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Imido Complexes of Titanium Bearing η^2-Pyrazolato Ancillary Ligand Sets

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Treatment of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) with Grignard (CH_3MgCl, $C_6H_5CH_2MgCl$) or organolithium ($LiCH_2Si(CH_3)_3$) reagents (2 equiv) afforded the dialkyl derivatives dimethylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (93%), dibenzylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (43%), and bis(methyltrimethylsilyl)bis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (49%). Analogous methylation of chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) with CH_3MgCl afforded methyltris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (52%). Attempted alkylation of trichloro(3,5-di-*tert*-butylpyrazolato)titanium(IV) with CH_3MgCl (3 equiv) afforded dimethylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (35%), along with extensive decomposition. This experiment indicates that trimethyl(3,5-di-*tert*-butylpyrazolato)titanium(IV) is unstable at ambient temperature. The reactivity of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) and dimethylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) toward primary amines was studied. Treatment of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) with excess *tert*-butylamine afforded *tert*-butylimido(chloro)(3,5-di-*tert*-butylpyrazolato)titanium(IV) dimer (10%), chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (56%), and *tert*-butylammonium chloride (85%). Analogous treatment of dimethylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) with *tert*-butylamine gave the monomeric imido complex *tert*-butylimidobis(3,5-di-*tert*-butylpyrazolato)(*tert*-butylamine)titanium(IV) (33%). Addition of pyridine to the reaction between dimethylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) and *tert*-butylamine or isopropylamine afforded the pyridine adducts *tert*-butylimidobis(3,5-di-*tert*-butylpyrazolato)(pyridine)titanium(IV) (80%) and isopropylimidobis(3,5-di-*tert*-butylpyrazolato)(*tert*-butylamine)titanium(IV) (46%), respectively. Treatment of dimethylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) with 1-amino-4-methylpiperazine led to the hydrazide(1−) complex 1-amido-4-methylpiperazine(methyl)bis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (64%), which contains both a titanium−methyl bond and a primary hydrazide(1−) ligand. It is proposed that the thermal stability of this compound arises from bidentate coordination of the hydrazide(1−) ligand, which places the reactive nitrogen−hydrogen bond distal to the titanium−methyl bond. The reactivity of *tert*-butylimidobis(3,5-di-*tert*-butylpyrazolato)(*tert*-butylamine)titanium(IV) toward acetylenes, nitriles, and ketones is discussed. The X-ray crystal structures of bis(methyltrimethylsilyl)bis(3,5-di-*tert*-butyl-pyrazolato)titanium(IV), *tert*-butylimido(chloro)(3,5-di-*tert*-butylpyrazolato)titanium(IV) dimer, and isopropylimidobis(3,5-di-*tert*-butylpyrazolato)(*tert*-butylamine)titanium(IV) were determined.

Introduction

We have recently described the synthesis, structure, and properties of a series of early transition metal complexes that contain η^2-pyrazolato ligands.[1−5] Prior to our reports, the only structurally characterized d-block metal complex bearing a η^2-pyrazolato ligand was $[Cp_2Zr(C_3H_3N_2)(THF)]BPh_4\cdot(THF)_{0.5}$.[6] While extensive research has established that mid to late transition metal complexes exhibit either bridging or η^1-pyrazolato ligand coordination modes,[7] the analogous situation with the early transition metals has not received enough attention to make general statements. Our work and the result of Erker[6] suggested that η^2-pyrazolato ligands might be common among the early transition metals. Since there has been considerable recent interest in the development of new ancillary ligand sets for reactive early transition metal complexes,[8−11] we wondered if the η^2-pyrazolato ligand would be sufficiently stable to serve as a spectator ligand. The η^2-pyrazolato coordination

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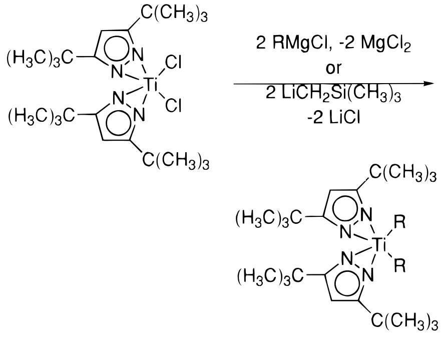
mode would be most desirable for such applications, since reactions involving the basic nitrogen lone pairs of electrons associated with η^1-structures would be eliminated or attenuated. Moreover, bridging pyrazolato ligands could lead to intractable or poorly soluble oligomeric complexes. We recently demonstrated that titanium complexes bearing both chloride and η^2-pyrazolato ligands have significant structural and chemical analogy with cyclopentadienyltitanium trichloride and titanocene dichloride.[4] Titanium complexes bearing cyclopentadienyl ligands are widely used in many reactive systems,[12] and it seemed possible that titanium complexes bearing η^2-pyrazolato ligands might serve in similar roles.

Herein we describe the synthesis, structure, and reactivity of complexes that contain the bis(η^2-3,5-di-*tert*-butylpyrazolato)titanium(IV) structural fragment. The starting material for this chemistry, dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV),[3,4] is easily prepared in high yield and can be alkylated with organolithium or organomagnesium reagents to afford the dialkyl derivatives in moderate to high yields. There is no evidence for side reactions that involve the pyrazolato ligands. Monomeric and dimeric imido complexes result upon treatment of the dichloro or dialkyl complexes with primary alkylamines. The reactivity of the monomeric imido complexes toward unsaturated organic molecules is presented. Finally, the crystal structures of representative complexes are described. The combined results suggest that η^2-pyrazolato ligands are stable during several types of reactions that occur at the titanium center and may therefore find utility as new ancillary ligands for early transition metal complexes.

Results

Synthesis of Alkyl Derivatives. Treatment of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV)[3,4] with 2 equiv of methylmagnesium chloride, benzylmagnesium chloride, or methyltrimethylsilyllithium afforded dimethylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (**1**, 93%), dibenzylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (**2**, 43%), and bis(methyltrimethylsilyl)bis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (**3**, 49%), respectively, as yellow (**1**, **3**) or red (**2**) crystalline solids (eq 1).



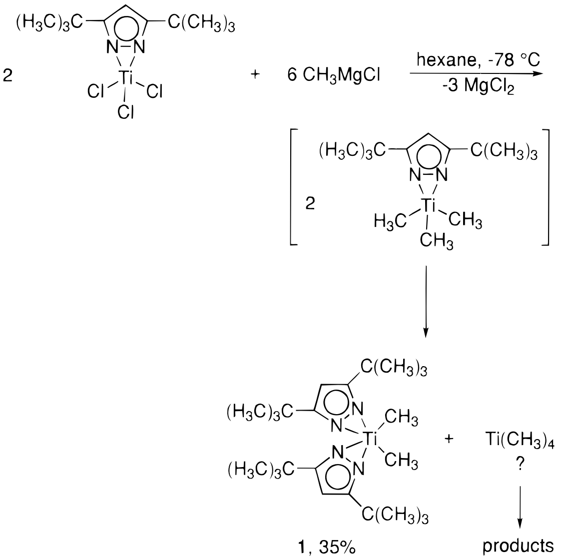
(1)

1, R = CH_3, 93%
2, R = $CH_2C_6H_5$, 43%
3, R = $CH_2Si(CH_3)_3$, 49%

Compounds **1**−**3** are air sensitive in solution and in the solid state, but are stable at ambient temperature for at least weeks under argon. A benzene-d_6 solution of **1** did not show any changes in its ^{1}H NMR spectrum after heating at 70 °C for 48 h. Structures of **1**−**3** were assigned by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, infrared spectroscopy, microanalysis, and an X-ray structure determination for **3** (vide infra).

