H76A	170	2 310	5 058	8.29
H36B	3021	8 482	4 129	7.32	H76B	–252	3 744	5 042	8.29
H36C	2885	9 133	4 760	7.32	H76C	–267	2 773	5 549	8.29
H37A	4478	13 108	4 920	6.56	H77A	320	5 646	6 997	9.27
H37B	4285	11 519	5 068	6.56	H77B	–200	4 488	6 487	9.27
H37C	3957	12 907	5 351	6.56	H77C	–142	6 199	6 445	9.27
H38A	3754	15 245	4 617	7.23	H78A	2049	7 403	7 072	8.91
H38B	2948	15 553	4 409	7.23	H78B	1230	7 538	7 069	8.91
H38C	3444	15 359	3 944	7.23	H78C	1606	8 325	6 632	8.91
H39A	1807	14 337	3 650	6.90	H79A	2828	6 702	6 227	9.44
H39B	1440	12 810	3 258	6.90	H79B	2481	6 917	5 571	9.44
H39C	2048	13 711	3 052	6.90	H79C	2800	5 418	5 690	9.44
H40A	1832	8 990	3 644	6.00	H80A	2044	3 404	5 000	9.69
H40B	1573	9 978	3 150	6.00	H80B	1539	4 414	4 649	9.69
H40C	1338	10 257	3 765	6.00	H80C	1244	2 803	4 719	9.69

[a] Thermal parameters are of the form $\exp[-B((\sin^2\theta)/\lambda^2)]$.

structurally characterized appears to be $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$.[23] The Ti-C(carbonyl) bond lengths for this complex (2.030 (11) Å) compare favorably with the Ti-N bond lengths for **1** (av = 2.017 (12) Å), as do the two Ti-N distances (2.035 (17) Å) for $(\eta^5\text{-}C_5H_5)_2Ti(NCO)_2$.[25] The conventional end-on N_2 bonding mode for **1**, as for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, is of special significance. It is therefore reasonable to assume the same linear TiN≡NTi arrangement for the parent compound $\{(\eta^5\text{-}C_5H_5)_2Ti\}_2N_2$, rather than the doubly bent or edge-on TiN_2Ti arrangements suggested earlier.[4,5,9,10]

The binuclear structures for **1** and $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ cast considerable doubt on the claim by one of us (J.E.B.) that a monomeric bis(pentamethylcyclopentadienyl)titanium(II) dinitrogen complex, $(\eta^5\text{-}C_5Me_5)_2TiN_2$, forms when solutions of **1** or $(\eta^5\text{-}C_5Me_5)_2Ti$ are cooled below −20 °C under N_2. On the basis of NMR and IR data $(\eta^5\text{-}C_5Me_5)_2TiN_2$ was interpreted to exist in both end-on, $(\eta^5\text{-}C_5Me_5)_2Ti(\eta^1\text{-}N_2)$, and edge-on, $(\eta^5\text{-}C_5Me_5)_2Ti(\eta^2\text{-}N_2)$, forms in solution. However, ^1H and ^{15}N NMR and IR spectra subsequently obtained for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$[26,27] were noted to be conspicuously similar to those for this unstable dinitrogen complex of $(\eta^5\text{-}C_5Me_5)_2Ti$. We therefore began to suspect that the stoichi-

Table V. Bond Angles (deg)[a]

