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E. Brady, W. Lukens, J.R. Telford, and G. Mitchell

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Bis(pentamethylcyclopentadienyl)titanium Amide

**Elizabeth Brady, Wayne Lukens,
Jason R. Telford, and Greg Mitchell**

**Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 (USA)**

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Abstract. $(\text{Me}_5\text{C}_5)_2\text{TiNH}_2$ is a bent metallocene with the NH_2 group oriented to maximize the π -interaction between nitrogen and titanium. The Ti-N bond length is short [1.944(2) Å], consistent with increased π -bonding.

Comment. The title compound was synthesized as part of an investigation of metal-ligand π bonding in titanium(III) compounds. Since the electronically favored orientation of the NH_2 group is the most sterically hindered, the relative strength of the electronic and steric effects can be examined. If steric effects dominate, the plane of the NH_2 ligand should be perpendicular to the plane formed by the titanium atom and the two centroids of the pentamethylcyclopentadienyl ligands. On the other hand, if electronic effects dominate, the titanium atom, and the two centroids, and the NH_2 group, acting as a π -donor, will all lie in the same plane.

Atomic parameters are given in Table 1. Selected distances and angles are given in Table 2. An ORTEP (Johnson, 1965) drawing of $(\eta^5\text{-Me}_5\text{C}_5)_2\text{TiNH}_2$ is given in Figure 1. The NH_2 ligand is in the proper orientation for the filled p-orbital of nitrogen to interact with the empty b_2 orbital of $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Ti}$ enabling the NH_2 ligand to act as a π -donor. The Ti - N distance is also quite short at 1.944(2) Å. Similar nitrogen to metal π -bonding is also seen in $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Hf(H)NHMe}$ (Hillhouse, Bulls, Santarsiero, and Bercaw, 1998) as evidenced by the similar orientation of the methyl amide group. In the only other crystallographically characterized bis(pentamethylcyclopentadienyl)-titanium(III) amide, bis(pentamethylcyclopentadienyl)titanium N-methyl-N-phenyl amide (Feldman and Calabrese, 1991), the amide ligand is perpendicular to the plane formed by the titanium atom and the two cyclopentadienyl ring centroids, preventing the nitrogen p-orbital from interacting with the b_2 orbital of the $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Ti}$ fragment. The Ti - N bond length of 2.054(2) Å is considerably longer than that found in the title compound.

The titanium(IV) metallocene, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{NC}_4\text{H}_4)_2$ (Bynum, Hunter, Rogers, and Atwood, 1980), nicely demonstrates the difference in bond lengths due to π -bonding. The compound possesses two pyrrole ligands, one of which is in the correct orientation for the nitrogen p-orbital to interact with the empty $1a_1$ orbital of the metallocene. The other pyrrole ring is perpendicular to the first and thus unable to act as a π -donor towards the low lying $1a_1$ orbital. The Ti-N bond length for the pyrrole acting as a π -donor is 2.070(5) Å while the T-N bond length for the non π -bonding pyrrole is 2.100(4) Å. Curiously, in the analogous zirconium compound (Bynum, Hunter, Rogers, and Atwood, 1980), the bond lengths are almost identical.

* Address correspondence to this author.