Similar reactions of chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) and trichloro(3,5-di-*tert*-butylpyrazolato)titanium(IV) with methylmagnesium chloride were also studied (eqs 2, 3). In the first case (eq 2),

$$(tBu_2pz)_3TiCl + CH_3MgCl \xrightarrow[\text{-}MgCl_2]{\text{hexane, 0 °C}} \underset{\mathbf{4},\ 52\%}{(tBu_2pz)_3TiCH_3} \qquad (2)$$



(3)

methyltris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (**4**, 52%) was obtained as yellow crystals after crystallization from hexane. However, the reaction of trichloro(3,5-di-*tert*-butylpyrazolato)titanium(IV) with methylmagnesium chloride (3 equiv) was more complicated (eq

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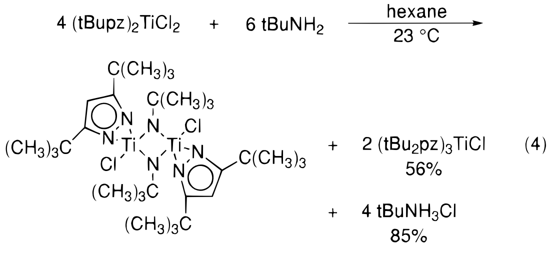
3). A yellow suspension immediately resulted when the reagents were mixed at −78 °C. However, upon warming to ambient temperature, the solution gradually turned to a black color. Workup afforded **1** in 35% yield as the sole tractable product. This result implies that trimethyl(3,5-di-*tert*-butylpyrazolato)titanium(IV) is unstable at or near room temperature. A possible route to the formation of **1** involves a redistribution reaction of trimethyl(3,5-di-*tert*-butylpyrazolato)titanium(IV) to afford **1** and tetramethyltitanium. Tetramethyltitanium is known to be thermally unstable and decomposes near −78 °C to metallic titanium and other products in the absence of donor ligands.[13] Due to the low-yield formation of **1**, the preparation of trimethyl(3,5-di-*tert*-butylpyrazolato)titanium(IV) was not pursued further.

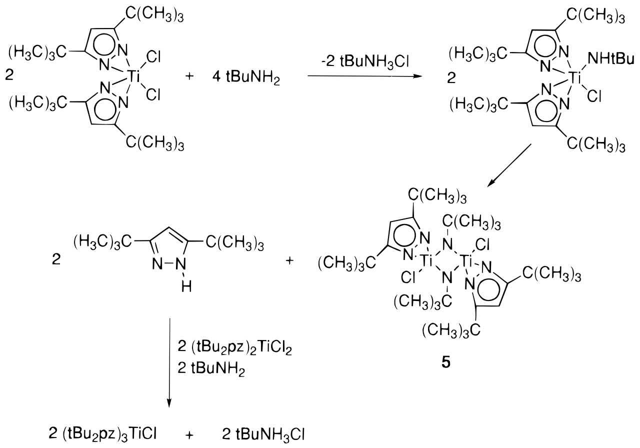
Reactivity of Bis(3,5-di-*tert*-butylpyrazolato)titanium(IV) Derivatives with Primary Amines. The reactivity of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) with *tert*-butylamine was examined as a route to a complex bearing *tert*-butylimido ligands (eq 4). When the reaction was run in hexane at ambient temperature for 16 h, the hexane solution gradually took on a deep orange coloration and a fine white precipitate formed. Upon workup, the white precipitate was determined to be *tert*-butylammonium chloride (85% of theory) by comparison of its ^{1}H and ^{13}C{^{1}H} NMR spectra with those of authentic material. A pale orange powder was obtained after decanting the hexane layer from the *tert*-butylammonium chloride and removing the hexane under reduced pressure. Analysis of the powder by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy showed it to be a 30:70 mixture of imido complex **5** and chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV).[4,5a] Pure **5** was obtained as dark orange crystals in 10% yield by fractional crystallization. Further crystallization afforded chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) as pure yellow crystals in 56% yield. Intermediate crops of crystals were mixtures of **5** and chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV), which is why the yields were substantially reduced from the 33% and 67% theoretical values, respectively. The composition of **5** was established by a combination of spectral and analytical data and by an X-ray crystal structure determination (vide infra).



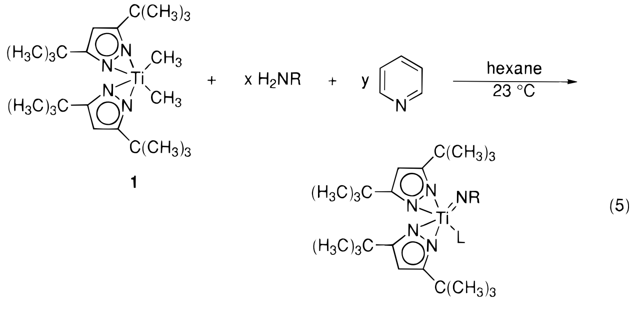
5, 10%

A reaction path that rationalizes the products is outlined in Scheme 1. Treatment of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) with *tert*-butylamine would result in the formation of a *tert*-butylamide complex along with production of *tert*-butylammonium chloride. A similar reaction occurs upon treatment of titanocene dichloride with primary amines to afford stable complexes of the formula $Cp_2Ti(NHR)(Cl)$.[14] The *tert*-butylamide complex then eliminates 3,5-di-*tert*-butylpyrazole to afford the fragment $(tBu_2pz)Ti(NtBu)(Cl)$, which dimerizes to give **5**. Finally, 3,5-di-*tert*-butylpyrazole reacts with dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) in the presence of *tert*-butylamine to afford chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) and *tert*-butylammonium chloride. We have reported that chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) can be prepared in high yield by treatment of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) with 3,5-di-*tert*-butylpyrazole using triethylamine as a base to neutralize the hydrogen chloride that is generated.[4] It is clear that *tert*-butylamine plays a role similar to that of triethylamine in the present reaction.

Scheme 1. Proposed Reaction Path



We next examined the reaction of the dimethyl derivative **1** with primary amines. Use of *tert*-butylamine led to elimination of methane (2 equiv) to afford the monomeric imido complex **6** (33%) after crystallization from hexane (eq 5). In **6**, the neutral *tert*-butylamine ligand completes the coordination sphere and stabilizes the potentially reactive terminal imido linkage. However, **6** was exceptionally soluble in hexane and was correspondingly difficult to isolate. More tractable compounds were obtained by replacing the neutral primary amine donor with a pyridine ligand. Treatment of **1** with *tert*-butylamine or isopropylamine (5 equiv) in the presence of pyridine (5 equiv) afforded the imido complexes **7** (80%) and **8** (46%) as orange solids after crystallization from hexane. The structures of **6**−**8** were



6, x = 2, y = 0, R = $C(CH_3)_3$, L = $H_2NC(CH_3)_3$
7, x = 1, y = 1, R = $C(CH_3)_3$, L = py
8, x = 1, y = 1, R = $CH(CH_3)_2$, L = py

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[13] For leading references, see: Berthold, H. J.; Groh, G. *Z. Anorg. Allg. Chem.* **1963**, *319*, 230. Thiele, K. H.; Müller, J. Z. *Z. Anorg. Allg. Chem.* **1968**, *362*, 113.

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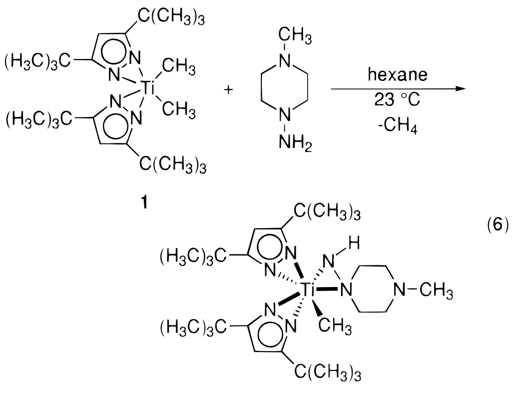
established from the spectral and analytical data and by an X-ray crystal structure determination for **8**. The ^{13}C NMR chemical shifts of the carbons attached to the imido nitrogens in **6**−**8** resonated between 65.6 and 68.74 ppm. Such chemical shifts are about 10 ppm more shielded than the related resonance associated with the bridging imido ligand in **5**. The −80 °C ^{1}H NMR spectrum of **8** showed a single resonance for the *tert*-butyl methyl groups on the pyrazolato ligands.

