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Structural Diversity in the Reaction of Mono- and Disubstituted Pyrazoles with Titanium Tetrachloride. Importance of Hydrogen Bonding and Trends in *cis*/*trans* Geometry of Binary Adducts with Unidentate Ligands

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Treatment of titanium tetrachloride with 3,5-di-*tert*-butylpyrazole affords the complexes $[3,5\text{-}(C(CH_3)_3)_2C_3H_3N_2]_2[TiCl_6]$ and $(3,5\text{-}(C(CH_3)_3)_2C_3HN_2)_2TiCl_2$ in 37 and 42% yields, respectively. An analogous reaction with 3,5-dimethylpyrazole, 3-methylpyrazole, 4-bromopyrazole, and 4-iodopyrazole leads to the formation of corresponding $TiCl_4L_2$ binary adducts in 30−86% yields. Crystal structures of $[3,5\text{-}(C(CH_3)_3)_2C_3H_3N_2]_2[TiCl_6]$, $(3,5\text{-}(C(CH_3)_3)_2C_3HN_2)_2TiCl_2$, $TiCl_4(3,5\text{-}(CH_3)_2C_3H_2N_2)_2$, and $TiCl_4(4\text{-}IC_3H_3N_2)_2$ were determined. $[3,5\text{-}(C(CH_3)_3)_2C_3H_3N_2]_2[TiCl_6]$ crystallizes in the space group *C*2/*c* with $a = 18.892(4)$ Å, $b = 7.1200(10)$ Å, $c = 24.461(6)$ Å, $\beta = 103.78(2)°$, and $Z = 4$. $(3,5\text{-}(C(CH_3)_3)_2C_3HN_2)_2TiCl_2$ crystallizes in the space group $P2_1/n$ with $a = 12.283(10)$ Å, $b = 17.891(8)$ Å, $c = 12.580(6)$ Å, $\beta = 90.96(4)°$, and $Z = 4$. $TiCl_4(3,5\text{-}(CH_3)_2C_3H_2N_2)_2$ crystallizes in the space group *C*2/*c* with $a = 12.087(2)$ Å, $b = 12.922(3)$ Å, $c = 10.403(2)$ Å, $\beta = 92.08(2)°$, and $Z = 4$. $TiCl_4(4\text{-}IC_3H_3N_2)_2$ crystallizes in the space group *C*2/*c* with $a = 9.252(2)$ Å, $b = 8.660(2)$ Å, $c = 19.652(4)$ Å, $\beta = 102.14(3)°$, and $Z = 4$. An analysis of factors governing the *cis*/*trans* geometry of MCl_4L_2 (M = Ti, Zr, Hf) complexes is offered.

Introduction

Titanium tetrahalides characteristically react with Lewis bases to form binary adducts of the formula TiX_4L_2. We recently reported that adducts of titanium tetrachloride with σ-donor ligands act as single-source precursors in a chemical vapor deposition reactor to titanium nitride, titanium phosphide, and titanium disulfide thin films.[1] Many octahedral titanium(III) and titanium(IV) complexes of the composition $[TiA_4L_2]^n$ (A = molecule or ion with a Cl, Br, O, or N donor atom; L = molecule or ion with an I, Cl, F, O, or N atom; $n = -2$ to $+1$) have been studied by various spectroscopic methods and X-ray diffraction.[2−4] Despite the large number of complexes that have been characterized, the driving forces for a certain complex to adopt *cis* or *trans* geometry are still unclear. Herein we report on the reaction of titanium tetrachloride with a small range of substituted pyrazoles. X-ray crystal structures of 3,5-di-*tert*-butylpyrazolium hexachlorotitanate(IV), bis(3,5-di-*tert*-butylpyrazolato)dichlorotitanium(IV), *trans*-bis(3,5-dimethylpyrazole)tetrachlorotitanium(IV), and *cis*-bis(4-iodopyrazole)tetrachlorotitanium(IV) demonstrate that the solid state structures adopted by the complexes are extremely sensitive to the pyrazole substituents and to nitrogen−hydrogen−chlorine hydrogen bonding. In addition, an analysis of factors governing the *cis*/*trans* stereochemistry of the MCl_4L_2 (M = Ti, Zr, Hf) complexes is offered.

Results

Titanium tetrachloride reacts with 2 equiv of 3,5-di-*tert*-butylpyrazole in dichloromethane to afford the ionic complex 3,5-di-*tert*-butylpyrazolium hexachlorotitanate(IV) (**1**) and the molecular complex bis(3,5-di-*tert*-butylpyrazolato)dichlorotitanium(IV) (**2**) in 37 and 42% yields, respectively (eq 1). Complex **1** was isolated as pale yellow crystals by diffusion of hexane into the reaction solution. The complex was character-

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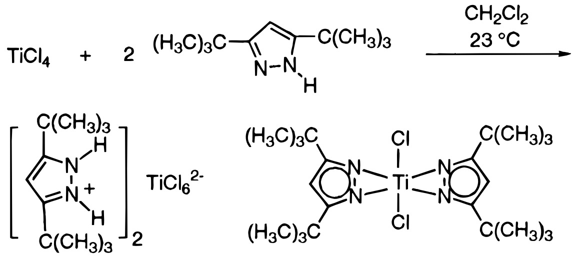
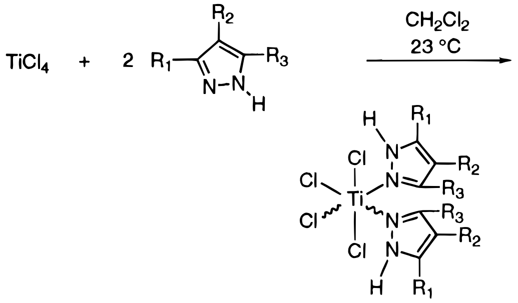


(1)

1, 37% **2**, 42%

ized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, infrared spectroscopy, microanalysis, and an X-ray crystal structure determination (vide infra). The presence of hydrogen bonding involving the nitrogen−hydrogen bonds was suggested by weak infrared stretches at 3208, 3158, and 3131 cm^{-1}. To isolate **2**, the reaction was performed in hexane, in which **1** is insoluble. Light yellow crystals of **2** separated after filtration and cooling the solution to −20 °C. The formulation of **2** was assigned on the basis of the data obtained by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, infrared spectroscopy, microanalysis, and an X-ray crystal structure determination (vide infra).

