Synthesis, Structure, and Properties of Group 4 and 5 Metal Pyrazolato Chloride Complexes

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Treatment of titanium tetrachloride with 3,5-di-*tert*-butylpyrazole (2 equiv) and triethylamine (2 equiv) in toluene afforded dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (93%). A similar reaction with 3 equiv of 3,5-di-*tert*-butylpyrazole and triethylamine gave chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (91%). Trichloro-(3,5-di-*tert*-butylpyrazolato)titanium(IV) was prepared in 93% yield through reaction of titanium tetrachloride with 1-trimethylsilyl-3,5-di-*tert*-butylpyrazole (1 equiv) in toluene. Treatment of zirconium and hafnium tetrachlorides with 3,5-di-*tert*-butylpyrazolatopotassium (4 equiv) in toluene afforded the homoleptic pyrazolato complexes tetrakis(3,5-di-*tert*-butylpyrazolato)zirconium(IV) (90%) and tetrakis(3,5-di-*tert*-butylpyrazolato)hafnium-(IV) (68%). Analogous reaction of 3,5-di-*tert*-butylpyrazolatopotassium ($\geq$3 equiv) with niobium and tantalum pentachlorides gave dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V) (98%) and dichlorotris(3,5-di-*tert*-butylpyrazolato)tantalum(V) (83%). Reaction of the complexes tetrakis(3,5-di-*tert*-butylpyrazolato)metal(IV) (metal = Zr, Hf) and dichlorotris(3,5-di-*tert*-butylpyrazolato)metal(V) (metal = Nb, Ta) with the metal tetrachlorides and metal pentachlorides, respectively, in dichloromethane afforded the complexes chlorotris(3,5-di-*tert*-butylpyrazolato)metal(IV) (metal = Zr, 89%; Hf, 97%) and trichlorobis(3,5-di-*tert*-butylpyrazolato)metal(V) (metal = Nb, 90%; Ta, 84%). Crystal structures of trichloro(3,5-di-*tert*-butylpyrazolato)titanium(IV), chlorotris(3,5-di-*tert*-butylpyrazolato)hafnium(IV), and dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V) were determined. Trichloro-(3,5-di-*tert*-butylpyrazolato)titanium(IV) crystallizes in the space group $C2/c$ with $a = 22.6542(8)$ Å, $b = 9.5147(3)$ Å, $c = 16.5329(6)$ Å, $\beta = 113.5780(10)°$, and $Z = 8$. Chlorotris(3,5-di-*tert*-butylpyrazolato)hafnium(IV) crystallizes in the space group $P2_1/c$ with $a = 10.4529(7)$ Å, $b = 10.1437(6)$ Å, $c = 36.986(3)$ Å, $\beta = 93.3080(10)°$, and $Z = 4$. Dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V) crystallizes in the space group $P2_1/c$ with $a = 10.2051(3)$ Å, $b = 38.3650(12)$ Å, $c = 9.7585(3)$ Å, $\beta = 93.3280(10)°$, and $Z = 4$. Kinetic analysis of a dynamic process observed for dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V) is described. The results of this study suggest that η^2-pyrazolato donors may be useful ancillary ligands in the development of new reactive early transition metal complexes.

Introduction

Cyclopentadienyl ligands have played an extremely important role in the development of early transition metal chemistry, and there are now many important reactive systems that employ cyclopentadienyl-based complexes.[1] A recent theme in organometallic chemistry has been to develop new ancillary ligand sets for early transition metal complexes that have the stabilizing characteristics of cyclopentadienyl ligands but do not possess the same degree of steric and electronic saturation that is observed in many cyclopentadienyl-based complexes. Oxygen- and nitrogen-based ligands are attractive candidates for such applications because of the extremely strong bonds formed between these hard donor atoms and high-valent early transition metal centers. Recent examples of ligands that have been pursued in this vein include alkoxides,[2] amidinates,[3] and pyrazolylborates,[4] as well as many others.[5]

Ligands derived from five-membered nitrogen-rich heterocycles, such as pyrazolate and substituted derivatives,[6] represent intriguing potential ligands for early transition metals, since the