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Table 1. Atomic Parameters

$$B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

Starred Atoms Refined with Isotropic Thermal Parameters

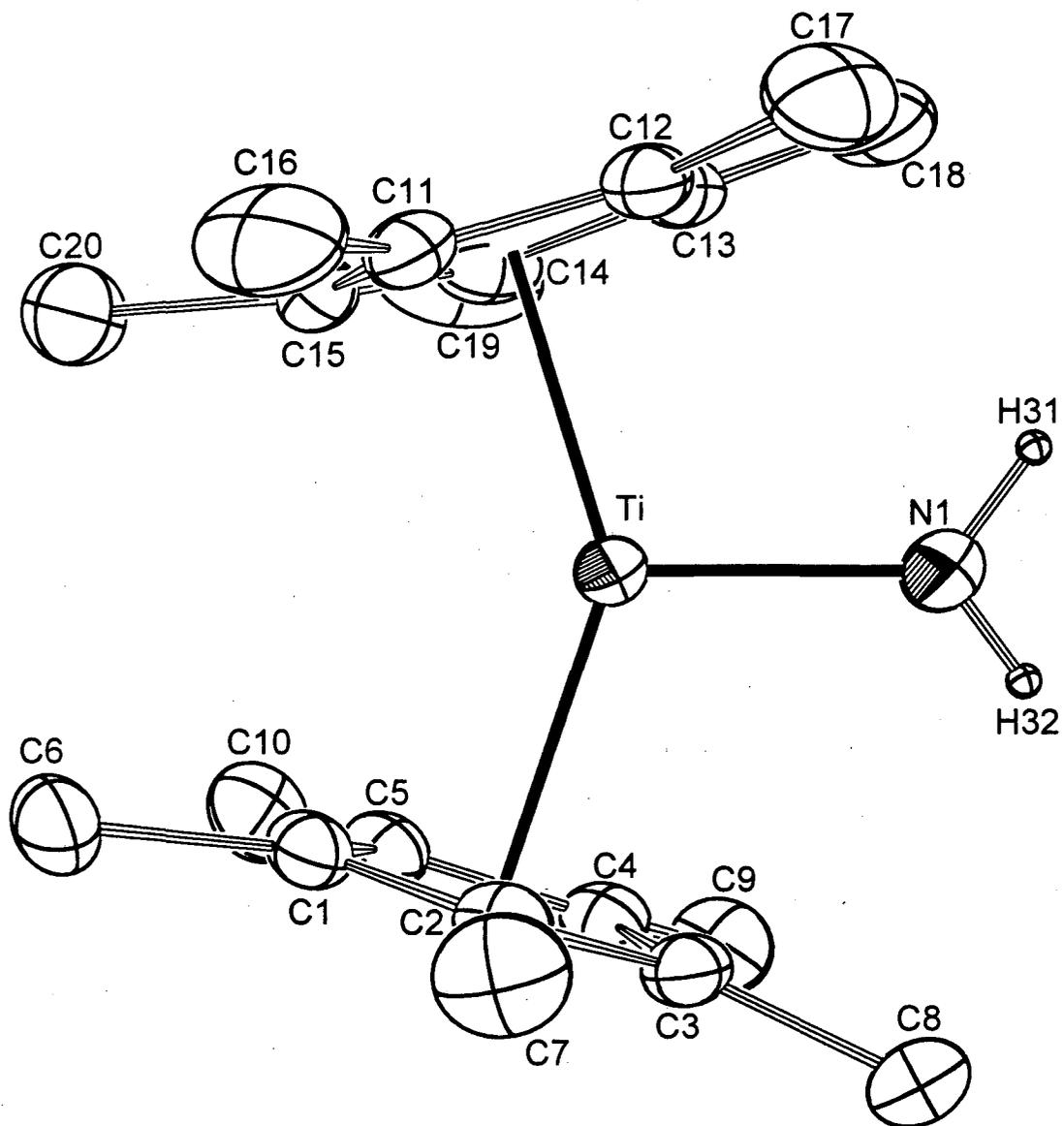
Atom	X	y	Z	Beq(Å ²)
Ti	0.11498(1)	0.23016(1)	0.40310(1)	1.529(5)
N1	0.1327(2)	0.1761(1)	0.5261(1)	3.69(4)
C1	0.1354(2)	0.1684(1)	0.2533(1)	2.01(3)
C2	0.0893(2)	0.0911(1)	0.3043(1)	2.00(3)
C3	0.2006(2)	0.0696(1)	0.3794(1)	1.98(3)
C4	0.3126(2)	0.1360(1)	0.3768(1)	2.00(3)
C5	0.2730(2)	0.1971(1)	0.2989(1)	2.01(3)
C6	0.0606(2)	0.1994(2)	0.1592(1)	2.85(4)
C7	-0.0451(2)	0.0339(2)	0.2768(1)	3.22(4)
C8	0.2035(2)	-0.0152(1)	0.4433(1)	2.84(4)
C9	0.4533(2)	0.1383(2)	0.4415(1)	3.08(4)
C10	0.3702(2)	0.2698(2)	0.2667(1)	3.09(4)
C11	-0.0822(2)	0.3342(1)	0.3476(1)	2.31(3)
C12	-0.0692(2)	0.3286(1)	0.4440(1)	2.04(3)
C13	0.0605(2)	0.3724(1)	0.4849(1)	2.16(3)
C14	0.1296(2)	0.4031(1)	0.4135(1)	2.57(3)
C15	0.0385(2)	0.3828(1)	0.3287(1)	2.58(3)
C16	-0.2126(2)	0.3043(2)	0.2800(2)	4.53(5)
C17	-0.1803(2)	0.2856(2)	0.4914(2)	3.76(4)
C18	0.1126(2)	0.3910(2)	0.5854(1)	3.71(4)
C19	0.2647(3)	0.4613(2)	0.4263(2)	5.52(6)
C20	0.0541(3)	0.4264(2)	0.2375(2)	5.38(5)