Ti1-N1-N2	176.8	C31-C32-C37	124.4
Ti2-N2-N1	178.1	C33-C32-C37	125.6
Ti3-N3-N4	176.9	C32-C33-C38	127.8
Ti4-N4-N3	177.8	C34-C33-C38	123.8
N1-Ti1-R1	106.8	C33-C34-C39	126.1
N1-Ti1-R2	107.5	C35-C34-C39	126.3
R1-Ti1-R2	145.8	C31-C35-C40	125.1
N2-Ti2-R3	107.5	C34-C35-C40	124.9
N2-Ti2-R4	106.9	C41-C42-C43	108.8
R3-Ti2-R4	145.6	C42-C43-C44	108.0
N3-Ti3-R5	107.4	C43-C44-C45	107.0
N3-Ti3-R6	107.3	C44-C45-C41	107.1
R5-Ti3-R6	145.3	C45-C41-C42	109.1
N4-Ti4-R7	106.5	C42-C41-C46	126.8
N4-Ti4-R8	107.3	C41-C42-C47	124.7
R7-Ti4-R8	146.1	C43-C42-C47	126.0
C1-C2-C3	107.7	C42-C43-C48	125.1
C2-C3-C4	108.9	C44-C43-C48	126.7
C3-C4-C5	107.1	C43-C44-C49	125.4
C4-C5-C1	108.6	C45-C44-C49	126.6
C5-C1-C2	107.6	C41-C45-C50	124.7
C2-C1-C6	124.7	C44-C45-C50	127.5
C5-C1-C6	126.5	C51-C52-C53	109.8
C1-C2-C7	125.6	C52-C53-C54	107.0
C3-C2-C7	126.2	C53-C54-C55	108.1
C2-C3-C8	125.4	C54-C55-C51	108.6
C4-C3-C8	125.3	C55-C51-C52	106.4
C3-C4-C9	127.3	C52-C51-C56	127.6
C5-C4-C9	124.9	C55-C51-C56	125.3
C1-C5-C10	126.4	C51-C52-C57	124.0
C4-C5-C10	123.6	C53-C52-C57	125.9
C11-C12-C13	108.0	C52-C53-C58	127.2
C12-C13-C14	108.1	C54-C53-C58	125.3
C13-C14-C15	107.5	C53-C54-C59	124.0
C14-C15-C11	108.2	C55-C54-C59	126.3
C15-C11-C12	108.1	C51-C55-C60	123.3
C12-C11-C16	124.5	C54-C55-C60	127.5
C15-C11-C16	127.1	C61-C62-C63	107.3
C11-C12-C17	126.3	C62-C63-C64	108.9
C13-C12-C17	125.3	C63-C64-C65	107.6
C12-C13-C18	127.0	C64-C65-C61	107.9
C14-C13-C18	124.4	C65-C61-C62	108.3
C13-C14-C19	124.4	C62-C61-C66	124.7
C15-C14-C19	127.1	C65-C61-C66	126.3
C11-C15-C20	125.6	C61-C62-C67	123.3
C14-C15-C20	125.2	C63-C62-C67	128.1
C21-C22-C23	107.0	C62-C63-C68	125.4
C22-C23-C24	109.6	C64-C63-C68	124.2
C23-C24-C25	107.1	C63-C64-C69	125.4
C24-C25-C21	108.3	C65-C64-C69	126.7
C25-C21-C22	108.0	C61-C65-C70	125.8
C22-C21-C26	126.0	C64-C65-C70	125.7
C25-C21-C26	124.8	C71-C72-C73	106.3
C21-C22-C27	127.5	C72-C73-C74	109.9
C23-C22-C27	125.0	C73-C74-C75	107.2
C22-C23-C28	123.3	C74-C75-C71	110.5
C24-C23-C28	126.7	C75-C71-C72	106.1
C23-C24-C29	128.4	C72-C71-C76	125.7
C25-C24-C29	123.6	C75-C71-C76	126.8
C21-C25-C30	126.6	C71-C72-C77	126.9
C24-C25-C30	124.2	C73-C72-C77	126.5
C31-C32-C33	109.1	C72-C73-C78	125.4
C32-C33-C34	107.7	C74-C73-C78	124.3
C33-C34-C35	107.2	C73-C74-C79	126.7
C34-C35-C31	109.4	C75-C74-C79	125.7
C35-C31-C32	106.5	C71-C75-C80	126.1
C32-C31-C36	126.0	C74-C75-C80	122.5
C35-C31-C36	127.3		

[a] The estimated standard deviations are: Ti–N–N, 0.4°; N–Ti–R, 0.3°; R–Ti–R, 0.3°; C–C–C, 0.5°.