Analogous treatment of titanium tetrachloride with 2 equiv of 3,5-dimethylpyrazole, 4-iodopyrazole, 4-bromopyrazole, and 3-methylpyrazole afforded the adducts bis(3,5-dimethylpyrazole)tetrachlorotitanium(IV) (**3**, 86%), bis(4-iodopyrazole)-tetrachlorotitanium(IV) (**4**, 86%), bis(4-bromopyrazole)tetrachlorotitanium(IV) (**5**, 76%), and bis(5-methylpyrazole)tetrachlorotitanium(IV) (**6**, 30%), respectively, as orange-red crystalline solids (eq 2). The formulation of **3**−**6** as adducts rested upon microanalyses, infrared spectra, and X-ray structure determinations for **3** and **4** (vide infra). Unfortunately, **3**−**6** were insoluble in unreactive NMR solvents, which precluded solution structural analysis. The presence of hydrogen bonding involving the nitrogen−hydrogen bonds was evident by weak absorptions observed between 3100 and 3300 cm^{-1} in the infrared spectra of **3**−**6**.



(2)

3, R$_1$, R$_3$ = CH$_3$, R$_2$ = H, 86%
4, R$_1$, R$_3$ = H, R$_2$, = I, 86%
5, R$_1$, R$_3$ = H, R$_2$ = Br, 76%
6, R$_1$ = CH$_3$, R$_2$, R$_3$ = H, 30%

In order to understand the molecular geometries, the X-ray crystal structures of **1**−**4** were determined. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2−5, and perspective views are presented in Figures 1−4. Further data are available in the Supporting Information.

Complex **1** is an ionic compound consisting of a hexachlorotitanate(IV) anion and two 3,5-di-*tert*-butylpyrazolium cations. The titanium atom is situated on a crystallographic 2-fold axis, and as a result, there are only three unique titanium−chlorine bond distances, Ti−Cl(1) (2.269(2) Å), Ti−Cl(2) (2.464(2) Å), and Ti−Cl(3) (2.3070(14) Å). The environment about the titanium atom is a distorted octahedron with the *cis* chlorine−titanium−chlorine angles ranging from 85.57(6) to 94.93(9)° and the *trans* angles spanning 172.97(10) and 175.32(7)°. The hexachlorotitanate anion is bonded to the two pyrazolium cations by two pairs of hydrogen bonds: N(1)−H(1N)···Cl(2) and N(2)−H(2N)···Cl(2) with distances of 3.205 and 3.188 Å and N−H···Cl angles of 163.1 and 172.8°, respectively. Remarkably, involvement of the Cl(2) atom in both of these interionic interactions results in a significant elongation of the Ti−Cl(2) distance to 2.464(2) Å, compared to the Ti−Cl(1) and Ti−Cl(3) bonds. The Ti−Cl(2) bond length is also longer than the average titanium−chlorine distance of 2.341(9) Å found in other hexachlorotitanate(IV) ions.[4] Apparently, the increased Ti−Cl(2) bond length causes a reduction in the electron density on titanium, which enables the other chlorine atoms to approach more closely to the central metal. In related compounds **3** and **4**, hydrogen bonds of the type Ti−Cl···H−N do not lead to appreciable lengthening of the titanium−chlorine bonds. It is also possible that some of the observed lengthening of the Ti−Cl(2) bond could be due to reduced librational motion of Cl(2), which could make the Ti−Cl(2) bond distance slightly longer than the Ti−Cl(1) and Ti−Cl(3) values. However, such an effect would be small and cannot account for the 0.157−0.195 Å elongations that are observed.

The molecular structure of complex **2** is shown in Figure 2. The titanium atom possesses approximate tetrahedral geometry, if the centers of the nitrogen−nitrogen bonds in the 3,5-di-*tert*-butylpyrazolato moieties are considered as unidentate ligands. The pseudotetrahedral angles around the titanium atom span 100.5−113.3°. The titanium−chlorine bond lengths (2.247(4) and 2.251(3) Å) are typical and compare well to those in **1**. The 3,5-di-*tert*-butylpyrazolato ligands are symmetrically coordinated in an η^2-fashion, with the titanium−nitrogen distances ranging from 1.972(9) to 1.986(8) Å. These values are slightly shorter than those of the titanium−nitrogen bonds found in tetrakis(dimethylpyrazolato)titanium(IV) (average = 2.047(36) Å)[5a] and tetrakis(diphenylpyrazolato)titanium(IV) (average = 2.057(24) Å).[5a] The shorter titanium−nitrogen bonds in **2** can be rationalized by the presence of two chlorine atoms, which make the central metal more electrophilic and less crowded, relative to that in tetrakis(3,5-dimethylpyrazolato)titanium(IV).[5a] Consequently, a closer approach of the nitrogen atoms to the titanium atom in **2** ensues. The nitrogen−nitrogen distances (1.377(9) and 1.381(9) Å) and the bite angles (40.8(3) and 40.8(3)°) of the bidentate ligands in **2** are similar to the corresponding values found in pyrazolato and hydrazido complexes of titanium: 1.364(7) Å and 38.9(4)° in tetrakis(3,5-dimethylpyrazolato)titanium(IV),[5a] 1.364(4) Å and 38.69(8)° in tetrakis-(3,5-diphenylpyrazolato)titanium(IV),[5a] 1.42(1) Å and 42.6(2)° in Ti(OAr-2,6-^{i}Pr$_2$)$_2$(η^2-PhNNPh)(py)$_2$,[6a] and 1.339 Å and 39.8° in Cp$_2$Ti(η^2-PhNNPh).[6b]

