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Molecular Structure of μ-Pyrazole-bis(η^5-cyclopentadienyl)titanium(III), a Dimeric Titanium(III) Compound with a Bridging Organic Group

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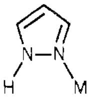
The first molecular structure of a dimeric titanium(III) compound with an organic bridge, $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$, Pz = pyrazole, has been determined by X-ray diffraction techniques. The compound crystallizes in the monoclinic space group $P2_1/n$ with cell parameters $a = 8.073$ (2) Å, $b = 7.961$ (3) Å, $c = 17.834$ (5) Å, and $\beta = 94.54$ (2)°. The title compound has two dimeric molecules per unit cell and a calculated density of 1.430 g/cm^3 (observed density 1.42 (1) g/cm^3). Full-matrix least-squares refinement based on 1994 reflections leads to agreement factors of $R = 0.061$ and $R_w = 0.071$. In the solid state, $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$ possesses a crystallographic inversion center and a structure in which two coplanar pyrazolide anions bridge between two titanium atoms. The four nitrogen atoms from the pyrazolide groups and the titanium atoms form a six-membered ring which is in a chair configuration with one titanium atom occupying a position 0.40 Å above the plane of the pyrazolide groups and the other titanium atom located 0.40 Å below the same plane. The structure of $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$ is discussed in relation to the bonding in other low-valent titanium compounds and in other metal complexes where pyrazole is a ligand.

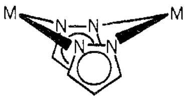
Introduction

The bifunctionality and unsaturation of pyrazole give it an interesting coordination chemistry as a ligand.[1] η^1 coordination (I) of the pyrazole group is found for the neutral pyrazole molecule and has been described in several crystal structures.[2] Compounds such as $(\eta^5\text{-}C_5H_5)Co(C_2H_3N_2)(C_3H_3N_2H)$ ionize an amine proton from one pyrazole atom to give a neutral monomeric compound.[3] Coordination of pyrazole to one metal site has been most extensively investigated in the poly(1-pyrazolyl)borates,[1] and several crystal structural studies have been reported of poly(1-pyrazolyl)borates with transition metals such as ruthenium, rhodium, molybdenum, and copper.[4-7] Crystallographic and NMR studies of $(C_2H_5)_2B(C_3H_3N_2)Mo(CO)_2(\eta^3\text{-2-phenylallyl})$ show not only strong C–H···Mo interactions but also the presence of "ring-flips" that arise from changes in the conformation of the six-membered ring formed by the four pyrazolyl nitrogen atoms, the boron atom, and the central molybdenum atom.[5,8] Further evidence of both the wide variety of coordination geometries and the tendency of poly(1-pyrazolyl)borates to exhibit stereochemical nonrigidity is found with the compound $[(HB(C_3H_3N_2)_3)Cu]_2$.[7] This Cu(I) dimeric compound has both bridging and terminal pyrazolyl groups in the solid state, but the solution NMR spectrum indicates the presence of only one type of pyrazolyl signal down to −130 °C.



I

II



III

The anion of pyrazole can function as a 1,2 bridge (II) and this configuration leads to polymeric compounds with the stoichiometry $M(Pz)_n$ for univalent cations of copper, silver, and several other metals.[10]

Compounds with the formula $L_xM(Pz)_2ML_x$ and structures analogous to III have been prepared where M is Rh and Pd.[11] When L_x is an allyl group and the metal atom is palladium, the compound gives an NMR signal which is consistent with the presence of stereochemical nonrigidity. The temperature dependence of the NMR spectrum indicates a mechanism involving rotation of allyl groups and a molecular structure in a boat configuration shown in III. In contrast, there is evidence that binuclear compounds such as $Cu(acac)_2(Pz)_2$ and $Cu_2(acac)_2OH(Pz)$, where acac is the anion of acetylacetone, have a structure in which the pyrazolide bridges lie in the same plane as the two copper atoms.[12] The preliminary report of the X-ray crystal structure of the binuclear copper compound R–Cu_2(Pz) (R is the di-2′-hydroxyanil of 2-hydroxy-5-methylisophthalaldehyde) confirms the coplanarity of the pyrazole groups with the two Cu atoms.[13] The novel compound $(CO)_3Mn(Pz)_3Mn(CO)_3$ with three 1,2-η^2-pyrazolide groups gives an NMR signal consistent with a molecular structure which has D_{3h} symmetry.[14]