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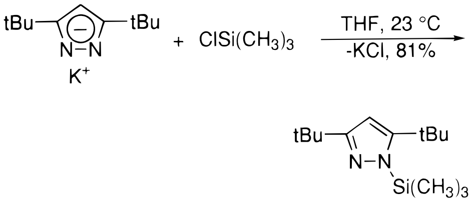
parent heterocycles are easily deprotonated to form monoanionic donors with flexible coordination ability. The strong metal–nitrogen bonds formed with these ligands should lead to thermodynamically robust complexes. Furthermore, the degree of steric crowding about the coordination sphere could be easily controlled by choice of the organic groups attached to the carbon atoms. The coordination chemistry of pyrazolato ligands has been extensively explored in complexes of the middle to late transition metals. Structurally documented coordination modes include η^1-bonding to a single metal ion or μ_2-bonding between two metal centers.[6] η^2-Pyrazolato ligand coordination is well established for f-block metals,[7] but prior to our work it had only been documented in one complex of the d-block metals.[8] We have recently reported a series of titanium, tantalum, potassium, and magnesium complexes that bear η^2-pyrazolato ligands.[9−13] A combination of synthetic work and theoretical studies has demonstrated that η^2-pyrazolato bonding is preferred over the η^1-binding mode unless the coordination sphere is sterically congested.

As part of the general development of early transition metal complexes bearing pyrazolato ligands, we sought to develop synthetic procedures to complexes that contain both pyrazolato and chloride donor ligands. Such species would be analogues of well-known group 4 metallocene dichlorides and group 5 metallocene trichlorides.[14] Herein we report the preparation and characterization of a family of group 4 and 5 metal pyrazolato chloride complexes. These complexes are easily synthesized, possess good solubilities in organic solvents, and exhibit excellent thermal stability. The crystal structures of representative complexes are described, and include the first examples of hafnium and niobium complexes bearing η^2-pyrazolato ligands. In addition to providing further examples of η^2-pyrazolato ligand coordination among the early transition metals, the complexes described herein represent potentially useful starting materials for the preparation of new reactive early transition metal complexes.

Results

Preparation of Pyrazolato Chloride Complexes. Treatment of titanium tetrachloride with a mixture of 3,5-di-*tert*-butylpyrazole (2 equiv) and triethylamine (2 equiv) in toluene at 0 °C afforded dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (**1**, 93%) as a yellow solid. We have previously reported that treatment of titanium tetrachloride with 3,5-di-*tert*-butylpyrazole in the absence of an additional nitrogen base affords **1** (42%) along with the ionic complex 3,5-di-*tert*-butylpyrazolium hexachlorotitanate(IV) (37%).[11] Addition of triethylamine avoids formation of the ionic compound and leads to much higher yields of **1**. Prolonged treatment (ca. 10 days) of titanium tetrachloride with excess (≥3 equiv) 3,5-di-*tert*-butylpyrazole and triethylamine in toluene afforded chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (**2**, 91%). We have recently described an alternate synthesis of **2** that involves the reaction of titanium tetrachloride with 3,5-di-*tert*-butylpyrazolatopotassium (≥3 equiv).[12] The structures of **1** and **2** were established by a combination of spectral and analytical techniques. The crystal and molecular structure of **1** has been previously reported.[11]

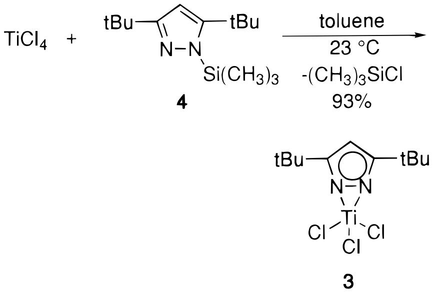
Next, we sought to prepare trichloro(3,5-di-*tert*-butylpyrazolato)titanium(IV) (**3**). However, treatment of titanium tetrachloride with 1 equiv of 3,5-di-*tert*-butylpyrazole and triethylamine in toluene afforded **1** as the exclusive product. A well-established preparative route to cyclopentadienyltitanium trichloride and ring-substituted derivatives thereof entails the treatment of titanium tetrachloride with a silylated cyclopentadiene.[15] Accordingly, the reaction of 1-trimethylsilyl-3,5-di-*tert*-butylpyrazole (**4**) with titanium tetrachloride was examined as a route to **3**. Compound **4** was prepared in 81% yield by treatment of potassium 3,5-di-*tert*-butylpyrazolate with chlorotrimethylsilane (eq 1), as described in the Experimental Section.