Compound **3** is molecular with intermolecular hydrogen bonding. The complex adopts a distorted octahedral geometry with the two pyrazole ligands *trans* to each other. Atoms Ti(1), Cl(1), and Cl(3) occupy a crystallographic 2-fold axis, and therefore only half of the molecule is crystallographically independent. The titanium−chlorine bond lengths (average = 2.288(23) Å) are typical for terminal distances. The titanium−nitrogen bond length (2.146(5) Å) compares well with other Lewis acid/base titanium/nitrogen interactions (vide infra). The *cis* angles about the titanium atom range from 85.7(2) to 94.3(2)°, while the *trans* angles span 171.5(3)−180.0°. Weak

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Table 1. Experimental Crystallographic Data for **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{22}H_{42}Cl_6N_4Ti$	$C_{22}H_{38}Cl_2N_4Ti$	$C_{10}H_{16}Cl_4N_4Ti$	$C_6H_6Cl_4N_4I_2Ti$
fw	623.20	477.36	381.97	577.65
space group	*C*2/*c*	P2$_1$/n	*C*2/*c*	*C*2/*c*
a (Å)	18.892(4)	12.283(10)	12.087(2)	9.252(2)
b (Å)	7.1200(10)	17.891(8)	12.922(3)	8.660(2)
c (Å)	24.461(6)	12.580(6)	10.403(2)	19.652(4)
β (deg)	103.78(2)	90.96(4)	92.08(3)	102.14(3)
V (Å^3)	3195.6(11)	2764(3)	1623.8(6)	1539.4(6)
Z	4	4	4	4
T (K)	295(2)	295(2)	295(2)	170(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.295	1.147	1.562	2.492
μ (mm^{-1})	0.787	0.517	1.176	5.245
T(max)/T(min)	0.784/0.629	n/a	0.810/0.622	0.631/0.424
$R(F)$ (%)[a]	5.82	8.82	7.34	6.50
$R(wF^2)$ (%)[a]	13.51	16.82	13.73	15.12

[a] Quantity minimized: $R(wF^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]\}^{1/2}$. $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$; $I > 2\sigma(I)$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Ti(1)−Cl(3)	2.269(2)	Ti(1)−Cl(2)	2.464(2)
Ti(1)−Cl(1)	2.3070(14)		
Cl(3)−Ti(1)−Cl(3)#1	94.93(9)	Cl(3)#1−Ti(1)−Cl(2)#1	175.32(7)
Cl(3)−Ti(1)−Cl(1)	92.52(6)	Cl(1)−Ti(1)−Cl(2)#1	87.52(6)
Cl(3)#1−Ti(1)−Cl(1)	92.23(6)	Cl(3)−Ti(1)−Cl(2)	175.33(6)
Cl(1)−Ti(1)−Cl(1)#1	172.97(10)	Cl(1)−Ti(1)−Cl(2)	87.32(6)
Cl(3)−Ti(1)−Cl(2)#1	89.75(5)	Cl(2)#1−Ti(1)−Cl(2)	85.57(7)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Ti−N(4)	1.972(9)	Ti−Cl(1)	2.247(4)
Ti−N(1)	1.977(8)	Ti−Cl(2)	2.251(3)
Ti−N(3)	1.981(8)	N(1)−N(2)	1.381(9)
Ti−N(2)	1.986(8)	N(3)−N(4)	1.377(9)
N(4)−Ti−N(3)	40.8(3)	N(4)−Ti−Cl(2)	98.7(2)
N(1)−Ti−N(2)	40.8(3)	N(1)−Ti−Cl(2)	135.2(2)
N(4)−Ti−Cl(1)	136.0(2)	N(3)−Ti−Cl(2)	110.6(2)
N(1)−Ti−Cl(1)	96.9(2)	N(2)−Ti−Cl(2)	94.6(2)
N(3)−Ti−Cl(1)	95.3(2)	Cl(1)−Ti−Cl(2)	100.5(2)
N(2)−Ti−Cl(1)	113.3(2)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**

Ti−N(1)	2.146(5)	Ti−Cl(2)	2.297(2)
Ti−Cl(3)	2.254(3)	Ti−Cl(1)	2.303(3)
N(1)−Ti−N(1)#1	171.5(3)	Cl(2)−Ti−Cl(2)#1	179.9(2)
N(1)−Ti−Cl(3)	94.3(2)	N(1)−Ti−Cl(1)	85.7(2)
N(1)−Ti−Cl(2)	88.07(14)	Cl(3)−Ti−Cl(1)	180.0
N(1)#1−Ti−Cl(2)	91.92(14)	Cl(2)−Ti−Cl(1)	89.96(8)
Cl(3)−Ti−Cl(2)	90.04(8)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4**