Table VI. Bond Distances (Å)[a]

Ti1-N1	2.005	C14-C15	1.413
Ti2-N2	2.016	C15-C11	1.400
Ti3-N3	2.033	C11-C16	1.492
Ti4-N4	2.013	C12-C17	1.499
N1-N2	1.165	C13-C18	1.498
N3-N4	1.155	C14-C19	1.500
Ti1-R1[b]	2.065	C15-C20	1.490
Ti1-R2[b]	2.061	C21-C22	1.406
Ti2-R3[b]	2.072	C22-C23	1.402
Ti2-R4[b]	2.069	C23-C24	1.392
Ti3-R5[b]	2.071	C24-C25	1.407
Ti3-R6[b]	2.063	C25-C21	1.407
Ti4-R7[b]	2.070	C21-C26	1.488
Ti4-R8[b]	2.063	C22-C27	1.490
Ti1-C1	2.394	C23-C28	1.509
Ti1-C2	2.375	C24-C29	1.506
Ti1-C3	2.401	C25-C30	1.513
Ti1-C4	2.385	C31-C32	1.404
Ti1-C5	2.378	C32-C33	1.412
Ti1-C11	2.374	C33-C34	1.421
Ti1-C12	2.403	C34-C35	1.401
Ti1-C13	2.385	C35-C31	1.420
Ti1-C14	2.374	C31-C36	1.487
Ti1-C15	2.384	C32-C37	1.502
Ti2-C21	2.387	C33-C38	1.497
Ti2-C22	2.377	C34-C39	1.488
Ti2-C23	2.403	C35-C40	1.500
Ti2-C24	2.400	C41-C42	1.375
Ti2-C25	2.390	C42-C43	1.380
Ti2-C31	2.396	C43-C44	1.407
Ti2-C32	2.403	C44-C45	1.420
Ti2-C33	2.385	C45-C41	1.385
Ti2-C34	2.382	C41-C46	1.491
Ti2-C35	2.394	C42-C47	1.505
Ti3-C41	2.388	C43-C48	1.494
Ti3-C42	2.391	C44-C49	1.488
Ti3-C43	2.373	C45-C50	1.488
Ti3-C44	2.391	C51-C52	1.398
Ti3-C45	2.384	C52-C53	1.399
Ti3-C51	2.385	C53-C54	1.415
Ti3-C52	2.385	C54-C55	1.395
Ti3-C53	2.383	C55-C51	1.421
Ti3-C54	2.398	C51-C56	1.482
Ti3-C55	2.377	C52-C57	1.505
Ti4-C61	2.379	C53-C58	1.507
Ti4-C62	2.381	C54-C59	1.494
Ti4-C63	2.384	C55-C60	1.497
Ti4-C64	2.403	C61-C62	1.409
Ti4-C65	2.416	C62-C63	1.412
Ti4-C71	2.385	C63-C64	1.398
Ti4-C72	2.385	C64-C65	1.417
Ti4-C73	2.392	C65-C61	1.410
Ti4-C74	2.374	C61-C66	1.486
Ti4-C75	2.363	C62-C67	1.496
C1-C2	1.414	C63-C68	1.525
C2-C3	1.399	C64-C69	1.483
C3-C4	1.412	C65-C70	1.496
C4-C5	1.405	C71-C72	1.443
C5-C1	1.409	C72-C73	1.394
C1-C6	1.501	C73-C74	1.379
C2-C7	1.498	C74-C75	1.378
C3-C8	1.500	C75-C71	1.387
C4-C9	1.481	C71-C76	1.478
C5-C10	1.501	C72-C77	1.477
C11-C12	1.409	C73-C78	1.507
C12-C13	1.403	C74-C79	1.510
C13-C14	1.413	C75-C80	1.522