4

(1)

Treatment of **4** (1 equiv) with titanium tetrachloride (1 equiv) in toluene at 0 °C afforded **3** as a yellow crystalline solid in 93% yield (eq 2). Use of excess **4** did not lead to the formation of **1** or **2**, and only **3** was formed. The structure of **3** was established by spectral and analytical techniques. The presence of a monomeric complex in the solid state was confirmed by an X-ray crystal structure determination (vide infra).



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(2)

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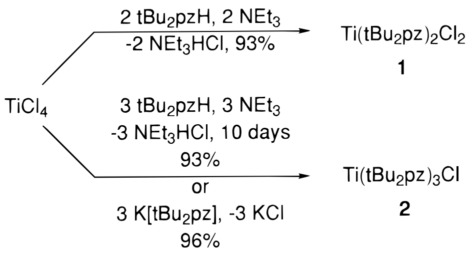
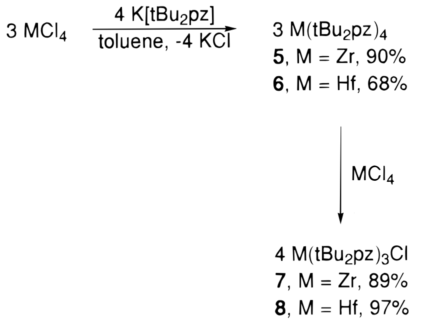
Scheme 1. Preparation of **1** and **2**



Scheme 2. Preparation of **5**−**8**



Scheme 3. Preparation of **9**−**12**

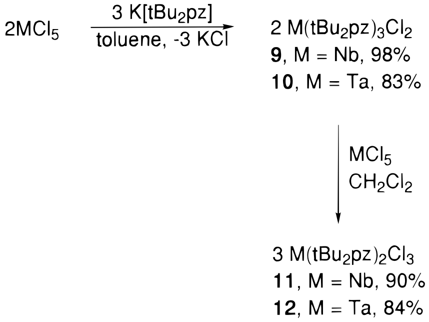


Table 1. Experimental Crystallographic Data for **3**, **8**, and **9**

	3	**8**	**9**
empirical formula	$C_{11}H_{19}Cl_3N_2Ti$	$C_{33}H_{57}N_6ClHf$	$C_{33}H_{57}Cl_2N_6Nb$
fw	333.53	751.79	701.66
space group	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*
a (Å)	22.6542(8)	10.4529(7)	10.2051(3)
b (Å)	9.5147(3)	10.1437(6)	38.3650(12)
c (Å)	16.5329(6)	36.986(3)	9.7585(3)
β (deg)	113.5780(10)	93.3080(10)	93.3280(10)
V (Å^3)	3266.1(2)	3915.1(4)	3814.2(2)
Z	8	4	4
T (K)	295(2)	295(2)	295(2)
λ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^3)	1.357	1.275	1.222
μ (mm^{-1})	0.997	2.760	0.484
$R(F)$ (%)^a	4.85	5.82	4.98
$R_w(F)$ (%)	10.81	7.14	9.85

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w(F) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

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

Ti(1)−N(1)	1.955(2)	Ti(1)−N(2)	1.963(2)
Ti(1)−Cl(1)	2.1717(11)	Ti(1)−Cl(2)	2.1901(11)
Ti(1)−Cl(3)	2.2084(12)	N(1)−N(2)	1.384(3)
N(1)−Ti(1)−N(2)	41.36(9)	N(1)−Ti(1)−Cl(1)	115.84(8)
N(2)−Ti(1)−Cl(1)	101.00(8)	N(1)−Ti(1)−Cl(2)	124.23(8)
N(2)−Ti(1)−Cl(2)	99.59(8)	Cl(1)−Ti(1)−Cl(2)	108.37(5)
N(1)−Ti(1)−Cl(3)	96.14(8)	N(2)−Ti(1)−Cl(3)	137.15(8)
Cl(1)−Ti(1)−Cl(3)	104.74(5)	Cl(2)−Ti(1)−Cl(3)	103.95(5)