Ti−N(1)	2.235(7)	Ti−Cl(2)	2.280(2)
Ti−Cl(1)	2.265(2)	I-C(2)	2.048(9)
N(1)#1−Ti−N(1)	83.4(4)	N(1)−Ti−Cl(2)	85.8(2)
N(1)−Ti−Cl(1)#1	172.4(2)	Cl(1)#1−Ti−Cl(2)	95.23(9)
N(1)−Ti−Cl(1)	89.1(2)	Cl(1)−Ti−Cl(2)	92.88(9)
Cl(1)#1−Ti−Cl(1)	98.32(14)	Cl(2)−Ti−Cl(2)#1	167.6(2)
N(1)#1−Ti−Cl(2)	84.9(2)		

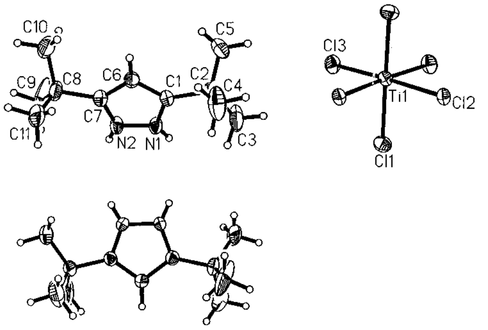

Figure 1. Perspective view of $[3,5\text{-}(C(CH_3)_3)_2C_3H_3N_2]_2[TiCl_6]$ (**1**) with thermal ellipsoids at the 30% probability level.

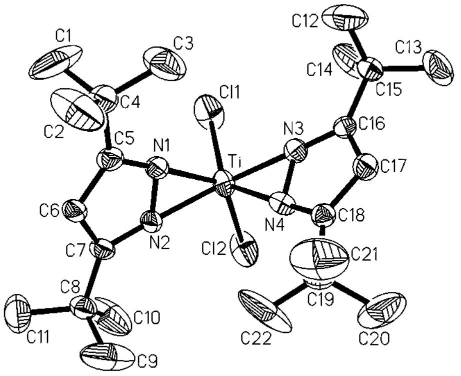

Figure 2. Perspective view of $(3,5\text{-}(C(CH_3)_3)_2C_3H_3N_2)_2TiCl_2$ (**2**) with thermal ellipsoids at the 30% probability level.

hydrogen bonding occurs in N(2)−H(2)···Cl(2) with a nitrogen−chlorine distance of 3.479 Å and nitrogen−hydrogen−chlorine angle of 154.6°.

Adduct **4** is molecular with *cis* pyrazole ligands. The coordination sphere exhibits significant deviations from ideal octahedral geometry, with the *cis* angles ranging from 83.4(4) to 98.32(14)°, while the *trans* angles span 167.6(2)−172.4(2)°. The titanium−chlorine distances (2.265(2) and 2.280(2) Å) are typical, but the titanium−nitrogen bond (2.235(7) Å) is substantially longer than that of **2** and related compounds. An intermolecular hydrogen bond occurs in N(2)−H(2)···Cl(1), with a nitrogen−chlorine distance of 3.514 Å and nitrogen−hydrogen−chlorine angle of 145.4°.

Hydrogen bonding detected in adducts **1**, **3**, and **4** is probably responsible for the observed distortion of the titanium atom environment from ideal octahedral geometry. Complex **1** contains one titanium−chlorine bond (Ti−Cl(2)) which is 0.157−0.195 Å longer than the other titanium−chlorine distances. A unit cell diagram emphasizing close nitrogen−chlorine contacts is shown in Figure 5. Since there is not a strong π-donor group *trans* to the elongated bond, the observed phenomenon can be explained by the formation of two hydrogen bonds with the Cl(2) atom. Hexachlorotitanate(IV) anions found in $[AsPh_4]_2TiCl_6\cdot 2CH_2Cl_2$,[4a] $[CH_3Ph_3P]_2TiCl_6$,[4b] $[(15\text{-crown-}5)Mg(CH_3CN)_2]TiCl_6$,[4c] and $[C_{16}H_{18}NO_2]_2TiCl_6\cdot 2C_6H_6$,[4d,e] in which hydrogen bonding is not possible, are far less distorted.

Figures 6 and 7 show intermolecular hydrogen bonding that occurs between the nitrogen−hydrogen bonds and a chlorine atom in an adjacent molecule in **3** and **4**. The nitrogen−chlorine distances in **3** (N(2)−Cl(2) 3.479 Å) and **4** (N(2)−Cl(1) 3.514

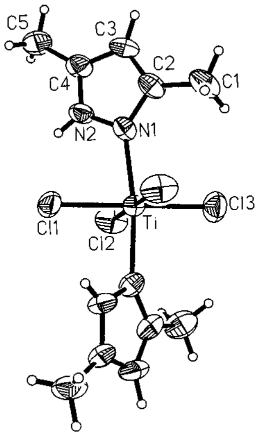

Figure 3. Perspective view of $TiCl_4(3,5\text{-}(CH_3)_2C_3H_2N_2)_2$ (**3**) with thermal ellipsoids at the 30% probability level.

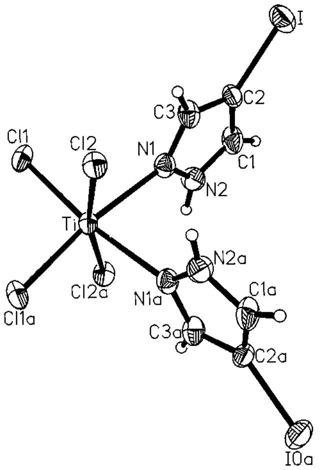

Figure 4. Perspective view of $TiCl_4(4\text{-}IC_3H_2N_2)_2$ (**4**) with thermal ellipsoids at the 30% probability level.