Examples of early transition-metal complexes with pyrazole ligands are limited to compounds with poly(1-pyrazolyl)borates. Manzer has reported the preparation of several titanium complexes including the dimeric compound $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)_2B(Pz)_2Ti(\eta^5\text{-}C_5H_5)_2][BPh_4]$ (Ph = phenyl).[15] The reaction of $K[HB(Pz)_3]$ with $TiCl_4$ has been reported by Kouba and Wreford.[16]

In this paper we present the synthesis and characterization by X-ray crystallography of the compound $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$. This study represents the first structural determination of a dimeric Ti(III) compound with an organic bridge and one of the few structures in which pyrazole is present in a 1,2-η^2 configuration. We have previously reported the structures of several halogen-bridged dimers such as $[(\eta^5\text{-}C_5H_4CH_3)_2TiX]_2$ (X = Br and Cl).[17] In the accompanying paper we report the EPR spectra and magnetic properties of the title compound along with those of several other binuclear Ti(III) compounds.[18]

Experimental Section

The synthetic work was carried out in a Vacuum Atmospheres drybox in a helium atmosphere. Solvents were distilled under a nitrogen atmosphere from sodium and benzophenone. Bis(cyclopentadienyl)titanium monochloride was prepared by a published procedure.[19] Pyrazole was purchased from Aldrich Chemical Co. The elemental and mass spectral analyses were performed at the University of Illinois School of Chemical Sciences. Computer calculations were done on a Sigma 5 computer at the Materials Research Laboratory at the University of Illinois.

μ-Pyrazole-bis(η^5-cyclopentadienyl)titanium(III). The synthesis was carried out in a drybox. Pyrazole (0.50 g, 7.3 mmol) and sodium sand (0.20 g, 8.7 mmol) were reacted in 20 mL of tetrahydrofuran (THF) for 12 h to produce the sodium salt of pyrazole. The excess solid sodium was then removed. Bis(cyclopentadienyl)titanium monochloride (1.60 g, 7.5 mmol) was dissolved in 20 mL of THF and was then added to the pyrazole salt solution to give a blue solution.

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Table I. Crystallographic Data for $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$

Compound: $C_{26}H_{26}N_4Ti_2$ (mol wt 490.32)
Lattice system: monoclinic
Space group: $P2_1/n$ (centrosymmetric)
Z: 2 dimers per unit cell
Cell parameters: $a = 8.073$ (2) Å
$b = 7.961$ (3) Å
$c = 17.834$ (5) Å
$\beta = 94.54$ (2)°
Density: obsd, 1.42 (1) g/cm^3; calcd, 1.430 g/cm^3
Wavelength: Mo Kα (λ 0.710 69 Å)
$R = 0.061$; $R_w = 0.071$
Scan rate: 2.0°/min
2θ limits: 2-50°
Linear absorption: $\mu = 7.51$ cm^{-1}
Reflections: 1994 of which 1258 were observed ($F_o^2 > 3\sigma(F_o^2)$)
Crystal dimensions: 0.36 × 0.38 × 0.24 mm

Table II. Interatomic Distances (Å) for the Nonhydrogen Atoms in $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$