Table 2. Selected distances and angles

Ti-N1	1.944(2) Å	Ti-Cp1	2.071 Å
Ti-Cp2	2.070 Å	Ti-Cp(ave)	2.40(1) Å
Ti-C1	2.415(2) Å	Ti-C11	2.388(2) Å
Ti-C2	2.385(2) Å	Ti-C12	2.390(2) Å
Ti-C3	2.396(2) Å	Ti-C13	2.402(2) Å
Ti-C4	2.386(2) Å	Ti-C14	2.375(2) Å
Ti-C5	2.402(2) Å	Ti-C15	2.412(2) Å
H31-N1-H32	108(2) °	H31-N1-Ti	126(2) °
H32-N1-Ti	126(2) °	Cp1-Ti-Cp2	144.3 °
Cp1-Ti-N1	108.7 °	Cp2-Ti-N1	107.0 °

Cp1 and Cp2 are the centroids of the cyclopentadienyl rings.

Figure 1



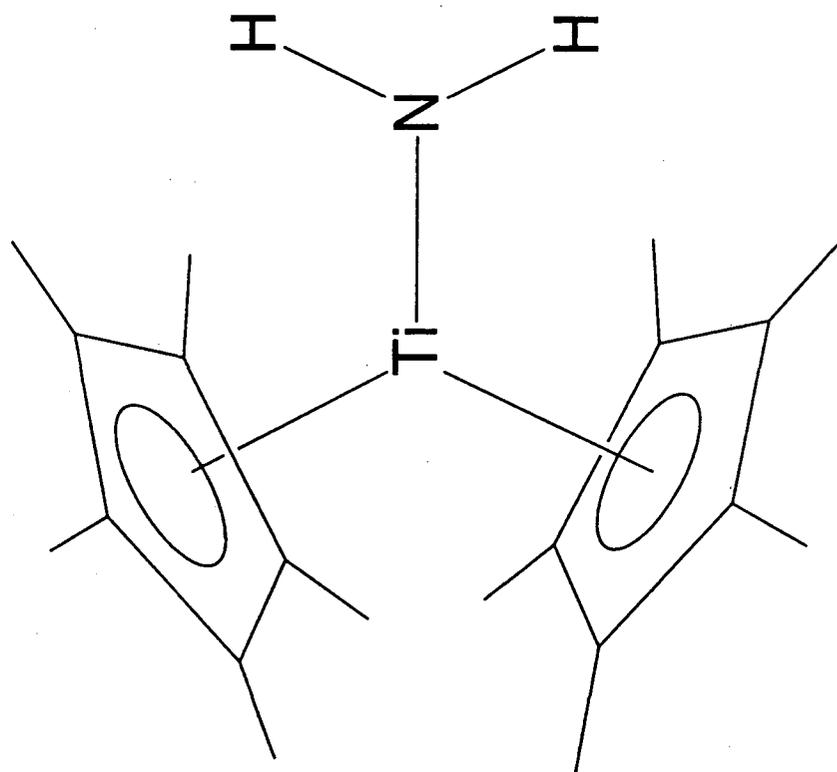
APPENDIX 2

Experimental form to be completed for each structure (hard-copy submission)