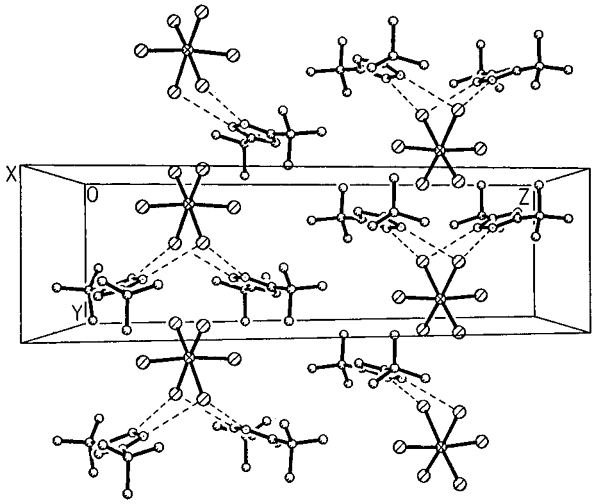

Figure 5. Unit cell view of **1** along the *a* axis, emphasizing the nitrogen–hydrogen–chlorine hydrogen bonding interactions.

Å) are longer than those in **1**, suggesting much weaker hydrogen bonds. However **3**–**6**, once crystallized, become insoluble in common organic solvents. Such insolubility appears to be due to hydrogen bonding, which creates an extended network. Unexpectedly, the titanium–nitrogen bond in *trans* complex **3** is 0.089 Å shorter than that in *cis* adduct **4**. In neither of these complexes does hydrogen bonding result in appreciable lengthening of bond distances between the titanium atom and hydrogen-bonded chlorine atom.

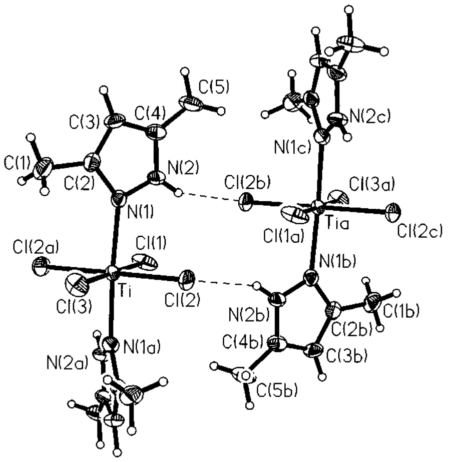

Figure 6. View of **3**, emphasizing the nitrogen–hydrogen–chlorine hydrogen bonding interactions. Thermal ellipsoids are at the 30% probability level.

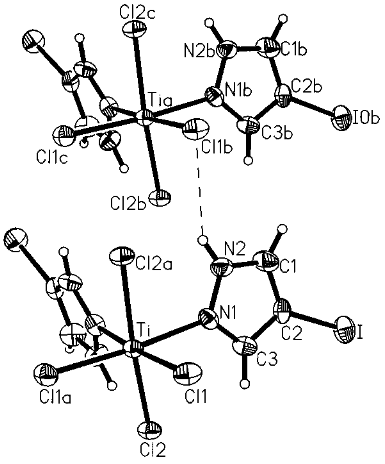

Figure 7. View of **4**, emphasizing the nitrogen–hydrogen–chlorine hydrogen bonding interactions. Thermal ellipsoids are at the 30% probability level.

Discussion

Several models have been proposed in the literature to explain trends in *cis*/*trans* geometry of octahedral metal complexes of the formula TiA_4B_2.[2g,7–10] Furthermore, *cis*–*trans* isomerization for titanium tetrachloride adducts of tetrahydrofuran (THF), tetramethylphosphorodiamidic chloride, and trimethylphosphine oxide has been observed[10] and the structures of both *cis*- and *trans*-$TiCl_4(THF)_2$ have been reported.[2d,e] In the following paragraphs, we rationalize the geometries observed in **1**–**4** and compare these results with related structures from the literature.

The adduct **4** crystallizes in the *cis* configuration with 4-iodopyrazole ligands. It is well-known that 3-substituted pyrazoles are in dynamic equilibrium with the 5-substituted tautomers (Scheme 1).[11] The latter should be preferred during crystallization, since it yields the less sterically encumbered adduct. With two substituents on the pyrazole ring, the steric demand in the titanium coordination sphere increases and crystallization of the *trans* adduct becomes preferred, as observed for the 3,5-dimethylpyrazole adduct **3**. Having taken the aforementioned rationales into account, we tentatively assign

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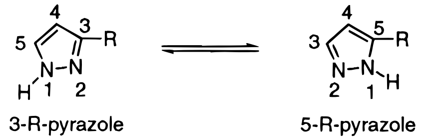
Table 6. Relevant Structural Information for Octahedral Complexes of Titanium and Hafnium[a]