We next sought to prepare hydrazide(2−) complexes that would be analogous to **6**−**8** through treatment of **1** with 1,1-dialkylhydrazines. Whereas 1,1-dimethylhydrazine and 1-aminopiperidine gave intractable mixtures, 1-amino-4-methylpiperazine afforded clear yellow crystals of (1-amido-4-methylpiperazine)(methyl)bis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (**9**) in 64% yield after crystallization from hexane (eq 6). Complex **9** was characterized by spectroscopic and analytical methods. Despite several data collections, crystals of **9** were found to be of insufficient quality to allow determination of the molecular structure by crystallographic methods. The most striking feature of **9** is the presence of the titanium−methyl bond, despite the acidic hydrogen bonded to the hydrazide(1−) ligand.



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(6)

9, 64%

We propose that the hydrazide(1−) ligand in **9** adopts a bidentate coordination mode in which the nitrogen−hydrogen bond is distal to the titanium−methyl bond. Such a structure would be very similar to those of dimethylamidotris(3,5-di-*tert*-butylpyrazolato)titanium(IV)[15] and chlorotris(3,5-di-*tert*-butylpyrazolato)hafnium(IV),[4] which contain chiral, seven-coordinate metal centers with η^2-pyrazolato ligands. Complex **9** could be refluxed in toluene for 18 h without decomposition or any reaction, as determined by ^{1}H NMR spectroscopy. To probe the origins of the thermal stability, the variable-temperature NMR spectra of **9** were recorded. In the ^{1}H NMR spectrum of **9** in toluene-d_8 at 20 °C, the piperazine ring hydrogens appeared as very broad resonances centered at δ 2.75 and 2.17. At −40 °C, sharper equal intensity multiplets for the piperazine ring hydrogens were observed at δ 2.78, 2.62, 2.22, and 2.05. Below −40 °C, **9** precipitated. The ^{13}C{^{1}H} NMR spectrum in benzene-d_6 at 20 °C showed the piperazine ring carbons at 60.13 and 54.15 ppm. These values can be compared to carbon chemical shifts of 59.77 and 55.36 ppm for the ring carbons of free 1-amino-4-methylpiperazine. We suggest that the sharpening of the ring ^{1}H NMR resonances upon cooling corresponds to freezing out of a dynamic process involving a chair−chair interconversion of the piperazine ring. The ^{1}H and ^{13}C{^{1}H} NMR data for **9** demonstrate that there are four chemically distinct sites for the protons and two chemically distinct sites for the carbon atoms. A static, chiral structure of the type proposed in eq 6 for **9** should have diastereotopic ring hydrogens and carbons on the piperazine ring, i.e., eight different hydrogen resonances and four different carbon resonances. Clearly, the solution structure of **9** is not static in the temperature range studied. One possibility is that the η^2-1-amido-4-methylpiperazine does not rotate fully on the NMR time scale, but only has enough motion to racemize the Δ and Λ isomers. Such a windshield wiper-like motion would lead to the observed number of resonances for the piperazine ring in **9**, but would not place the nitrogen−hydrogen bond near the titanium−methyl bond. Alternatively, the η^2-1-amido-4-methylpiperazine ligand may undergo rapid rotation on the NMR time scale, but the nitrogen−hydrogen and titanium−carbon bonds do not achieve the correct geometry for methane elimination. We are unable to differentiate between the two arguments with the limited data that could be collected. However, pyrazolato ligand rotation is fast, even at −40 °C, as evidenced by the sharp singlet that was observed for the *tert*-butyl methyl groups at this temperature. Rapid pyrazolato group rotation suggests that η^2-1-amido-4-methylpiperazine ligand rotation may also be fast and tends to support the idea that the correct transition state structure for methane elimination from **9** is not accessible at moderate temperatures.

Reactivity of 6 with Unsaturated Organic Compounds. The reactivity of zirconocene imido complexes toward unsaturated organic compounds has been extensively explored.[16] To provide a comparison, we examined the reactions of **6** with several organic compounds containing multiple bonds. Compound **6** was chosen for reactivity studies, since we reasoned that the pyridine ligands in **7** and **8** would be too strongly bonded to allow access of the unsaturated organic compounds to the titanium center. Treatment of **6** with diphenylacetylene or acetonitrile (3−4 equiv) in refluxing toluene for 24 h did not give any detectable reaction, as assessed by ^{1}H NMR spectroscopy, and **6** was recovered quantitatively. The reaction between **6** and benzophenone in benzene-d_6 was followed by NMR spectroscopy (eq 7). The ^{1}H and ^{13}C{^{1}H} NMR spectra after 48 h showed complete reaction and revealed resonances for *tert*-butylamine, the *tert*-butylimine of benzophenone, and new pyrazolato resonances that we propose correspond to an oxo complex **11**. Spectra taken after 0.5 h of reaction revealed complete consumption of **6**, with concomitant formation of free *tert*-butylamine, the *tert*-butylimine of benzophenone, and two compounds in a 68:32 ratio that only showed resonances from 3,5-di-*tert*-butylpyrazolato ligands. We propose that these latter two compounds correspond to oligomeric forms of

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[15] Guzei, I. A.; Baboul, A. G.; Yélamos, C.; Liable-Sands, L. M.; Rheingold, A. L.; Schlegel, H. B.; Winter, C. H. Manuscript in preparation.

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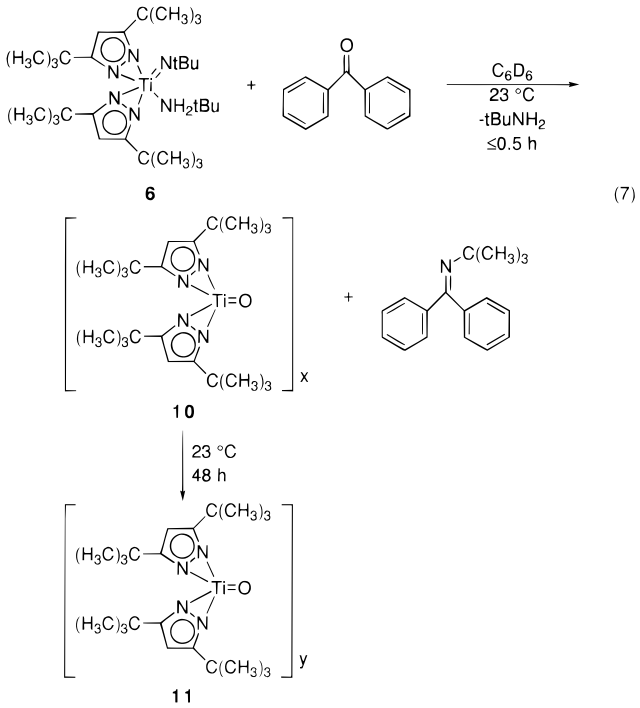

(7)

oxo complexes containing the bis(3,5-di-*tert*-butylpyrazolato)titanium(IV) fragment (**10**, **11**; $x \neq y$; $x, y \geq 2$).[17] The initial major compound **10** converted to **11** over about 48 h at 23 °C in benzene-d_6. To gain evidence that **10** and **11** were oxo complexes, the analogous reaction of **6** with acetophenone was conducted in an NMR tube. After 0.5 h, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy revealed complete conversion to free *tert*-butylamine and the *tert*-butylimine of acetophenone as the organic products. Additionally, **10** and **11** were observed in a 78:22 ratio. As per the case with benzophenone, **10** converted to **11** over 48 h at ambient temperature. Despite considerable effort, we were unable to provide more structural insight into **10** and **11**. The proposed structures are tentative, particularly with respect to the degree of oligomerization.

X-ray Crystal Structures of 3, 5, and 8. The X-ray crystal structures of **3**, **5**, and **8** were determined in order to establish the geometry about the metal centers and the bonding modes of the pyrazolato ligands. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2–4, and perspective views are presented in Figures 1–3. Further data are available in the Supporting Information.