The preparation of pyrazolato complexes of zirconium and hafnium was investigated next (Scheme 2). Treatment of zirconium tetrachloride and hafnium tetrachloride with 3,5-di-*tert*-butylpyrazolatopotassium (4 equiv) in toluene afforded the complexes tetrakis(3,5-di-*tert*-butylpyrazolato)zirconium(IV) (**5**, 90%)[16] and tetrakis(3,5-di-*tert*-butylpyrazolato)hafnium(IV) (**6**, 68%), respectively, as colorless solids. Reaction of **5** and **6** with zirconium tetrachloride and hafnium tetrachloride (3:1 proportion) in dichloromethane for 16 h gave chlorotris(3,5-di-*tert*-butylpyrazolato)zirconium(IV) (**7**, 89%) and chlorotris(3,5-di-*tert*-butylpyrazolato)hafnium(IV) (**8**, 97%), respectively, after workup. Alternatively, **7** and **8** could be prepared in a fashion similar to **1** and **2** by treatment of zirconium tetrachloride and hafnium tetrachloride with a mixture of 3,5-di-*tert*-butylpyrazole and triethylamine (3 equiv) in toluene. However, this procedure led to substantially lower yields (**7**, 31%; **8**, 35%) due to incomplete reaction after several days under reflux. Furthermore, separation of **7** or **8** from free 3,5-di-*tert*-butylpyrazole was difficult due to their similar solubilities. The compositions of **5**−**8** were established by a combination of spectral and analytical data. Furthermore, the structure of **8** was determined by X-ray crystallography (vide infra).

Treatment of niobium pentachloride and tantalum pentachloride with 3,5-di-*tert*-butylpyrazolatopotassium (3 equiv) in toluene at room temperature for 4 days gave dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V) (**9**, 98%) and dichlorotris(3,5-di-*tert*-butylpyrazolato)tantalum(V)[12] (**10**, 83%), respectively, as orange (**9**) and colorless (**10**) crystals (Scheme 3). Reaction of the metal chlorides with excess of 3,5-di-*tert*-butylpyrazolatopotassium (≥4 equiv) in refluxing toluene for 2 days did not lead to further chloride substitution, and only **9** and **10** were isolated. Treatment of **9** and **10** with the metal pentachlorides (2:1 ratio) in dichloromethane at room temperature for 24 h afforded trichlorobis(3,5-di-*tert*-butylpyrazolato)niobium(V) (**11**, 90%) and trichlorobis(3,5-di-*tert*-butylpyrazolato)tantalum(V) (**12**, 84%), respectively, as orange (**11**) and pale yellow (**12**) solids. Compounds **9**−**12** were characterized by spectral and analytical techniques and by an X-ray crystal structure determination for **9**.

Crystal Structures of 3, 8, and 9. The X-ray crystal structure of **3**, **8**, and **9** 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.

The molecular structure of complex **3** is shown in Figure 1. The coordination sphere about the titanium atom possesses approximate tetrahedral geometry (pseudotetrahedral angles span 103.95−116.64°), if the center of the nitrogen−nitrogen bond in the 3,5-di-*tert*-butylpyrazolato moiety is considered as a monodentate ligand. The titanium−chlorine bond lengths range between 2.17 and 2.21 Å. The 3,5-di-*tert*-butylpyrazolato ligand is coordinated in η^2 fashion with titanium−nitrogen bond lengths that are identical within 4σ. The titanium−chlorine and titanium−nitrogen distances in **3** are slightly shorter than the analogous values in **1** (Ti−N, 1.972−1.986 Å; Ti−Cl, 2.247−2.251 Å), whose structure we recently reported.[11] The more electrophilic and less-crowded central metal in **3** can bond more strongly to the ligands, rationalizing the shorter bond lengths. The nitrogen−

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(16) This complex will be described in a forthcoming publication: Guzei, I. A.; Yélamos, C.; Baboul, A. G.; Liable-Sands, L. M.; Rheingold, A. L.; Schlegel, H. B.; Winter, C. H., manuscript in preparation.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **8**