complex	A	L	Ti−A (Å)	T−L (Å)	Ti−L/Ti−A	*cis*/*trans*	ref
$TiCl_4(OAsPh_3)_2$	Cl	$OAsPh_3$	2.352(23)	1.895(5)	0.81	*trans*	2a
$TiCl_4(OPPh_3)_2$	Cl	$OPPh_3$	2.342(2)	1.923(3)	0.82	*trans*	1c
$TiCl_4(OP(NMe_2)_3)_2$	Cl	$OP(NMe_2)_3$	2.328(7)	1.945(3)	0.84	*trans*	2b
$[TiCl_4(N_3)_2]^{2-}$	Cl	N_3	2.352(10)	2.006(9)	0.85	*trans*	2c
$TiCl_4(THF)_2$	Cl	THF	2.395(9)	2.099(23)	0.88	*trans*	2d
$TiCl_4(THF)_2$	Cl	THF	2.293(2)	2.050(4)	0.89	*trans*	2e
$TiCl_4(PhCOOEt)_2$	Cl	PhCOOEt	2.261(41)	2.058(18)	0.91	*cis*	2f
$[TiCl_4(py)_2]^-$	Cl	py	2.405(3)	2.21(1)	0.92	*trans*	2g
$TiCl_4(DMP)_2$	Cl	DMP	2.288(23)	2.146(5)	0.94	*trans*	this work
$TiCl_4(THF)_2$	Cl	THF	2.265(23)	2.117(3)	0.94	*cis*	2e
$TiCl_4(Et_2O)_2$	Cl	Et_2O	2.269(16)	2.139(27)	0.94	*cis*	2g
$TiCl_4(Et_2O)_2$	Cl	Et_2O	2.249(35)	2.087(44)	0.94	*cis*	2h
$TiCl_4(py)_2$	Cl	py	2.290(4)	2.20(1)	0.96	*trans*	2i
$TiCl_4(CH_3CN)_2$	Cl	CH_3CN	2.240(29)	2.208(33)	0.97	*cis*	2j
$TiCl_4(4\text{-}Ipz)_2$	Cl	4-Ipz	2.273(11)	2.235(7)	0.98	*cis*	this work
$TiCl_4(R_1CN)$	Cl	R_2CN	2.244(23)	2.188(1)	0.98	*cis*	2k
$TiCl_4(HCN)_2$	Cl	HCN	2.254(49)	2.198(7)	0.98	*cis*	2l
$TiCl_4(R_2CN)$	Cl	R_1CN	2.241(43)	2.212(10)	0.99	*cis*	2m
$TiCl_4(SC_4H_8)_2$	Cl	SC_4H_8	2.256(27)	2.626(71)	1.16	*cis*	1e
$TiCl_4(HSC_6H_{12})_2$	Cl	HSC_6H_{12}	2.253(36)	2.655(12)	1.18	*cis*	1d
$TiBr_4(CH_3CN)_2$	Br	CH_3CN	2.418(48)	2.199	0.91	*cis*	2n
$[Ti(MeCN)_4Cl_2]^+$	MeCN	Cl^-	2.140(26)	2.280(13)	1.07	*trans*	2o
$[Ti(py)_4I_2]^+$	py	I^-	2.218(10)	2.747(1)	1.24	*trans*	2g
$[Ti(MeCN)_4I_2]^+$	MeCN	I^-	2.145	2.68(1)	1.25	*trans*	2p
$[Ti(H_2O)_4F_2]^+$	H_2O	F	2.087(12)	1.879(74)	0.90	*trans*	2q
$[Ti(THF)_4Cl_2]^+$	THF	Cl	2.096(42)	2.332	1.11	*cis*	2r
$[Ti(HOR_3)_4Cl_2]^+$	HOR_4	Cl	2.097(10)	2.325	1.11	*cis*	2s
$[Ti(THF)_4Cl_2]^+$	THF	Cl	2.080(16)	2.360(1)	1.14	*cis*	2t
$Ti(OR_4)_4(MeCN)_2$	OR_3	MeCN	1.845	2.235	1.21	*cis*	2u
$HfCl_4(THF)_2$	Cl	THF	2.444(4)	2.052(8)	0.84	*cis*	2a

[a] $R_1 = NC(CH_2)_3$; $R_2 = ((CH_3)_3Si)_2N(C_6H_4)$; R_3 = isopropyl; $OR_4 = OCH(CF_3)_2$; DMP = 3,5-dimethylpyrazole.

Scheme 1. Tautomerism of 3- and 5-Substituted Pyrazoles



the *cis* geometries to bis(4-bromopyrazole)tetrachlorotitanium(IV) (**5**) and bis(5-methylpyrazole)tetrachlorotitanium(IV) (**6**) with 5-substituted pyrazole ligands.

A substantial increase in the bulkiness of the substituents at the 3- and 5-positions (e.g., with 3,5-di-*tert*-butylpyrazole) prevents the pyrazole ligand from coordinating to the titanium atom via its nitrogen atoms. Instead, the ionic complex **1** and molecular complex **2** result. It should be noted that η^2-pyrazolato coordination by d-block metals is extremely rare and **2** is an accordingly significant molecule. We recently described several examples of η^2-pyrazolato ligand coordination in early transition metal complexes and have carried out molecular orbital calculations to understand the bonding.[5] We also note in passing that **2** bears a strong resemblance to titanocene dichloride, but is chiral. Derivatives of **2** may be useful as catalysts in olefin polymerization and organic derivatization schemes.

A comparison of the structural features of **3** and **4** with those of related adducts is given in Table 6. For complexes with titanium−ligand bond lengths above 2.05 Å, both *cis* and *trans* configurations are observed. However, when the titanium−ligand bond length is less than 2.05 Å, only the *trans* configuration is found. Strong π-donor ligands tend to form shorter bonds to titanium, since there are increased bonding interactions relative to a saturated donor analog (e.g., pyridine versus trimethylamine). While the titanium−ligand distances do not furnish information on the relative stability of the adducts, they do reflect comparative π-donor properties of different molecules and ions, provided that the radii of different donor atoms are taken into consideration.