Table 1. Experimental Crystallographic Data for 3, 5, and 8

	3	5	8
empirical formula	$C_{30}H_{60}N_4Si_2Ti$	$C_{15}H_{28}N_3ClTi$	$C_{30}H_{50}N_6Ti$
fw	580.90	333.75	542.66
space group	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$
a (Å)	10.0187(4)	12.4152(6)	10.399(10)
b (Å)	11.6437(5)	10.0217(5)	10.87(2)
c (Å)	16.7533(7)	15.7552(9)	15.79(2)
α (deg)	81.414(2)	90	94.67(8)
β (deg)	113.5780(10)	97.9090(10)	90.07(2)
γ (deg)	75.711(2)	90	106.63(7)
V (Å^3)	1860.17(13)	1941.6(2)	1704(4)
Z	2	4	2
T (K)	295(2)	295(2)	295(2)
λ (Å)	0.71073	0.71073	0.71073
ρ calcd (g cm^3)	1.037	1.1142	1.058
μ (mm^{-1})	0.316	0.574	0.276
$R(F)$ (%)	6.06	4.42	5.70
$Rw(F)$ (%)	12.52	12.01	12.57

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

Ti(1)–N(1)	2.015(4)	Ti(1)–N(3)	2.015(4)
Ti(1)–N(2)	2.028(3)	Ti(1)–N(4)	2.045(3)
Ti(1)–C(5)	2.079(3)	Ti(1)–C(1)	2.084(4)
N(1)–N(2)	1.370(4)	N(3)–N(4)	1.366(4)
N(1)–Ti(1)–N(3)	96.70(12)	N(1)–Ti(1)–N(2)	39.62(10)
N(3)–Ti(1)–N(2)	108.24(13)	N(1)–Ti(1)–N(4)	106.92(12)
N(3)–Ti(1)–N(4)	39.30(11)	N(2)–Ti(1)–N(4)	138.57(14)
N(1)–Ti(1)–C(5)	134.13(14)	N(3)–Ti(1)–C(5)	98.90(14)
N(2)–Ti(1)–C(5)	94.52(13)	N(4)–Ti(1)–C(5)	112.40(13)
N(1)–Ti(1)–C(1)	90.00(14)	N(3)–Ti(1)–C(1)	134.03(14)
N(2)–Ti(1)–C(1)	110.76(14)	N(4)–Ti(1)–C(1)	94.73(14)
C(5)–Ti(1)–C(1)	101.3(2)	Si(1)–C(1)–Ti(1)	122.9(2)
Si(2)–C(5)–Ti(1)	122.9(2)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5

Ti(1)–N(3)	1.854(2)	Ti(1)–N(3)#1	1.923(2)
Ti(1)–N(1)	2.030(2)	Ti(1)–N(2)	2.035(2)
Ti(1)–Cl(1)	2.2876(7)	N(1)–N(2)	1.386(3)
Ti(1)···Ti(1)#1	2.7670(7)		
N(3)–Ti(1)–N(3)#1	85.81(8)	N(3)–Ti(1)–N(1)	125.98(8)
N(3)#1–Ti(1)–N(1)	136.21(8)	N(3)–Ti(1)–N(2)	107.93(8)
N(3)#1–Ti(1)–N(2)	107.37(8)	N(1)–Ti(1)–N(2)	39.87(7)
N(3)–Ti(1)–Cl(1)	106.91(6)	N(3)#1–Ti(1)–Cl(1)	104.82(6)
N(1)–Ti(1)–Cl(1)	94.28(6)	N(2)–Ti(1)–Cl(1)	133.59(6)
C(12)–N(3)–Ti(1)	137.6(2)	C(12)–N(3)–Ti(1)#	128.1(2)
Ti(1)–N(3)–Ti(1)#	94.19(8)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 8

Ti(1)–N(6)	1.692(3)	Ti(1)–N(2)	2.027(3)
Ti(1)–N(4)	2.049(3)	Ti(1)–N(3)	2.109(3)
Ti(1)–N(5)	2.183(3)	Ti(1)–N(1)	2.251(4)
N(1)–N(2)	1.385(3)	N(3)–N(4)	1.387(3)
N(6)–Ti(1)–N(2)	111.22(14)	N(6)–Ti(1)–N(4)	103.3(2)
N(2)–Ti(1)–N(4)	109.85(12)	N(6)–Ti(1)–N(3)	111.8(2)
N(2)–Ti(1)–N(3)	131.80(11)	N(4)–Ti(1)–N(3)	38.93(9)
N(6)–Ti(1)–N(5)	97.65(14)	N(2)–Ti(1)–N(5)	102.76(12)
N(4)–Ti(1)–N(5)	130.94(10)	N(3)–Ti(1)–N(5)	92.09(10)
N(6)–Ti(1)–N(1)	148.47(11)	N(2)–Ti(1)–N(1)	37.33(10)
N(4)–Ti(1)–N(1)	90.86(13)	N(3)–Ti(1)–N(1)	96.97(12)
N(5)–Ti(1)–N(1)	93.79(13)	C(28)–N(6)–Ti(1)	172.7(3)

Complex **3** contains two η^2-pyrazolato ligands and two methyltrimethylsilyl groups. The titanium atom possesses approximate tetrahedral geometry, if the centers of the nitrogen–nitrogen bonds in the 3,5-di-*tert*-butylpyrazolato groups are considered to be monodentate ligands. The pseudotetrahedral angles about the titanium atom span 94.5–138.6°. The carbon–titanium–carbon angle associated with the methyltrimethylsilyl ligands (C(1)–Ti–C(5)) is 101.3(2)°. The 3,5-di-*tert*-butylpyrazolato ligands are symmetrically coordinated in a η^2-fashion, with the titanium–nitrogen distances ranging from 2.015 to 2.045 Å. These characteristics are

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(17) For crystal structures of terminal titanium oxo complexes with non-porphyrinato and non-phthalocyaninato ligands, see: Crescenzi, R.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1996**, *15*, 5456. Gallo, E.; Solari, E.; Franceschi, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1995**, *34*, 2495. De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 4505. Jeske, P.; Haselhorst, G.; Weyhermüller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1994**, *33*, 2462. Smith, M. R.; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7049. Bodner, A.; Jeske, P.; Weyhermüller, T.; Wieghardt, K.; Dubler, E.; Schmalle, H.; Nuber, B. *Inorg. Chem.* **1992**, *31*, 3737. Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1989**, *28*, 3602.

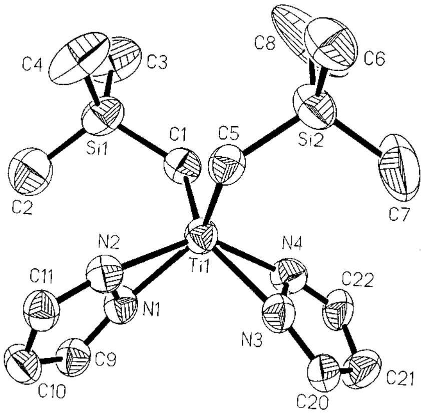

Figure 1. Perspective view of $(Bu^t{}_2pz)_2Ti(CH_2SiMe_3)_2$ (**3**) with thermal ellipsoids at the 50% probability level. The *tert*-butyl groups have been removed for clarity.

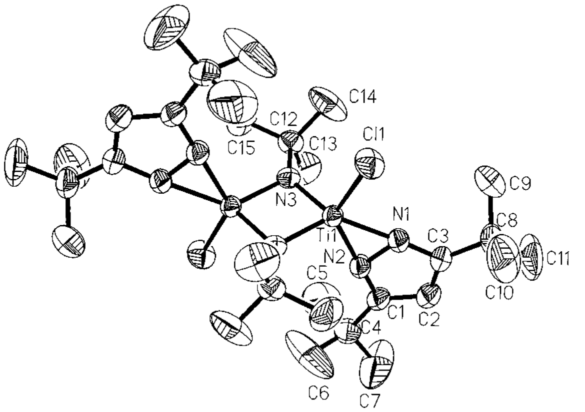

Figure 2. Perspective view of $[(Bu^t{}_2pz)TiCl(\mu\text{-}NtBu)]_2$ (**5**) with thermal ellipsoids at the 50% probability level.