[a] The estimated standard deviations are: Ti–N, 0.010; C–C, 0.014; Ti–C, 0.010; N–N, 0.014; Ti–R, 0.007 Å. [b] R1 = C1–C5 ring centroid; R2 = C11–C15 ring centroid; R3 = C21–C25 ring centroid; R4 = C31–C35 ring centroid; R5 = C41–C45 ring centroid; R6 = C51–C55 ring centroid; R7 = C61–C65 ring centroid; R8 = C71–C75 ring centroid.

ometry $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_n$ originally assigned this complex was, in fact, incorrect, and that this dinitrogen complex is rather the titanium analogue of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$. In order to reconcile these apparent contradictions, it should be noted that the stoichiometry of this complex was previously measured at residual N_2 pressures (ca. 0.005 Torr) substantially different from those maintained while obtaining NMR and IR spectra (ca. 1 atm). We have therefore examined the

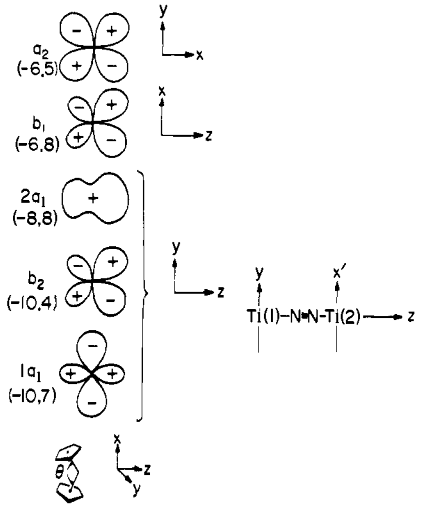

Figure 6. Contours of the five frontier orbitals of a bent, eclipsed $(\eta^5\text{-}C_5H_5)_2Ti$ fragment. Approximate energies (eV) from ref 29 for $\theta = 146°$ are given in parentheses.

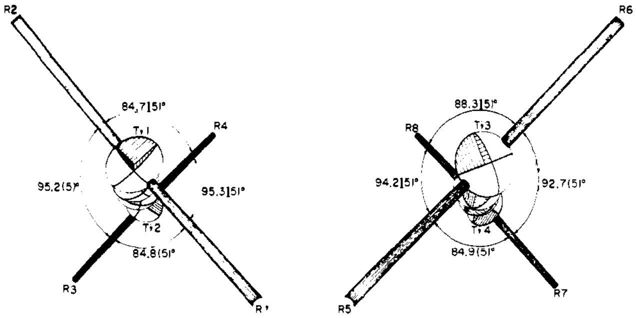

Figure 7. Skeletal view down the Ti–Ti axes revealing torsion angles.

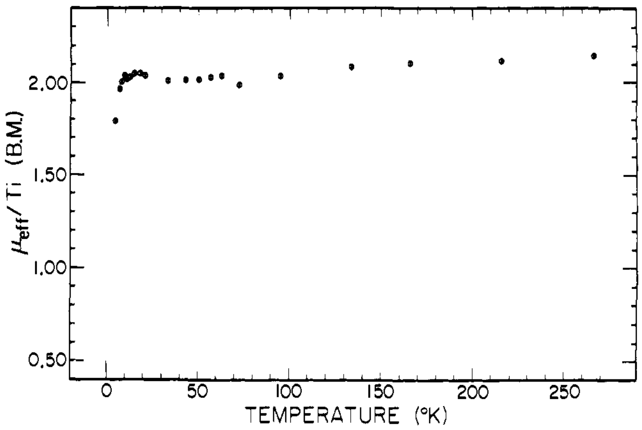

Figure 8. Temperature dependence of the magnetic moment (per Ti) for $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$.