Hf(1)−N(6)	2.132(5)	Hf(1)−N(5)	2.140(6)
Hf(1)−N(1)	2.146(5)	Hf(1)−N(3)	2.153(6)
Hf(1)−N(4)	2.156(5)	Hf(1)−N(2)	2.162(5)
Hf(1)−Cl(1)	2.392(2)	N(1)−N(2)	1.399(6)
N(3)−N(4)	1.396(6)	N(5)−N(6)	1.380(6)
N(6)−Hf(1)−N(5)	37.7(2)	N(6)−Hf(1)−N(1)	88.9(2)
N(5)−Hf(1)−N(1)	114.4(2)	N(6)−Hf(1)−N(3)	129.2(2)
N(5)−Hf(1)−N(3)	116.3(2)	N(1)−Hf(1)−N(3)	128.8(2)
N(6)−Hf(1)−N(4)	92.1(2)	N(5)−Hf(1)−N(4)	92.3(2)
N(1)−Hf(1)−N(4)	134.6(2)	N(3)−Hf(1)−N(4)	37.8(2)
N(6)−Hf(1)−N(2)	100.9(2)	N(5)−Hf(1)−N(2)	137.9(2)
N(1)−Hf(1)−N(2)	37.9(2)	N(3)−Hf(1)−N(2)	95.4(2)
N(4)−Hf(1)−N(2)	97.8(2)	N(6)−Hf(1)−Cl(1)	122.7(2)
N(5)−Hf(1)−Cl(1)	93.13(14)	N(1)−Hf(1)−Cl(1)	91.16(14)
N(3)−Hf(1)−Cl(1)	92.83(14)	N(4)−Hf(1)−Cl(1)	124.91(13)
N(2)−Hf(1)−Cl(1)	113.19(14)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **9**

Nb(1)−N(1)	2.074(3)	Nb(1)−N(5)	2.078(3)
Nb(1)−N(3)	2.077(3)	Nb(1)−N(6)	2.112(3)
Nb(1)−N(4)	2.126(3)	Nb(1)−N(2)	2.152(3)
Nb(1)−Cl(2)	2.4182(9)	Nb(1)−Cl(1)	2.4371(9)
N(1)−N(2)	1.356(3)	N(3)−N(4)	1.379(3)
N(5)−N(6)	1.376(3)		
N(1)−Nb(1)−N(5)	91.19(10)	N(1)−Nb(1)−N(3)	91.56(10)
N(5)−Nb(1)−N(3)	173.36(11)	N(1)−Nb(1)−N(6)	126.45(10)
N(5)−Nb(1)−N(6)	38.34(9)	N(3)−Nb(1)−N(6)	140.81(10)
N(1)−Nb(1)−N(4)	122.93(10)	N(5)−Nb(1)−N(4)	142.16(10)
N(3)−Nb(1)−N(4)	38.29(9)	N(6)−Nb(1)−N(4)	103.84(10)
N(1)−Nb(1)−N(2)	37.37(9)	N(5)−Nb(1)−N(2)	89.36(10)
N(3)−Nb(1)−N(2)	89.16(10)	N(6)−Nb(1)−N(2)	125.97(10)
N(4)−Nb(1)−N(2)	127.30(10)	N(1)−Nb(1)−Cl(2)	124.22(7)
N(5)−Nb(1)−Cl(2)	88.27(8)	N(3)−Nb(1)−Cl(2)	85.18(8)
N(6)−Nb(1)−Cl(2)	80.67(8)	N(4)−Nb(1)−Cl(2)	85.17(8)
N(2)−Nb(1)−Cl(2)	86.86(7)	N(1)−Nb(1)−Cl(1)	82.30(7)
N(5)−Nb(1)−Cl(1)	90.46(8)	N(3)−Nb(1)−Cl(1)	95.90(8)
N(6)−Nb(1)−Cl(1)	81.97(8)	N(4)−Nb(1)−Cl(1)	79.68(8)
N(2)−Nb(1)−Cl(1)	119.63(7)	Cl(2)−Nb(1)−Cl(1)	153.47(3)

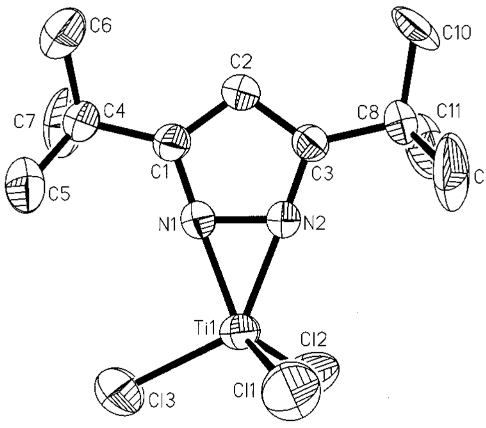


Figure 1. Perspective view of **3** with thermal ellipsoids at the 50% probability level.

nitrogen distance (1.384(3) Å) and the bite angle (N(1)−Ti−N(2) 41.36(9)°) of the pyrazolato ligand in **3** are similar to the corresponding values found in η^2-pyrazolato complexes of several main group and early transition metals.[9−13]