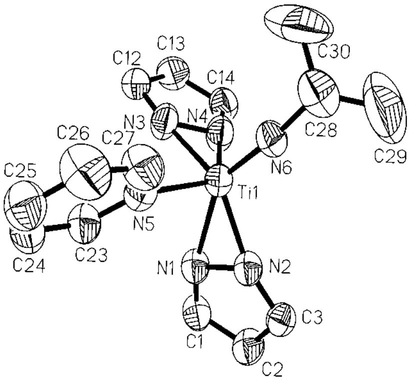

Figure 3. Perspective view of $(Bu^t{}_2pz)_2Ti(NiPr)(py)$ (**8**) with thermal ellipsoids at the 50% probability level. The *tert*-butyl groups have been removed for clarity.

similar to those found in dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) ((Ti−N 1.972−1.986 Å, Cl−Ti−Cl 100.5(2)°).[3] The slightly longer titanium−nitrogen distances in **3**, as compared to dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV), can be rationalized by the change of two methyltrimethylsilyl ligands for the two chlorine atoms, which makes the central metal less electrophilic and more crowded in **3**. The titanium−carbon bond lengths and the titanium−carbon−silicon angles are typical and compare well to those found in other methyltrimethylsilyl derivatives of titanium.[18]

Complex **5** is dimeric, with one 3,5-di-*tert*-butylpyrazolato, one chloride, and one imido ligand per titanium atom. The dimer is held together by the two bridging imido ligands. Molecules of **5** lie on a crystallographic inversion center. Each titanium atom possesses approximate tetrahedral geometry, if the centers of the nitrogen−nitrogen bonds in the 3,5-di-*tert*-butylpyrazolato groups are considered to be monodentate ligands. The pyrazolato groups are symmetrically coordinated in a η^2-fashion, with titanium−nitrogen distances of 2.030(2) and 2.035(2) Å. These values are identical to the related values observed in **3**. The titanium chlorine bond length (2.2876(7) Å) is slightly longer than the values found in dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (2.247−2.251 Å).[3] The difference probably reflects the less electrophilic metal center present in **5**, due to the strong donor characteristics of the imido ligands. The titanium−nitrogen bond lengths associated with the imido linkages (Ti−N(3) 1.854(2), Ti−N(3)#1 1.923(2) Å) are longer than the average value for known monomeric alkylimido complexes (1.704 Å)[19−22] and are similar to those found in other structurally characterized dimeric titanium imido complexes.[23] The geometry at the bridging nitrogen atoms is nearly trigonal planar (sum of angles = 359.9(5)°). The structural and bonding characteristics of dinuclear imido complexes with core structures similar to that of **5** have been the subject of a recent theoretical study.[20]

Complex **8** is a monomeric complex that bears two η^2-pyrazolato, one isopropylimido, and one pyridine ligand. The titanium atom possesses approximate tetrahedral geometry, if the centers of the nitrogen−nitrogen bonds in the 3,5-di-*tert*-butylpyrazolato groups are considered to be monodentate ligands. The pseudo-tetrahedral angles around the titanium atom span 90.8−148.5°. The titanium−nitrogen−carbon angle associated with the imido ligand (172.7(3)°) is nearly linear and is consistent

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(18) For selected examples of structurally characterized titanium complexes with methyltrimethylsilyl ligands, see: Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5981. Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390. Chesnut, R. W.; Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Polyhedron* **1987**, 6, 2019. Gómez-Sal, P.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R.; Carreras, S. M. *J. Organomet. Chem.* **1989**, *375*, 59. Eisch, J. J.; Caldwell, K. R.; Werner, S.; Krüger, C. *Organometallics* **1991**, *10*, 3417. McAlexander, L. H.; Hung, M.; Li, L.; Diminnie, J. B.; Xue, Z.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1996**, *15*, 5231.

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(21) Monomeric titanium imido complexes reported to date show an average titanium−nitrogen bond distance of 1.704 Å: Swallow, D.; McInnes, J. M.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1998**, 2253. Stewart, P. J.; Blake, A. J.; Mountford, P. *Organometallics* **1998**, *17*, 3271. Hagadorn, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355. Dunn, S. C.; Mountford, P.; Robson, D. A. *J. Chem. Soc., Dalton Trans.* **1997**, 293. Blake, A. J.; Collier, P. E.; Gade, L. H.; McPartlin, M.; Mountford, P.; Schubart, M.; Scowen, I. J. *J. Chem. Soc., Chem. Commun.* **1997**, 1555. Dunn, S. C.; Mountford, P.; Shishkin, O. V. *Inorg. Chem.* **1996**, *35*, 1006. Collier, P. E.; Dunn, S. C.; Mountford, P.; Shishkin, O. V.; Swallow, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3743. Dunn, S. C.; Batsanov, A. S.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2007. Duchateau, R.; Williams, A. J.; Gambarotta, S.; Chiang, M. Y. *Inorg. Chem.* **1991**, *30*, 4863. Bai, Y.; Noltemeyer, M.; Roesky, H. W. *Z. Naturforsch.* **1991**, *B46*, 1357.

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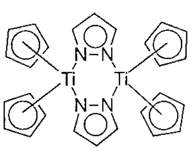
with triple bonding between titanium and nitrogen. The titanium−nitrogen distance in the imido group (1.692(3) Å) is similar to the related distances in known monomeric imido complexes.[19−22] One of the pyrazolato ligands is bonded to the titanium atom with essentially ideal η^2-bonding (Ti−N(4) 2.049(3), Ti−N(3) 2.109(3) Å), while the other pyrazolato ligand adopts a "slipped" η^2-bonding mode (Ti(1)−N(2) 2.027(3), Ti(1)−N(1) 2.251(4) Å). In the "slipped" η^2-ligand, one titanium−nitrogen bond is 0.224 Å longer than the other. We have found this type of bonding in situations where the coordination sphere is extremely crowded.[2] It is also likely that the extremely strong trans-influence of the imido ligand weakens the bonding between titanium and nitrogen(1). Nitrogen(1) is the nitrogen atom that is closest to being trans to the imido group.

Discussion

Since early transition metal complexes containing η^2-pyrazolato ligands remain very rare,[7] it is instructive to compare the titanium complexes prepared herein with previous titanium pyrazolato complexes that have been structurally characterized. In 1978, Fieselman and Stucky reported the crystal structure of μ-pyrazolatobis(cyclopentadienyl)titanium(III) (**12**), which contains bridging pyrazolato ligands.[24] We have recently reported the crystal structures of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV),[3] tetrakis(3,5-dimethylpyrazolato)titanium(IV) (**13**),[1] and tetrakis(3,5-diphenylpyrazolato)titanium(IV) (**14**).[1] Complex **12** possesses d^1 titanium(III) centers, while **13** and **14** possess the d^0 titanium(IV) oxidation state. It is possible that a partially filled d-shell destabilizes the η^2-pyrazolato coordination mode through filled/filled d-orbital/pyrazolato repulsive interactions. The question of η^2-pyrazolato ligand coordination in d-block metal complexes with partially filled d-shells remains open, but we are working on this issue both experimentally and theoretically.



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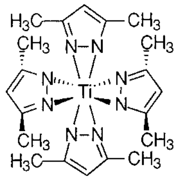

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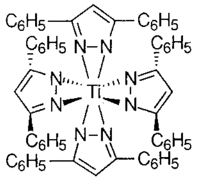

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A central goal of the present study was to determine if the η^2-pyrazolato ligand would be inert enough to serve as an ancillary ligand in reactive early transition metal complexes. In this regard, we envisioned that there would be a significant analogy between cyclopentadienyl and η^2-pyrazolato ligands.[4] Since many reactive systems employ cyclopentadienyltitanium fragments,[12] new reactive complexes with unique steric and electronic characteristics might be constructed from pyrazolato building blocks. From the experiments described herein, we predict that the bis(η^2-pyrazolato) ligand set will be stable during transformations that do not lead to the generation of acidic element−hydrogen bonds in the coordination sphere. When acidic element−hydrogen bonds are generated in the coordination sphere, the stability of the pyrazolato ligands will depend on the other ligands present about the metal. If other highly reactive metal−ligand bonds are present, i.e., titanium−alkyl linkages, the pyrazolato ligands should be preserved. If, however, the other ligands in the coordination sphere are unreactive, i.e., chloride ligands, then the pyrazolato ligand may be eliminated as the neutral pyrazole. We are continuing to explore these predictions in the context of olefin polymerizations promoted by catalysts derived from **1**−**3** and related molecules.[25]

The results of this study suggest that the pyrazolato ligand can be added to the list of new useful ligands for early transition metals. Related ligands that have been the subject of much recent study in early transition metal systems include alkoxides,[8] amidinates,[9] and pyrazolylborates,[10] as well as many others.[11] The structural and electronic features of η^2-pyrazolato ligand coordination may impart unique reactivity patterns to metal centers that bear these groups.