Ti-Ti'[a]	4.339 (3)	C(1)-C(2)	1.333 (9)
Ti-N(1)	2.206 (5)	C(2)-C(3)	1.363 (8)
Ti-N(2)	2.183 (5)	C(4)-C(5)	1.390 (10)
Ti-C(4)	2.391 (8)	C(5)-C(6)	1.402 (10)
Ti-C(5)	2.366 (7)	C(6)-C(7)	1.402 (10)
Ti-C(6)	2.362 (7)	C(7)-C(8)	1.350 (11)
Ti-C(7)	2.431 (7)	C(8)-C(4)	1.367 (10)
Ti-C(8)	2.431 (8)	C(9)-C(10)	1.353 (12)
Ti-C(9)	2.354 (8)	C(10)-C(11)	1.359 (18)
Ti-C(10)	2.380 (10)	C(11)-C(12)	1.322 (16)
Ti-C(11)	2.364 (12)	C(12)-C(13)	1.311 (13)
Ti-C(12)	2.370 (9)	C(13)-C(9)	1.309 (12)
Ti-C(13)	2.346 (8)	Ti-plane 1[b]	2.086
Av Ti-C bond	2.379 (30)	Ti-plane 2[b]	2.077
N(1)-N(2)	1.312 (6)	Ti-plane 4[b]	−0.398
N(1)-C(1)	1.350 (8)	Ti'-plane 4[b]	0.398
N(2)-C(3)	1.312 (6)	Ti-plane 5[b]	−0.416
		Ti'-plane 5[b]	0.416

[a] See Table VI for the atoms that define the planes. [b] The prime (') indicates atoms generated by the inversion center in the middle of the dimer unit.

After 12 h of stirring the reaction mixture turned green and a light green precipitate was formed. The volume of the solution was reduced to 10 mL under reduced pressure, and the solution was filtered to remove the green powder. The product was extracted several times with a total of 80 mL of refluxing toluene. This solution was filtered, while hot, and gave on slow cooling 0.22 g of green rod-shaped, air-sensitive crystals in 12% yield. Anal. Calcd for $C_{26}H_{26}N_4Ti_2$: C, 63.69; H, 5.35; N, 11.43; Ti, 19.54. Found: C, 63.90; H, 5.40; N, 11.40; Ti, 19.34. The dimeric configuration was confirmed by the mass spectrum which showed a parent ion peak at mass number 490 (calcd 490).

Collection and Reduction of X-ray Data. Several rod-shaped crystals were cleaved and placed in thin-walled capillaries. This operation was performed outside of the drybox because the crystals decompose only slightly over the period of a day on exposure to oxygen. The capillary tubes were then placed in a vacuum desiccator, which was subsequently evacuated and refilled several times with nitrogen. The open ends of the capillaries were plugged and the tubes were sealed in a flame so that they retained their inert atmospheres.

The crystal symmetry and space groups were determined from Weissenberg and precession photographs to be monoclinic and $P2_1/n$. The systematic extinctions were $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$. The cell parameters, as obtained by least-squares fitting of ten hand-centered diffractometer reflections, are $a = 8.073$ (2) Å, $b = 7.961$ (3) Å, $c = 17.834$ (5) Å, and $\beta = 94.54$ (2)°. The density was found to be 1.42 (1) g/cm^3 by flotation in a 2-bromopropane–carbon tetrachloride solution and is in agreement with the calculated value of 1.430 g/cm^3 assuming a cell with two dimer units. Table I has additional crystallographic information.

A crystal with dimensions 0.36 × 0.38 × 0.24 mm was mounted with the [010] axis parallel to the axis of the capillary. Intensity data were collected by the θ-2θ scan technique on a Picker FACS-I diffractometer using Mo Kα radiation. A scan rate of 2°/min was used, and three standard reflections were monitored after every 100 reflections. These standard reflections showed no systematic changes with time during data collection. The intensities of 1994 independent reflections were measured of which 1258 were observed using the criterion $F_o^2 > 3\sigma(F_o^2)$, where F_o is the observed structure factor and $\sigma(F_o^2)$ is the standard deviation. The intensities were corrected for background counts and Lorentz–polarization factors. No absorption corrections ($\mu = 7.51$ cm^{-1}) were made. The error due to the neglect of absorption is estimated to be less than ±5%.