CRYSTAL DATA	
Compound [e.g. (1), (2) etc.]	
Chemical formula $C_{20}H_{32}NTi$	Crystal system monoclinic
M_r 334.38	Space group $P2_1/n$
a (Å) 9.601(2)	α (°) 90
b (Å) 13.690(2)	β (°) 100.83(1)
c (Å) 14.808(2)	γ (°) 90
Z 4	D_m ($Mg\ m^{-3}$) too air sensitive
V (Å ³) 1911.6(9)	D_x ($Mg\ m^{-3}$) 1.62
Radiation $MoK\alpha$	No. of reflections for lattice parameters 24
Wavelength (Å) 0.71073	θ range for lattice parameters (°) $14 < \theta < 16$
Absorption coefficient (mm^{-1}) 43.96	Temperature (K) 183
Crystal source Crystallization from hexane	
Crystal colour Dark Purple	Crystal description black
Crystal size (mm) 0.50 x 0.50 x 0.30	
DATA COLLECTION	
Diffractometer type CAD-4	Collection method $\omega/2\theta$
Absorption correction type (circle appropriate description) analytical integration empirical (refdelf) sphere cylinder none	Absorption correction (T_{min} , T_{max}) $T_{max} = 1.19$ $T_{min} = 0.85$
No. of reflections measured 4844	R_{int} N/A
No. of independent reflections 4393	θ_{max} (°) 27.5
No. of observed reflections 3799	No. of standard reflections (and interval) 3, 1 hour
Criterion for observed $F^2 > 3\sigma(F^2)$	Variation of standards no loss
h_{min} 0	h_{max} 12
k_{min} 0	k_{max} 17
l_{min} -19	l_{max} 18

REFINEMENT	
Treatment of hydrogen atoms (circle appropriate entry, or describe in box below) refall refxyz refU noref	F, F^2 or I F
R 0.0353	No. of parameters refined 328
wR 0.0447	No. of reflections used in refinement 3571
S 1.988	Weighting scheme $w = 1/\sigma(F_o)^2$
$(\Delta/\sigma)_{max}$ 0	$(\Delta\rho)_{min}$ ($e \text{ \AA}^{-3}$) -0.10
Extinction correction method (if applied) Secondary	$(\Delta\rho)_{max}$ ($e \text{ \AA}^{-3}$) 0.29
Primary- and secondary-extinction values 7×10^{-7}	Source of atomic scattering factors International Tables
<p>Enter below in grammatically correct text details of any novel or unusual features of the experimental procedure, method used to measure density, discussion of absolute structure and justification of unusually high R values or shift-to-e.s.d. values > 1.0 should be included (attach extra sheet if necessary).</p>	
<p>A chemical structural diagram should be attached to this form.</p>	
<p>The remainder of the manuscript should consist of: (i) double-spaced typed text and tables set out under the standard subheadings of § 3 of the full Notes; (ii) figures and figure legends; (iii) supplementary data for deposition (see § 4); (iv) signed Transfer of Copyright Agreement form; and (v) letter of submission.</p>	

Experimental. The title compound was synthesized from $(\eta^5\text{-Me}_5\text{C}_5)_2\text{TiCH}_3$ and NH_3 . Dark crystals were grown by slowly cooling a saturated hexane solution. A dark air-sensitive crystal was mounted on the end of a quartz capillary tube with a drop of Paratone N oil. Atomic f for Ti, N, C and H from *International Tables* (1974); structure refinement using MOLEN (Delft Instruments, 1990) and local unpublished programs.



LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720