Experimental Section

General Considerations. All manipulations were carried out under argon using Schlenk line or glovebox techniques. Hexane and toluene were distilled from sodium just prior to use. Tetrahydrofuran was distilled from a purple solution of sodium/benzophenone ketyl immediately prior to use. The primary amines and pyridine (purchased from Aldrich Chemical Co.) were distilled from sodium and calcium hydride, respectively. Methylmagnesium chloride (3.0 M in tetrahydrofuran) and benzylmagnesium chloride (1.0 M in diethyl ether) were used as received from Aldrich Chemical Co. Methyltrimethylsilyllithium was purchased from Aldrich Chemical Co. as a 1.0 M solution in hexane, but was used as white solid after removing the solvent under reduced pressure. 1-Amino-4-methylpiperazine was used as received from Acros. Dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV)[3,4] and chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV)[4] were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as Nujol mulls unless stated otherwise. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 500, 300, 125, or 75 MHz. Chemical shifts (δ, ppm) are given relative to residual protons or to the carbon of the solvent. Melting points were determined in sealed capillary tubes under argon and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Preparation of Dimethylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (1). A 3.0 M solution of methylmagnesium chloride in tetrahydrofuran (3.10 mL, 9.21 mmol), diluted in tetrahydrofuran (30 mL), was slowly added to a solution of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (2.00 g, 4.19 mmol) in hexane (60 mL) at 0 °C. The reaction mixture

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was allowed to warm to room temperature and was stirred for 20 h. The volatile components were removed under reduced pressure, and the resultant yellow solid was extracted with hexane (60 mL). Filtration of the hexane extract through a 2 cm pad of Celite on a coarse glass frit afforded a yellow solution. Removal of the solvent under reduced pressure gave **1** as a yellow crystalline solid (1.67 g, 93%): dec 90 °C; IR (Nujol, cm^{-1}) 1528 (w), 1508 (s), 1363 (s), 1252 (s), 1234 (s), 1206 (w), 1102 (w), 1020 (m), 944 (w), 883 (w), 812 (s), 719 (m); ^{1}H NMR (CDCl$_3$, 22 °C, δ) 6.68 (s, 2H, ring C***H***), 1.43 (s, 6H, TiC***H***$_3$), 1.30 (s, 36H, C(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$, 22 °C, ppm) 160.89 (***C***C(CH$_3$)$_3$), 109.84 (ring ***C***H), 68.19 (Ti***C***H$_3$), 32.31 (C***C***(CH$_3$)$_3$), 30.72 (CC(***C***H$_3$)$_3$).

Anal. Calcd for $C_{22}H_{44}N_4Ti$: C, 66.03; H, 10.16; N, 12.83. Found: C, 64.82; H, 9.36; N, 12.73.

Preparation of Dibenzylbis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (2). A 1.0 M solution of benzylmagnesium chloride in diethyl ether (3.01 mL, 3.06 mmol), diluted with diethyl ether (30 mL), was slowly added to a solution of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (0.730 g, 1.53 mmol) in toluene (50 mL) at 0 °C. During the addition, the initial yellow color turned to deep red. After stirring at room temperature for 16 h, the volatile components were removed under reduced pressure and the resultant red solid was extracted with hexane (50 mL). Filtration of the hexane extract through a 1 cm pad of Celite on a coarse glass frit gave a red solution. This solution was concentrated under reduced pressure to ca. 10 mL. After 2 days at −20 °C, deep red crystals of **2** (0.39 g, 43%) were isolated by decanting the hexane solution: mp 109−112 °C; IR (Nujol, cm^{-1}) 3057 (w), 1593 (s), 1571 (w), 1527 (w), 1507 (s), 1485 (s), 1360 (s), 1286 (w), 1250 (m), 1229 (m), 1205 (m), 1087 (w), 1028 (m), 1017 (m), 986 (s), 889 (w), 813 (s), 794 (m), 747 (s), 720 (m), 693 (s), 656 (s); ^{1}H NMR (C$_6$D$_6$, 22 °C, δ) 7.06 (m, 4H, Ph meta-C***H***), 6.80−6.84 (m, 6H, Ph ortho-C***H*** and para-C***H***), 6.70 (s, 2H, pz ring C***H***), 3.45 (s, 4H, C***H***$_2$Ph), 1.23 (s, 36H, C(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C, ppm) 160.53 (***C***C(CH$_3$)$_3$), 146.37 (Ph ipso-***C***), 128.24 (Ph ortho-***C***H), 127.84 (Ph meta-***C***H), 122.79 (Ph para-***C***H), 111.66 (pz ring ***C***H), 95.25 (***C***H$_2$C$_6$H$_5$), 32.36 (C***C***(CH$_3$)$_3$), 30.77 (CC(***C***H$_3$)$_3$).

Anal. Calcd for $C_{36}H_{52}N_4Ti$: C, 73.44; H, 8.90; N, 9.52. Found: C, 73.21; H, 9.01; N, 9.65.

Preparation of Bis(methyltrimethylsilyl)bis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (3). A 100 mL Schlenk flask was charged with dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (0.70 g, 1.47 mmol), methyltrimethylsilyllithium (0.28 g, 2.93 mmol), and hexane (90 mL). The reaction mixture was stirred at ambient temperature for 24 h. At this point, the reaction mixture was filtered through a 2 cm pad of Celite on a coarse glass frit to afford a clear yellow solution. The volume of this solution was concentrated to about 10 mL under reduced pressure. Crystallization at −20 °C for 2 days afforded **3** as yellow crystals (0.42 g, 49%): dec 136 °C; IR (Nujol, cm^{-1}) 1508 (m), 1363 (m), 1252 (m), 1240 (s), 1206 (w), 1092 (s), 1019 (m), 990 (w), 898 (s), 844 (m), 816 (s), 740 (w), 720 (m), 698 (w), 677 (w); ^{1}H NMR (C$_6$D$_6$, 22 °C, δ) 6.70 (s, 2H, pz ring C***H***), 2.82 (s, 4H, C***H***$_2$SiMe$_3$), 1.36 (s, 36H, C(C***H***$_3$)$_3$), 0.00 (s, 18H, CH$_2$Si(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C, ppm) 160.96 (***C***C(CH$_3$)$_3$), 111.00 (pz ring ***C***H), 91.60 (***C***H$_2$SiMe$_3$), 32.52 (C***C***(CH$_3$)$_3$), 31.02 (CC(***C***H$_3$)$_3$), 2.05 (CH$_2$Si(***C***H$_3$)$_3$).

Anal. Calcd for $C_{30}H_{60}N_4Si_2Ti$: C, 62.03; H, 10.41; N, 9.64. Found: C, 61.82; H, 10.51; N, 9.54.

Preparation of Methyltris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (4). In a fashion similar to the preparation of **1**, chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (0.60 g, 0.96 mmol) and a 3.0 M solution of methylmagnesium chloride in tetrahydrofuran (0.35 mL, 1.06 mmol) were reacted to afford **4** as large yellow crystals (0.30 g, 52%): mp 155 °C; IR (Nujol, cm^{-1}) 1505 (m), 1363 (s), 1252 (m), 1233 (m), 1205 (w), 1019 (m), 997 (w), 804 (s), 718 (m); ^{1}H NMR (C$_6$D$_6$, 22 °C, δ) 6.55 (s, 3H, pz ring C***H***), 2.31 (s, 3H, TiC***H***$_3$), 1.25 (s, 54H, C(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C, ppm) 159.15 (***C***C(CH$_3$)$_3$), 108.75 (pz ring ***C***H), 68.80 (Ti***C***H$_3$), 32.22 (C***C***(CH$_3$)$_3$), 30.85 (CC(***C***H$_3$)$_3$).

Anal. Calcd for $C_{34}H_{60}N_6Ti$: C, 67.97; H, 10.07; N, 13.99. Found: C, 67.62; H, 10.12; N, 14.06.