The molecular structure of **8** is presented in Figure 2. Compound **8** is a 7-coordinate monomer bearing three η^2-pyrazolato groups and one chlorine atom. The geometry about the hafnium atom can be envisioned as distorted tetrahedral, if the center of the nitrogen−nitrogen bond in each 3,5-di-*tert*-butylpyrazolato moiety is considered as monodentate ligand. The hafnium−chlorine bond distance is 2.392(2) Å. The η^2-pyrazolato ligands are characterized by hafnium−nitrogen bond lengths that span 2.132−2.162 Å. The narrow range for the hafnium−nitrogen bond distances implies that the pyrazolato ligands are coordinated to hafnium with idealized η^2-bonding. The nitrogen−nitrogen bond lengths (1.380−1.399 Å) and the bite angles associated with the pyrazolato ligands (37.7−37.9°) are similar to the values found in **3** and related pyrazolato complexes that we have reported.[9−13] Interestingly, the pyrazolato ligands in **8** are canted with respect to each other, yielding chiral molecules. Inspection of the unit cell reveals two molecules with Δ configuration and two molecules with Λ configuration, indicating that the compound crystallizes as the racemate.

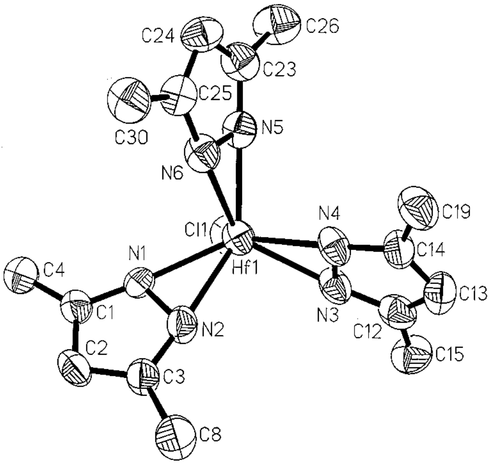


Figure 2. Perspective view of **8** with thermal ellipsoids at the 50% probability level. The *tert*-butyl methyl groups have been removed for clarity.

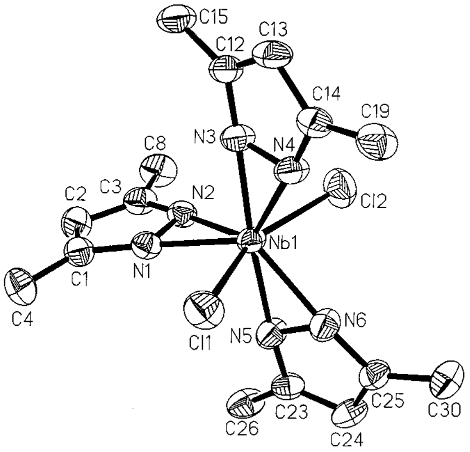


Figure 3. Perspective view of **9** with thermal ellipsoids at the 50% probability level. The *tert*-butyl methyl groups have been removed for clarity.

The molecular structure of **9** is presented in Figure 3. The coordination sphere contains two chlorine atoms and three η^2-pyrazolato ligands. The coordination geometry can be envisioned as distorted trigonal bipyramidal if the centers of the nitrogen−nitrogen bonds in the 3,5-di-*tert*-butylpyrazolato groups are considered as monodentate ligands. The two coplanar pyrazolato ligands correspond to the axial groups of the trigonal bipyramid. Deviation from the idealized 180° angle formed by the center of the nitrogen−nitrogen bond each of these pyrazolato ligands and the niobium atom (pz(centroid)−Nb−pz(centroid) 140.04°) illustrates the geometrical distortions that originate from the axial 3,5-di-*tert*-butylpyrazolato ligands. To accommodate the steric bulk of the *tert*-butyl groups in the axial ligands, the axial pyrazolato ligands are bent away from the third pyrazolato ligand, toward the side of the molecule containing the chlorine atoms. Such a pyrazolato ligand arrangement leads to the wide Cl(1)−Nb−Cl(2) angle of 153.47(3)°. The equatorial plane consists of two chlorine atoms and one pyrazolato ligand whose ring atoms lie in a plane that is approximately perpendicular to the plane of the other two pyrazolato ligands. This ligand arrangement appears to correspond to the minimum energy disposition of the bulky *tert*-butyl groups. The pyrazolato ligands are bonded to niobium in a slightly asymmetric fashion (Nb−N(1) 2.074(3), Nb−N(2) 2.152(3) Å; Nb−N(3) 2.077(3), Nb−N(4) 2.126(3) Å; Nb−N(5) 2.078(3), Nb−N(6) 2.112(3) Å), in which one niobium−nitrogen bond distance within each pyrazolato ligand is 0.034−0.078 Å longer than the other. We have previously suggested that such asymmetric pyrazolato bonding can be attributed to steric crowding in the coordination sphere.[10] The coordination sphere in **9** is certainly very crowded, and accommodation of the steric interactions is the likely cause of the observed asymmetric bonding. The niobium−chlorine bond lengths are 2.4182(9) and 2.4371(9) Å. These values are within the normal range for this linkage but are longer than terminal niobium−chlorine bond lengths that we have found in several niobium imido chloride complexes (range 2.271−2.380 Å).[17] Again, the crowded coordination sphere that is present in **9** probably causes a slight lengthening of the niobium−chlorine bond lengths in this molecule.