Table III. Bond Angles (deg) for the Nonhydrogen Atoms in $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$

N(1)-Ti-N(2)'	91.6 (2)	C(5)-C(6)-C(7)	106.6 (8)
Ti-N(1)-N(2)	132.1 (4)	C(6)-C(7)-C(8)	108.5 (8)
Ti-N(2)'-N(1)'	132.5 (4)	C(7)-C(8)-C(4)	109.5 (8)
N(2)-N(1)-C(1)	108.2 (6)	C(10)-C(9)-C(13)	107.4 (12)
N(1)-N(2)-C(3)	106.5 (5)	C(9)-C(10)-C(11)	105.4 (12)
N(2)-C(3)-C(2)	111.1 (6)	C(10)-C(11)-C(12)	108.4 (13)
C(1)-C(2)-C(3)	103.4 (6)	C(11)-C(12)-C(13)	107.8 (13)
N(1)-C(1)-C(2)	110.9 (7)	C(9)-C(13)-C(12)	110.9 (11)
C(5)-C(4)-C(8)	108.0 (8)	Plane 1-Ti-plane 2[a]	110.9 (11)
C(4)-C(5)-C(6)	107.4 (7)		

[a] See Table VI for the atoms that define the planes.

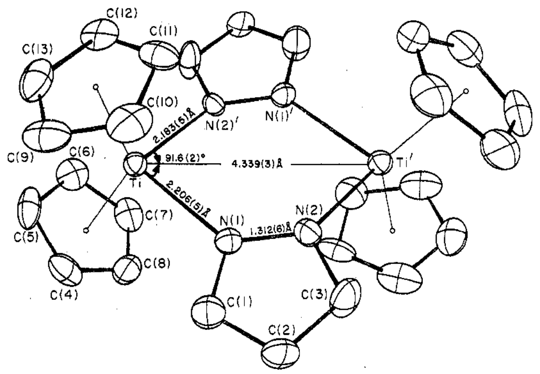


Figure 1. Crystal structure of $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$. An inversion center is present in the center of the dimer which generates the full molecule from the asymmetric unit.

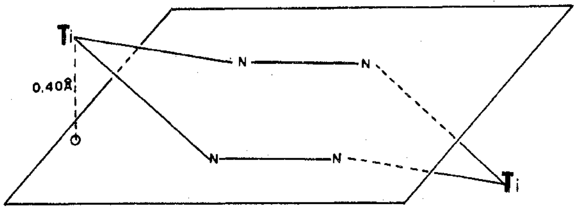


Figure 2. Schematic drawing indicating the deviation of the titanium atoms from the plane of the pyrazole atoms. Only the nitrogen atoms of the pyrazole molecule are shown and the cyclopentadiene rings are omitted for clarity.

Structure Solution and Refinement. From a Patterson map it was possible to establish the coordinates of the titanium atom.[20] A Fourier map based on the phases derived from a structure factor calculation with the titanium atom coordinates yielded the locations of the two nitrogen atoms. The remainder of the atomic positions were found in subsequent Fourier maps. The structure was refined isotropically through several cycles of least squares to $R = 0.117$ and $R_w = 0.132$.[21] After two cycles of anisotropic refinement, the locations of the hydrogen atoms were calculated.[20] In subsequent refinements the hydrogen atomic positions were not refined and the hydrogen atomic isotropic temperature factors were set equal to a value of $B_c + 1$, where B_c is the value of the temperature factor found for the isotropically refined carbon atom to which a given hydrogen atom is attached. After two more cycles of refinement, the positions of the hydrogen atoms were recalculated. Refinement, using all data, converged to final agreement factors of $R = 0.061$ and $R_w = 0.071$. The most intense peak in the final difference Fourier was 0.72 e/Å^3. This peak was located between the titanium atom and C(4). The final atomic positions are in Tables IV and VII, and the final temperature factors are in Table V.