Reaction of Trichloro(3,5-di-*tert*-butylpyrazolato)titanium(IV) with Methylmagnesium Chloride. A 3.0 M solution of methymagnesium chloride in tetrahydrofuran (1.20 mL, 3.60 mmol), diluted with tetrahydrofuran (30 mL), was slowly added to a suspension of trichloro(3,5-di-*tert*-butylpyrazolato)titanium(IV) (0.400 g, 1.20 mmol) in hexane (50 mL) at −78 °C. After 0.25 h at this temperature, the yellow solution was allowed to warm to ambient temperature and was stirred for 3 h to afford a black suspension. The volatile components were removed under reduced pressure, and the resultant black solid was extracted with hexane (60 mL). Filtration of the hexane extract through a 2 cm pad of Celite on a coarse glass frit afforded a yellow solution. Removal of the solvent under reduced pressure afforded **1** (0.18 g, 35%) as a yellow crystalline solid. The ^{1}H and ^{13}C{^{1}H} NMR spectra of this solid were identical to those of authentic **1**.

Preparation of *tert*-Butylimido(chloro)(3,5-di-*tert*-butylpyrazolato)titanium Dimer (5). *tert*-Butylamine (0.400 mL, 3.66 mmol) was added to a solution of dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (0.35 g, 0.73 mmol) in hexanes (40 mL). After stirring at room temperature for 16 h, the orange solution was separated from a fine white powder by filtration. The powder was isolated and dried to yield *tert*-butylammonium chloride (0.068 g, 85%). The volatile components were removed from the filtrate under reduced pressure to afford an orange solid. Analysis of this solid by ^{1}H NMR showed it to be a 30:70 mixture of **5** and chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV). Fractional crystallization from hexane (5 mL) at −15 °C gave pure **5** as dark orange crystals (0.050 g, 10%). Intermediate fractions obtained were mixtures of orange crystals of **5** and yellow crystals of chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV). The last fraction, obtained by cooling the solution to −20 °C for 20 days, afforded pure chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (0.26 g, 56%) as yellow crystals. Spectral and analytical data for **5**: mp 246 °C dec; IR (Nujol, cm^{-1}) 1508 (m), 1363 (m), 1308 (w), 1252 (w), 1236 (w), 1173 (m), 1017 (w), 988 (w), 816 (m), 720 (m), 664 (s); ^{1}H NMR (C$_6$D$_6$, 22 °C, δ) 6.63 (s, 2H, pz ring C***H***), 1.59 (s, 36H, CC(C***H***$_3$)$_3$), 0.96 (s, 18H, NC(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C, ppm) 162.14 (***C***C(CH$_3$)$_3$), 110.97 (pz ring ***C***H), 77.60 (N***C***(CH$_3$)$_3$), 32.95 (C***C***(CH$_3$)$_3$), 31.24 (NC(***C***H$_3$)$_3$), 31.08 (CC(***C***H$_3$)$_3$).

Anal. Calcd for $C_{30}H_{56}N_6Cl_2Ti_2$: C, 53.98; H, 8.46; N, 12.59. Found: C, 53.60; H, 8.61; N, 12.79.

tert-Butylammonium chloride and chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) were identified by comparison of their ^{1}H and ^{13}C{^{1}H} NMR spectra with those of authentic materials.

Preparation of *tert*-Butylimidobis(3,5-di-*tert*-butylpyrazolato)(*tert*-butylamine)titanium(IV) (6). *tert*-Butylamine (0.480 mL, 4.58 mmol) was added to a solution of **1** (0.40 g, 0.92 mmol) in toluene (30 mL) at ambient temperature. After stirring for 3 days at room temperature, the volatile components were removed under reduced pressure. The resultant orange solid was extracted with hexane (40 mL), and the hexane extract was filtered through a 1 cm pad of Celite on a coarse glass frit. The yellow-orange filtrate was concentrated to a volume of about 10 mL. Crystallization at −20 °C for 24 h afforded **6** as orange crystals (0.17 g, 33%): mp 149 °C dec; IR (Nujol, cm^{-1}) 3312 (m), 1569 (m), 1524 (s), 1404 (m), 1285 (w), 1261 (m), 1160 (w), 1091 (s), 1039 (m), 1026 (m), 799 (s), 727 (w), 676 (w), 660 (w); ^{1}H NMR (C$_6$D$_6$, 22 °C, δ) 6.23 (s, 2H, pz ring C***H***), 3.38 (s broad, 2H, N***H***$_2$Bu^t), 1.42 (s, 36H, CC(C***H***$_3$)$_3$), 1.22 (s, 9H, NC(C***H***$_3$)$_3$), 1.10 (s, 9H, NH$_2$C(C***H***$_3$)$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 22 °C, ppm) 158.92 (***C***C(CH$_3$)$_3$), 102.27 (pz ring $\boldsymbol{C}$H), 68.39 ($N\boldsymbol{C}(CH_3)_3$), 51.14 ($NH_2\boldsymbol{C}(CH_3)_3$), 32.75 ($NC(\boldsymbol{C}H_3)_3$), 32.28 ($C\boldsymbol{C}(CH_3)_3$), 31.33 ($CC(\boldsymbol{C}H_3)_3$), 30.91 ($NH_2C(\boldsymbol{C}H_3)_3$).

Anal. Calcd for $C_{30}H_{58}N_6Ti$: C, 65.43; H, 10.62; N, 15.26. Found: C, 64.61; H, 10.56; N, 15.22.

Preparation of *tert*-Butylimidobis(3,5-di-*tert*-butylpyrazolato)(pyridine)titanium(IV) (7). *tert*-Butylamine (0.72 mL, 6.87 mmol) and pyridine (0.55 mL, 6.87 mmol) were added to a solution of **1** (0.60 g, 1.37 mmol) in toluene (30 mL). After stirring for 3 days at room temperature, the volatile components were removed under reduced pressure to afford an orange solid. The solid was extracted with hexane (40 mL). The resulting extract was filtered through a 1 cm pad of Celite on a coarse glass frit and was then concentrated in volume to ca. 20 mL. Crystallization at −20 °C for 24 h afforded **7** as orange crystals (0.61 g, 80%): mp 151 °C; IR (Nujol, cm^{-1}) 1604 (s), 1508 (s), 1360 (s), 1302 (m), 1248 (s), 1230 (s), 1211 (s), 1117 (m), 1070 (m), 1043 (m), 1018 (m), 999 (w), 990 (m), 801 (s), 792 (m), 758 (m), 723 (m), 696 (s), 642 (m); ^{1}H NMR (C_6D_6, 22 °C, δ) 9.07 (m, 2H, py ortho-C$\boldsymbol{H}$), 6.77 (m, 1H, py para-C$\boldsymbol{H}$), 6.53 (m, 2H, py meta-C$\boldsymbol{H}$), 6.32 (s, 2H, pz ring C$\boldsymbol{H}$), 1.43 (s, 36H, $CC(C\boldsymbol{H}_3)_3$), 1.26 (s, 9H, $NC(C\boldsymbol{H}_3)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 159.03 ($\boldsymbol{C}C(CH_3)_3$), 152.35 (py ortho-$\boldsymbol{C}$H), 138.43 (py para-$\boldsymbol{C}$H), 123.95 (py meta-$\boldsymbol{C}$H), 102.53 (pz ring $\boldsymbol{C}$H), 68.74 ($N\boldsymbol{C}(CH_3)_3$), 32.64 ($NC(\boldsymbol{C}H_3)_3$), 32.37 ($C\boldsymbol{C}(CH_3)_3$), 31.32 ($CC(\boldsymbol{C}H_3)_3$).

Anal. Calcd for $C_{31}H_{52}N_6Ti$: C, 66.88; H, 9.42; N, 15.10. Found: C, 66.92; H, 9.44; N, 15.10.