Table VII. Least-Squares Planes of the Cyclopentadienyl Rings[a]

Atom	Deviation, Å	Atom	Deviation, Å
	Ring 1		Ring 3
C1	−0.012	C21	−0.008
C2	0.017	C22	0.013
C3	−0.015	C23	0.013
C4	0.008	C24	0.008
C5	0.003	C25	0.000
C6	−0.300	C26	−0.287
C7	−0.096	C27	−0.097
C8	−0.214	C28	−0.204
C9	−0.165	C29	−0.184
C10	−0.254	C30	−0.225
	Ring2		Ring 4
C11	0.013	C31	0.013
C12	−0.011	C32	−0.010
C13	0.004	C33	0.003
C14	0.004	C34	0.005
C15	−0.011	C35	−0.011
C16	−0.055	C36	−0.053
C17	−0.174	C37	−0.267
C18	−0.151	C38	−0.184
C19	−0.206	C39	−0.117
C20	−0.276	C40	−0.235
	Ring 5		Ring 7
C41	0.000	C61	0.009
C42	−0.006	C62	−0.005
C43	0.010	C63	−0.002
C44	−0.010	C64	0.007
C45	0.006	C65	−0.010
C46	−0.169	C66	−0.167
C47	−0.198	C67	−0.287
C48	−0.073	C68	−0.299
C49	−0.260	C69	−0.113
C50	−0.166	C70	−0.220
	Ring 6		Ring 8
C51	0.003	C71	−0.004
C52	−0.009	C72	0.009
C53	0.012	C73	−0.011
C54	−0.010	C74	0.009
C55	0.005	C75	−0.003
C56	−0.177	C76	−0.286
C57	−0.179	C77	−0.081
C58	−0.106	C78	−0.199
C59	−0.332	C79	−0.116
C60	−0.162	C80	−0.239

[a] A positive deviation is a deviation toward the titanium atom.

stoichiometry of this dinitrogen complex under the same conditions as those for the NMR and IR experiments. We indeed find that $(\eta^5\text{-}C_5Me_5)_2Ti$ absorbs 1.41 mol N_2/mol Ti in toluene at −80 °C under 0.85 atm N_2, close to that ratio required for $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$.[28] The apparent 1:1 stoichiometry obtained previously arose because under reduced pressure at −80 °C the solution undoubtedly contains a mixture of **1** and $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$. No evidence appears to remain, therefore, in support of any dinitrogen complex of titanocene (or zirconocene) containing N_2 bonded edge-on to the metal.

A qualitative description of the Ti-N_2 bonding for **1** may be formulated (as for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$) by suitable combinations of dinitrogen lone pair, π, and π^* orbitals with those of the bent bis(η^5-cyclopentadienyl)titanium(II) fragments (Figure 6). As is seen (Figure 7), all RTi···TiR torsion angles are nearly 90° (average 90.0 (4.8)°). If each $(C_5Me_5)_2Ti$ approximates an eclipsed $(C_5H_5)_2Ti$ unit (C_{2v} symmetry) and RTi···TiR torsion angles assume exactly 90°, then the dimer possesses perfect D_{2d} symmetry.

The two $(C_5H_5)_2Ti$ orbitals of interest in considering the bonding in the dimer are $1a_1$ and b_2 (Figure 6).[29] In the D_{2d} dimer the two fragment $1a_1$ orbitals transform as $a_1 + b_2$ and the two fragment b_2 orbitals form a degenerate e combination. The dimer a_1 orbital may be expected to interact with the N_2 σ_g and thus be somewhat destabilized; the b_2 will mix with the lower lying N_2 σ_u, and should be destabilized less. Whether the e set should go up or down is difficult to anticipate, since it should interact with both π and π^* N_2 orbitals, the former pushing e up, the latter down. A calculation by Hoffmann and Thorn[30] indicates that the interaction with N_2 π^* dominates, and hence e is stabilized. The calculated level ordering is shown below:

a_1 — −10.61
b_2 — −10.67
e — −11.17 eV

Four electrons, two from each $(\eta^5\text{-}C_5Me_5)_2Ti$ unit, are to go into this scheme. The calculated level ordering would dictate a high-spin $e^2b_2{}^1a_1{}^1$ configuration, since the gap of only 0.5 eV is well below a reasonable electron pairing energy (ca. 2 eV) for a d^2 Ti(II) ion.