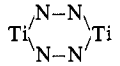
Table IV. Positional Parameters for the Nonhydrogen Atoms in $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$[a]

Atom	x	y	z
Ti	−0.0238 (1)	−0.0017 (2)	0.1203 (1)
N(1)	0.1155 (6)	−0.1557 (7)	0.0440 (3)
N(2)	0.1507 (6)	−0.1333 (7)	−0.0259 (3)
C(1)	0.2110 (12)	−0.2823 (11)	0.0735 (4)
C(2)	0.3119 (8)	−0.3398 (9)	0.0237 (4)
C(3)	0.2707 (10)	−0.2451 (11)	−0.0387 (4)
C(4)	−0.0923 (10)	−0.2498 (12)	0.1868 (6)
C(5)	−0.1584 (12)	−0.1129 (14)	0.2225 (4)
C(6)	−0.2812 (9)	−0.0421 (10)	0.1722 (6)
C(7)	−0.2912 (10)	−0.1436 (13)	0.1077 (5)
C(8)	−0.1755 (14)	−0.2657 (11)	0.1174 (5)
C(9)	0.1882 (19)	0.0694 (13)	0.2131 (8)
C(10)	0.2542 (13)	0.0935 (12)	0.1466 (12)
C(11)	0.1664 (25)	0.2224 (27)	0.1130 (7)
C(12)	0.0557 (17)	0.2737 (13)	0.1588 (11)
C(13)	0.0702 (15)	0.1808 (20)	0.2178 (6)

[a] The remainder of the dimer unit is generated by an inversion center which is located in the center of the molecule.

Results and Discussion

The solid-state structure of $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$ is dimeric and has a crystallographic center of inversion. Figure 1 shows the structure, which has two coplanar pyrazolide groups that bridge in a 1,2-η^2 linkage between two titanium atoms. Figure 2 shows that the resulting



moiety has a chair conformation with the titanium atoms displaced 0.40 Å above and below the plane containing the two pyrazolide groups. Tables II and III provide a partial listing of bond distances and angles.

The most unexpected results from this structural study are the coplanarity of the pyrazolide rings as indicated in Table VI and the deviation of the metal atoms from the plane occupied by both of the pyrazolide groups giving a chair conformation. Previous X-ray and NMR structural studies of dimetallic complexes with two bridging pyrazolide groups or with poly(1-pyrazolyl)borates indicate that the pyrazole groups usually are not in the same plane. The coplanarity of the pyrazolide moieties in this structure is apparently enforced by the cyclopentadienyl rings, which hinder tilting of the pyrazolide groups relative to their observed positions in Figure 1. The nonbonding contact distances between the cyclopentadienyl carbon atoms, C(8) and C(10), and the pyrazolide group atoms, N(1) and C(1), are C(8)–N(1) 2.91 (1) Å, C(8)–C(1) 3.29 (1) Å, C(10)–N(1) 2.87 (1) Å, and C(10)–C(1) 3.27 Å. These values are equal to or less than the expected van der Waals contact distances of 3.2–3.4 Å.[32] We estimate that the cyclopentadienyl carbon to cyclopentadienyl carbon (Cp–Cp) atomic distance across the dimer would be over 4 Å if the titanium atoms were in the same plane as the pyrazolide groups. Thus Cp–Cp interactions do not seem to be a factor in explaining the observed chair configuration. A possible result of the tilting of the ligands out of the plane of the metal is that occupied π orbitals of the pyrazolide groups have enhanced interaction with the electron-deficient titanium center. It is interesting to note in this regard that the displacement of titanium atom out of the plane of an aromatic, planar coordinating ligand is also observed in the structure of $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$, bpy = bipyridyl. The bipyridyl molecule is inclined upward 25° toward one of the cyclopentadienyl rings so that the titanium atom does not lie in the plane of the ligand.[23]