Nitrogen−hydrogen−chlorine hydrogen bonding is a prominent feature in the structures of **1**, **3**, and **4**. In **3** and **4**, these interactions are weak, as evidenced by the long nitrogen−chlorine distances. The hydrogen bonding does not have a significant effect on the bond lengths in **3** and **4** and is probably not a factor in the adoption of *cis* versus *trans* geometries. The weak interactions probably help to orient the molecules during crystallization and lead to the lowest energy packing. In **1**, nitrogen−hydrogen−chlorine hydrogen bonding is substantially stronger than that it is in **3** and **4** and leads to observable elongations of the titanium−chlorine bonds involved in the hydrogen bonding. The greater effect of hydrogen bonding in **1**, relative to **3** and **4**, is likely a result of having more polar interactions due to the cationic pyrazolium hydrogen bond donors and the hexachlorotitanate(IV) acceptor.

Finally, it is surprising that the small range of pyrazoles examined in this study provides such a broad array of structures upon interaction with titanium tetrachloride. The steric bulk of the pyrazole, as measured both by the substituent size (*tert*-butyl versus methyl) and by position (3,5 versus 4), is an important factor in determining the product(s) upon reaction with titanium tetrachloride. In **3** and **4**, the steric profile of the pyrazole ligands seems to dictate the adoption of *cis* or *trans* geometries. The other structure determinant is nitrogen−hydrogen−chlorine hydrogen bonding. Hydrogen bonding appears to be a major driving force for the formation of **1**, while in **3** and **4** it is a significant force in molecular packing but probably does not contribute to adoption of *cis* or *trans* geometries.

Experimental Section

General Considerations. All manipulations were performed under argon using either drybox or Schlenk-line techniques. Hexane and diethyl ether were distilled over sodium. All NMR solvents were dried over 4-Å molecular sieves. Dichloromethane was distilled from calcium hydride. 3,5-Dimethylpyrazole, 3-methylpyrazole, 4-methylpyrazole, 4-bromopyrazole, 4-iodopyrazole, and titanium tetrachloride were purchased (Aldrich Chemical Co. or Acros Organics) and used as received. 3,5-Di-*tert*-butylpyrazole was prepared according to a published procedure.[12]

^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained at 300 and 75 MHz, respectively, in chloroform-*d*. Infrared spectra were recorded using Nujol or Fluorolube mulls. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points are uncorrected.

Preparation of 3,5-Di-*tert*-butylpyrazolium Hexachlorotitanate(IV) (1). A 50-mL Schlenk flask was charged with titanium tetrachloride (0.310 mL, 2.82 mmol), 3,5-di-*tert*-butylpyrazole (2.032 g, 11.29 mmol), dichloromethane (20 mL), and a stir bar and was fitted with a rubber septum. After being stirred for 2 h, the dichloromethane solution was layered with hexane (ca. 50 mL), and the system was allowed to equilibrate for 24 h. The solvent was decanted, and the flask contents were vacuum dried to afford **1** as light yellow crystals (0.325 g, 37%): mp 221 °C dec; IR (Nujol, cm^{-1}) 3208 (w), 3158 (w), 3131 (w), 1601 (w), 1518 (w), 1337 (w), 1262 (w), 1250 (w), 1204 (w), 1181 (w), 984 (w), 807 (w); ^{1}H NMR (CDCl$_3$, 22 °C, δ) 12.76 (broad s, N***H***), 6.82 (s, ring C***H***), 1.27 (s, 2 C(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 22 °C, ppm) 158.18 (s, ***C***C(CH$_3$)$_3$), 100.33 (s, ring ***C***H), 31.85 (2 ***C***(CH$_3$)$_3$), 29.42 (2 C(***C***H$_3$)$_3$).

Anal. Calcd for $C_{22}H_{42}Cl_6N_4Ti$: C, 42.40; H, 6.79; N, 8.99. Found: C, 41.75; H, 6.54; N, 8.97.

Preparation of Bis(3,5-di-*tert*-butylpyrazolato)dichlorotitanium(IV) (2). A 50-mL Schlenk flask was charged with titanium tetrachloride (0.310 g, 2.82 mmol), 3,5-di-*tert*-butylpyrazole (2.032 g, 11.29 mmol), hexanes (20 mL), and a stir bar and was fitted with a rubber septum. After being stirred for 2 h, the solution was filtered, and the filtrate was cooled to −20 °C to afford **2** as light yellow crystals (0.283 g, 42%): mp 157 °C; IR (Nujol, cm^{-1}) 3230 (w), 3119 (w), 1734 (w), 1717 (w), 1700 (w), 1684 (w), 1653 (w), 1636 (w), 1597 (w), 1559 (w), 1541 (w), 1509 (m), 1485 (w), 1438 (m), 1367 (m), 1283 (w), 1253 (m), 1234 (m), 1204 (w), 1127 (w), 1019 (w), 1004 (w), 992 (w), 975 (w), 840 (m), 806 (w); ^{1}H NMR (CDCl$_3$, 22 °C, δ) 6.68 (s, ring C***H***), 1.29 (s, 2 C(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 22 °C, ppm)) 161.08 (s, ***C***C(CH$_3$)$_3$), 114.60 (s, ring ***C***H), 32.53 (2 ***C***(CH$_3$)$_3$), 30.18 (2 C(***C***H$_3$)$_3$).

Anal. Calcd for $C_{22}H_{38}Cl_2N_4Ti$: C, 55.35; H, 8.02; N, 11.74. Found: C, 56.81; H, 8.26; N, 12.22.