Microcrystalline samples of **1** exhibit a gram magnetic susceptibility of 5.83×10^{-6} cgsu at 25 °C. The corrected effective magnetic moment is thus only 2.18 (1) μ_B per Ti, intermediate between 1.73 μ_B spin-only (d^1 Ti(III)) and 2.87 spin-only (d^2 Ti(II)) values. Furthermore, the temperature dependence of the magnetic moment (Figure 8) indicates very little magnetic exchange between the two titanium centers; μ_{eff} is invariant to ca. 20 K. While the linear rather than bent $Ti\text{-}N_2\text{-}Ti$ geometry and preliminary EPR data[31] for **1** are in accord with a Ti(II)N≡NTi(II) system, it is difficult to reconcile the large negative orbital contribution to the magnetic moment required to reduce μ_{eff} to 2.18 μ_B. Puzzling also is the low magnetic moment (2.15 μ_B) for $(\eta^5\text{-}C_5Me_5)_2Ti$,[10,32] which from all presently available data appears to be a monomeric, high-spin d^2 system.

It may be concluded, however, that the calculated level ordering for $\{(\eta^5\text{-}C_5Me_5)_2Ti\}_2N_2$ is at least qualitatively in agreement with its magnetism. The dominant component of the TiN≡NTi bonding is thus π interaction of the two Ti b_2 orbitals with N_2 π^* orbitals. Interaction of the empty π-acceptor orbital on each Ti (b_1) with filled N_2 π orbitals further enhances the N_2 π^* interaction with the Ti b_2 π orbitals. Thus **1** falls into the general class of binuclear complexes, discussed in the preceding article, where N_2 bridges a π-donor to a π-acceptor metal. As for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$, the MN≡NM bonding for **1** may be viewed as a "push-pull" interaction in the two orthogonal planes along the TiN≡NTi axis. A reduction in bond order for the $\mu\text{-}N_2$ of **1** comparable to that for $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ is thus achieved.

The effect exerted on the MN≡NM bonding by the empty b_1 π-acceptor orbitals on each Ti in **1** is illustrated by comparison to $\{(C_6H_{11})_3P\}_2NiN{\equiv}NNi\{P(C_6H_{11})_3\}_2$,[33] which also possesses nearly perfect D_{2d} symmetry. Even though Ti(II) formally possesses eight fewer d electrons than Ni(0), the presence of low-lying empty π-type orbitals for Ti effects a reduction in $\mu\text{-}N_2$ bond order (av N-N distance 1.160 (7) Å) greater than that for the Ni dimer (N-N distance 1.12 Å). A sizable reduction in N-N bond order does not appear to guarantee N_2 activation, however. The observations that **1** liberates only minor amounts of reduced N_2 (5-20%)[34] when treated with HCl, while $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ and $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$[28] give nearly quantitative yields of hydrazine under identical conditions, are indicative of more stringent requirements. Indeed, the results of a labeling study of the reaction of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ with HCl suggest that here the terminal dinitrogen ligands play the deciding role.[27]

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Supplementary Material Available: structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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$$\sigma = \left[\sum_i (x_i - \bar{x})^2/(N - 1) \right]^{1/2}$$

where N is the number of observations, x_i.

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(34) It may well be that the ammonia and hydrazine formed in this reaction result from $\{(\eta^5\text{-}C_5Me_5)_2TiN_2\}_2N_2$, which is generated from 1 and liberated N_2 during the reaction with HCl.