The structure of the title compound given in Figure 1 provides indirect evidence for the "ring-flip" mechanism that has been proposed to explain the fluxional NMR behavior of several poly(1-pyrazolyl)borate compounds such as $(Pz)_2B(Pz)_2Mo(\eta^5\text{-}C_5H_5)(CO)_2$ and $Et_2B(Pz)_2Mo(\eta^5\text{-}C_5H_5)_2(CO)_2$. In this mechanism the boat conformation of the six-membered ring consisting of a central molybdenum atom, a boron atom, and four pyrazolyl nitrogen atoms inverts by the movement of the pyrazolyl rings and the boron atom. The coplanar pyrazolide rings observed in Figure 1 would have a similar geometry to the intermediate step in a "ring-flip" mechanism.

The Ti–Ti distance of 4.339 (3) Å is longer than that found in other dimeric titanium(III) compounds such as $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ (3.943 (2) and 3.968 (2) Å) and $[(\eta^5\text{-}C_5H_4CH_3)_2TiBr]_2$ (4.125 Å), where there is evidence for magnetic exchange via the direct overlap of metal orbitals.[17] The N–Ti–N angle of 91.6 (2)° in $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$ is close to the included angle of 93.15 (8)° found in the nonbridging d^0 compound $(\eta^5\text{-}C_5H_4CH_3)_2TiCl_2$.[22] In contrast the Cl–Ti–Cl angles of the d^1 halogen-bridged compounds, such as $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$, are much smaller with values of 77.1–78.6°. This difference is presumably inherent in the geometric constraints of the four-membered ring in $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ vs. those for the six-membered ring in $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$.

The two Ti–N bonds have approximately the same lengths (2.183 (5) and 2.206 (5) Å). The Ti–N bond distances are comparable with those found in $(\eta^5\text{-}C_5H_5)_2Ti(bpy)$ (2.14 (1) Å)[23] and $(\eta^5\text{-}C_5H_5)TiCl_2(quinoline)$ (2.224 (7) and 2.270 (10) Å).[24] The nitrogen–nitrogen contact distance across the dimeric unit (N(1) to N(2)′) of 3.148 (7) Å is the same as the van der Waals diameter for nitrogen of 3.1 Å.[32]

The coordination of pyrazole to two titanium atoms appears to have only minor effects on the structure of the pyrazole molecule. The N=N bond distance of 1.35 (1) Å in the

Table V. Anisotropic Thermal Parameters (×10³) for the Nonhydrogen Atoms in $[(\eta^5\text{-}C_5H_5)_2Ti(Pz)]_2$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	42 (1)	39 (6)	35 (2)	−6 (1)	3 (1)	−1 (1)
N(1)	59 (4)	46 (4)	38 (3)	14 (3)	5 (3)	4 (3)
N(2)	51 (4)	43 (4)	45 (3)	12 (10)	9 (3)	8 (3)
C(1)	135 (9)	82 (7)	64 (6)	61 (6)	20 (6)	21 (6)
C(2)	52 (5)	55 (5)	66 (5)	29 (4)	−1 (4)	0 (4)
C(3)	102 (7)	103 (7)	51 (5)	65 (6)	21 (5)	6 (5)
C(4)	79 (7)	78 (7)	87 (8)	7 (6)	27 (6)	42 (6)
C(5)	74 (7)	128 (9)	38 (5)	−45 (6)	11 (5)	0 (6)
C(6)	54 (5)	66 (8)	98 (6)	−26 (5)	28 (5)	−10 (6)
C(7)	59 (6)	82 (7)	82 (6)	−27 (5)	−1 (5)	4 (6)
C(8)	132 (10)	55 (6)	66 (6)	−23 (6)	42 (7)	−8 (6)
C(9)	105 (10)	62 (7)	133 (11)	−14 (6)	−98 (8)	−6 (7)
C(10)	31 (6)	236 (21)	195 (18)	−35 (8)	28 (8)	−158 (16)
C(11)	170 (18)	220 (22)	54 (6)	−166 (16)	−7 (9)	3 (10)
C(12)	119 (11)	37 (6)	173 (14)	−18 (7)	−86 (11)	4 (9)
C(13)	83 (9)	105 (10)	74 (8)	−31 (7)	16 (6)	−39 (7)