Preparation of *trans*-Bis(3,5-dimethylpyrazole)tetrachlorotitanium(IV) (3). A 50-mL Schlenk flask was charged with titanium tetrachloride (0.310 mL, 2.82 mmol), 3,5-dimethylpyrazole (0.542 g, 5.64 mmol), dichloromethane (20 mL), and a stir bar and was fitted with a rubber septum. After being stirred for 2 h, the dichloromethane solution was layered with diethyl ether (ca. 50 mL), and the system was allowed to equilibrate for 24 h. The solvent was decanted, and the flask contents were vacuum-dried to afford **3** as red crystals (0.927 g, 86%): mp 252 °C dec; IR (Nujol, cm^{-1}) 3233 (w), 3246 (w), 3204 (w), 3105 (w), 3035 (w), 2788 (b), 2711 (s, b), 2647 (s, b), 2520 (b), 1598 (m), 1570 (s), 1524 (w), 1351 (s), 1308 (m), 1281 (s), 1154 (m), 1048 (s), 1013 (s), 1010 (w), 971 (w), 851 (m), 788 (m), 773 (m), 738 (w), 717 (w), 689 (m, b), 661 (m), 647 (m).

Anal. Calcd for $C_{10}H_{16}Cl_4N_4Ti$: C, 31.44; H, 4.22; N, 14.67. Found: C, 31.40; H, 4.14; N, 14.21.

Preparation of *cis*-Bis(4-iodopyrazole)tetrachlorotitanium(IV) (4). To a hexane solution (30 mL) of 4-iodopyrazole (0.177 g, 0.91 mmol) was added titanium tetrachloride (0.050 mL, 0.46 mmol). Insoluble orange-red crystals (227 g, 86%) precipitated over 24 h: mp 229 °C dec; IR (Nujol, cm^{-1}) 3410 (w), 3318 (s), 3137 (m), 3128 (m), 1662 (w), 1509 (w), 1463 (m), 1375 (s), 1321 (m), 1053 (s), 1026 (m), 971 (s), 941 (s), 903 (s), 871 (m), 832 (m), 793 (w), 747 (m), 738 (m), 719 (m), 696 (m), 673 (s), 650 (s), 589 (s).

Anal. Calcd for $C_6H_6Cl_4I_2N_4Ti$: C, 12.48; H, 1.05; N, 9.70. Found: C, 12.68; H, 0.99; N, 9.66.

Preparation of *cis*-Bis(4-bromopyrazole)tetrachlorotitanium(IV) (5). In a fashion similar to the preparation of **3**, titanium tetrachloride (0.310 mL, 2.82 mmol) reacted with 4-bromopyrazole (0.829 g, 5.64 mmol) to afford **5** as a red powder (1.037 g, 76%): mp 210 °C dec; IR (Nujol, cm^{-1}) 3400 (w), 3308 (m), 3125 (m), 1661 (w), 1522 (w), 1470 (m), 1384 (m), 1327 (m), 1052 (m), 1024 (w), 971 (s), 952 (s), 903 (s), 876 (w), 836 (w), 741 (w), 683 (m), 666 (m), 649 (m), 594 (s), 587 (s).

Anal. Calcd for $C_6H_6Br_2Cl_4N_4Ti$: C, 14.90; H, 1.25; N, 11.58. Found: C, 15.02; H, 1.23; N, 11.38.

Preparation of *cis*-Bis(3-methylpyrazole)tetrachlorotitanium(IV) (6). In a fashion similar to the preparation of **3**, titanium tetrachloride (0.310 mL, 2.82 mmol) reacted with 3-methylpyrazole (0.462 g, 5.64 mmol) to afford **6** as a pale yellow powder (0.300 g, 30%): mp 248 °C dec; IR (Nujol, cm^{-1}) 3353 (s), 2964 (w), 2928 (w), 2853 (w), 1560 (m), 1538 (w), 1504 (w), 1489 (w), 1437 (w), 1419 (w), 1506 (w), 1382 (w), 1333 (w), 1322 (w), 1288 (m), 1262 (m), 1059 (m), 1041 (w), 1017 (w), 968 (s), 958 (s), 900 (m), 794 (m), 788 (m), 658 (m).

Anal. Calcd for $C_8H_{12}Cl_4N_4Ti$: C, 27.15; H, 3.24; N, 15.83. Found: C, 27.41; H, 3.67; N, 16.07.

Crystallography. The single-crystal X-ray diffraction experiments were performed on a Siemens P4 diffractometer for **1**, **3**, and **4** and on a Siemens P4/CCD diffractometer for **2**. The crystals were mounted in thin-walled capillaries in a drybox under an atmosphere of nitrogen.

The unit cell parameters for **1**, **3**, and **4** were obtained by the least-squares refinement of the angular settings of 36, 34, and 39 reflections, respectively. The data were corrected for Lorentz and polarization effects as well as for absorption. The absorption correction data were collected by the ψ-scan technique. In the case of **2**, 112 reflections with $I > 20\sigma(I)$ from 60 frames of 0.3° ω-scan data were used in the initial cell refinement. The systematic absences in the diffraction data were consistent with the reported space groups. For **1**, **3**, and **4** either of the monoclinic space groups *Cc* and *C*2/*c* was indicated; the latter was preferred on the basis of the chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. The Ti atoms in for **1**, **3**, and **4** resided on crystallographic 2-fold axes. Despite several recrystallizations, the crystals of **2** were of low quality, and only 1.03 Å resolution data were obtained.

All software and sources of the scattering factors are contained in the SHELXTL (version 5.0.3) program library[13] Siemens XRD, Madison, WI).

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Supporting Information Available: Tables S1−S20, listing full experimental details for data collection and refinement, atomic coordinates, bond distances and angles, and thermal parameters for **1**−**4** (14 pages). Ordering information is given on any current masthead page.

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