Preparation of Isopropylimidobis(3,5-di-*tert*-butylpyrazolato)(pyridine)titanium(IV) (8). In a fashion similar to the preparation of **7**, isopropylamine (0.390 mL, 4.58 mmol), pyridine (0.370 mL, 4.58 mmol), and **1** (0.40 g, 0.92 mmol) were reacted to afford **8** as orange crystals (0.23 g, 46%): mp 108 °C dec; IR (Nujol, cm^{-1}) 1604 (m), 1507 (m), 1360 (m), 1300 (m), 1250 (m), 1231 (s), 1111 (w), 1070 (w), 1044 (w), 1018 (m), 991 (w), 801 (s), 759 (w), 723 (w), 696 (m); ^{1}H NMR (C_6D_6, 22 °C, δ) 9.03 (m, 2H, py ortho-C$\boldsymbol{H}$), 6.80 (m, 1H, py para-C$\boldsymbol{H}$), 6.54 (m, 2H, py meta-C$\boldsymbol{H}$), 6.33 (s, 2H, pz ring C$\boldsymbol{H}$), 3.81 (septuplet, $J_{HH} = 6.6$ Hz, 1H, $NC\boldsymbol{H}(CH_3)_2$), 1.43 (s, 36H, $CC(C\boldsymbol{H}_3)_3$), 1.17 (d, $J_{HH} = 6.6$ Hz, 6H, $NCH(C\boldsymbol{H}_3)_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 159.10 ($\boldsymbol{C}C(CH_3)_3$), 152.24 (py ortho-$\boldsymbol{C}$H), 138.29 (py para-$\boldsymbol{C}$H), 124.00 (py meta-$\boldsymbol{C}$H), 102.65 (pz ring $\boldsymbol{C}$H), 65.60 ($N\boldsymbol{C}H(CH_3)_2$), 32.36 ($C\boldsymbol{C}(CH_3)_3$), 31.27 ($CC(\boldsymbol{C}H_3)_3$), 26.36 ($NCH(\boldsymbol{C}H_3)_2$).

Anal. Calcd for $C_{30}H_{50}N_6Ti$: C, 66.40; H, 9.29; N, 15.49. Found: C, 65.53; H, 9.00; N, 15.38.

Preparation of 1-Amido-4-methylpiperazine(methyl)bis(3,5-di-*tert*-butyl-pyrazolato)titanium(IV) (9). In a fashion similar to the preparation of **6**, 1-amino-4-methylpiperazine (0.620 mL, 5.15 mmol) and **1** (0.450 g, 1.03 mmol) were reacted in toluene (50 mL) to afford **9** as yellow crystals (0.35 g, 64%): mp 104−107 °C dec; IR (Nujol, cm^{-1}) 3292 (ν_{NH}, m), 1517 (m), 1507 (s), 1489 (w), 1362 (s), 1283 (m), 1251 (s), 1235 (s), 1206 (w), 1141 (w), 1092 (m), 1019 (m), 1003 (s), 926 (w), 809 (s), 794 (s), 706 (m), 668 (w); ^{1}H NMR (C_6D_6, 22 °C, δ) 6.84 (s broad, 1H, $N\boldsymbol{H}N(CH_2CH_2)_2NCH_3$), 6.38 (s, 2H, pz ring C$\boldsymbol{H}$), 2.76 (broad m, 4H, $NHN(C\boldsymbol{H}_2CH_2)_2NCH_3$), 2.16 (broad m, 4H, $NHN(CH_2C\boldsymbol{H}_2)_2NCH_3$), 2.02 (s, 3H, $NHN(CH_2CH_2)_2NC\boldsymbol{H}_3$), 1.34 (s, 36H, $CC(C\boldsymbol{H}_3)_3$), 1.11 (s, 3H, $TiC\boldsymbol{H}_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 158.25 ($\boldsymbol{C}C(CH_3)_3$), 106.43 (ring $\boldsymbol{C}$H), 60.12 ($NHN(\boldsymbol{C}H_2CH_2)_2NCH_3$), 54.15 ($NHN(CH_2\boldsymbol{C}H_2)_2NCH_3$), 49.50 ($Ti\boldsymbol{C}H_3$), 45.58 ($NHN(CH_2CH_2)_2N\boldsymbol{C}H_3$), 32.21 ($C\boldsymbol{C}(CH_3)_3$), 31.10 ($CC(\boldsymbol{C}H_3)_3$).

Anal. Calcd for $C_{28}H_{53}N_7Ti$: C, 62.78; H, 9.97; N, 18.30. Found: C, 62.54; H, 10.04; N, 18.34.

Reaction of 6 with Benzophenone. A 5 mm NMR tube was charged with **6** (0.040 g, 0.073 mmol), benzophenone (0.014 g, 0.077 mmol), and benzene-d_6 (1.00 mL). The tube was flame sealed, and the course of the reaction was monitored by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. For a description of the reaction, see the text.

Data for *tert*-butylamine: ^{1}H NMR (C_6D_6, 22 °C, δ) 0.98 (s, 9H), 0.68 (s, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 47.01 (s, $H_2N\boldsymbol{C}(CH_3)_3$), 37.70 (s, $H_2NC(\boldsymbol{C}H_3)_3$).

Data for the *tert*-butylimine of benzophenone: ^{1}H NMR (C_6D_6, 22 °C, δ) 7.83 (m, 4H, o-$C_6\boldsymbol{H}_2H_2'H''$), 7.12−6.95 (m, 6H, m,p-$C_6H_2\boldsymbol{H}_2'\boldsymbol{H}''$), 1.23 (s, 9H, $C(C\boldsymbol{H}_3)_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 142.21 (s, $\boldsymbol{C}{=}NtBu$), 140.31 (s, ipso-phenyl carbon), 129.56 (s, p-phenyl carbons), 128.69 (s, o- or m-phenyl carbons), 128.60 (s, o- or m-phenyl carbons), 57.02 (s, $\boldsymbol{C}(CH_3)_3$), 31.83 (s, $C(\boldsymbol{C}H_3)_3$).

Data for **10**: ^{1}H NMR (C_6D_6, 22 °C, δ) 6.33 (s, 2H), 1.29 (s, 36H);$^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 160.69 (s, $\boldsymbol{C}{-}C(CH_3)_3$), 107.41 (s, pz ring $\boldsymbol{C}{-}H$), 32.48 (s, $\boldsymbol{C}(CH_3)_3$), 30.68 (s, $C(\boldsymbol{C}H_3)_3$).

Data for **11**: ^{1}H NMR (C_6D_6, 22 °C, δ) 6.30 (s, 2H), 1.25 (s, 36H); $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C, ppm) 159.40 (s, $\boldsymbol{C}{-}C(CH_3)_3$), 106.81 (s, pz ring $\boldsymbol{C}{-}H$), 32.26 (s, $\boldsymbol{C}(CH_3)_3$), 30.73 (s, $C(\boldsymbol{C}H_3)_3$).

X-ray Crystal Structure Determination of 2, 5, and 8. Samples for X-ray structural determinations were mounted in thin-walled capillaries under a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A hemisphere of data was collected for each sample at 10 s/frame and integrated with the manufacturer's SMART and SAINT software, respectively. Absorption corrections were applied with Sheldrick's SADABS, and the structures were solved and refined using the programs of SHELXS-86 and SHELXL-93.[26]

For **2**, 10 793 total data were averaged to yield 7175 ($R_{int} = 0.072$) independent reflections. The compound crystallizes as a molecular complex with no associated solvent or ions. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound. The *tert*-butyl groups and trimethylsilyl groups in the molecule displayed a typical rotational disorder that is reflected in the large thermal parameters associated with these atoms.

For **5**, 10 662 total data were averaged to yield 4240 ($R_{int} = 0.038$) independent reflections. The compound crystallizes as a binuclear molecular complex with no associated solvents or ions. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound or were placed in observed positions and refined. The molecule occupies a crystallographic inversion center, but all atoms occupy general positions in the cell. The asymmetric unit consists of one-half dimer. Moderate disorder in the *tert*-butyl groups was observed and is reflected in the large thermal parameters associated with the atoms contained in these groups.

For **8**, 9174 total data were averaged to yield 6527 ($R_{int} = 0.038$) independent reflections. The compound crystallizes as a molecular complex with no associated solvent or ions. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound or were placed in observed positions and refined. The *tert*-butyl groups in the molecule displayed a typical rotational disorder. The two *tert*-butyl groups most subject to disorder were modeled with partial (occupancy = 0.5) carbon atoms, viz., C(5)−C(7) and C(20)−C(22).

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Supporting Information Available: Tables listing full experimental details for data collection and refinement, atomic coordinates, bond distances and angles, and thermal parameters for **3**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Sheldrick, G. *SHELX-S and SHELXL-93*; University of Göttingen: FDR, 1986 and 1993, respectively.