[a] The form of the thermal motion function is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table VI. Calculations of Planes in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(Pz)}]_2$ and Deviation from Planarity

Atoms	Distance, Å	Atoms	Distance, Å
Plane 1		Plane 2	
C(4)	0.006	C(9)	0.004
C(5)	−0.012	C(10)	−0.006
C(6)	0.014	C(11)	0.006
C(7)	−0.011	C(12)	−0.004
C(8)	0.003	C(13)	0.000
Plane 3		Plane 4	
N(1)	−0.008	N(1)	0.000
N(2)	0.003	N(1)′	0.000
C(1)	0.009	N(2)	0.000
C(2)	−0.007	N(2)′	0.000
C(3)	0.002		
Plane 5			
N(1)	−0.006	N(1)′	0.006
N(2)	0.004	N(2)′	−0.004
C(1)	0.009	C(1)′	−0.009
C(2)	−0.007	C(2)′	0.007
C(3)	0.002	C(3)′	−0.002

Table VII. Positional and Isotropic Thermal Parameters for the Hydrogen Atoms in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(Pz)}]_2$

Atom	*x*	*y*	*z*	B,[a] Å^2
H(1)	0.2074	−0.3235	0.1232	6.0
H(2)	0.3933	−0.4262	0.0306	7.2
H(3)	0.3200	−0.2577	−0.0848	7.3
H(4)	−0.0035	−0.3181	0.2084	6.3
H(5)	−0.1287	−0.0722	0.2715	6.8
H(6)	−0.3466	0.0557	0.1788	6.2
H(7)	−0.3662	−0.1321	0.0635	6.0
H(8)	−0.1534	−0.3516	0.0822	6.0
H(9)	0.2237	−0.0147	0.2491	7.7
H(10)	0.3416	0.0328	0.1263	7.4
H(11)	0.1803	0.2719	0.0647	7.9
H(12)	−0.0233	0.3627	0.1506	7.5
H(13)	0.0054	0.1908	0.2610	6.9

[a] Isotropic temperature factor.

uncoordinated pyrazole molecule[26] shows little change (1.312 (6) Å) on forming a 1,2-η^2 bond in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(Pz)}]_2$.

Other than the examples cited in the Introduction, there are only a few examples of the coordination of adjacent nitrogen atoms to two different metal atoms (M—N═N—M) as observed in the title compound. This configuration is found in Cr, Mo, and W complexes with 2,3-diazobicyclo[2.2.1]-hept-2-ene.[27] A crystal structure analysis of the trinuclear compound Ru(CO)_{10}(pyridazine) has confirmed that two nitrogen atoms of the pyridazine ring are coordinated to two different ruthenium atoms.[28] The parent compound diazene, HN═NH, has been complexed in a 1,2-η^2 fashion along with molecular nitrogen in a number of complexes.[31] Because several titanium compounds have been successfully employed in the reduction of molecular nitrogen to hydrazine or ammonia,[29] there is special interest in the ability of two titanium atoms to coordinate to adjacent nitrogen atoms. Bercaw and co-workers have isolated and characterized the compound $[(\eta^5\text{-C}_5(\text{CH}_3)_5)_2\text{Ti}]_2\text{N}_2$, which has a linear Ti—N≡N—Ti configuration.[30] The structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(Pz)}]_2$ provides a model for two titanium(III) atoms bonded to adjacent nitrogen atoms which have been partially reduced from the zero oxidation state.

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Registry No. $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti(Pz)}]_2$, 66324-41-2; $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}$, 60955-54-6.

Supplementary Material Available: A listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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(21) $R = \Sigma[|F_o| - |F_c|]/\sum|F_o|$ and $R_w = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$. Least-squares refinements were based on the minimization of $\Sigma w||F_o| - |F_c||^2$.
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