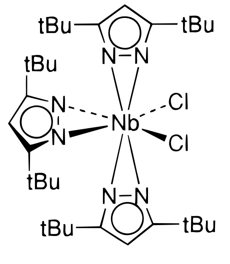
Variable Temperature NMR Behavior. The crystallographically characterized complexes **1**, **3**, **8**, and **9** possess monomeric structures in the solid state in which each *tert*-butyl group within a 3,5-di-*tert*-butylpyrazolato ligand should be magnetically and chemically inequivalent, if the dynamic processes that interconvert the *tert*-butyl groups are slow on the NMR time scale. To probe for such dynamic processes, these complexes were studied by low temperature ^{1}H NMR spectroscopy. Complexes **1**, **2**, and **8** did not show any dynamic behavior at or above −85 °C in toluene-d_8, implying that interconversion of the *tert*-butyl sites is rapid on the NMR time scale in this temperature range. However, the low-temperature ^{1}H NMR spectra of **9** exhibited a dynamic process. This kinetic event was investigated in detail.

At −85 °C in toluene-d_8, the ^{1}H NMR spectrum of **9** revealed three equal intensity *tert*-butyl resonances at δ 1.64, 1.59, and 0.94. The resonances at δ 1.64 and 1.59 merged into a single resonance at −58.0 °C. Upon warming between −70 and −30 °C, the peak at δ 0.94 became very broad and coalesced with the other *tert*-butyl resonance at about −33 °C. A sample with approximately half the concentration of **9** exhibited the same coalescence temperatures, suggesting that the process is intramolecular.

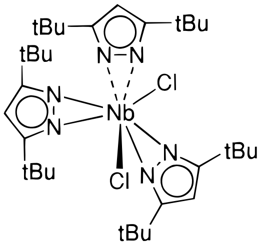
To gain further insight into the dynamic processes, the line-broadening kinetics were studied for the event. Details of the analysis are presented in the Experimental Section and in the Supporting Information. Rate constants were determined by simulating the ^{1}H NMR spectra at various temperatures using the program gNMR.[18] Analysis of the processes with coalescence temperatures of −58.0 and −33 °C as independent kinetic events yielded rates for the −58.0 °C process that were about half as fast as the −33 °C process at a given temperature. The factor of 2 relationship in rates suggested that two kinetic events were not independent but were actually the same process.[19] Moreover, the activation parameters for the separate processes were identical within experimental error. Accordingly, the ^{1}H NMR spectra taken between −72 and +5 °C were modeled using an $A_2B_2C_2$ process. Rate constants are presented in Table 5. Eyring analysis of the rate data afforded the activation parameters $\Delta H^\ddagger = 9.7 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = -2.7 \pm 2.4$ cal/K·mol, and $\Delta G^\ddagger(240\ \mathrm{K}) = 10.3$ kcal/mol. These data allow us to offer some insight into the character of the transition state. The transition state most likely corresponds to a square pyramidal-like species obtained by interconversion of the ground-state isomer **9** to one of the sterically more congested isomers **13** or **14**.[20] Isomers **13** and **14** should be higher in energy than **9**, due to placement of two (**13**) or three (**14**) bulky 3,5-di-*tert*-butylpyrazolato ligands in the equatorial plane. Conversion of **13** or **14** back to **9** by microscopic reverse of the forward process would afford scrambling of the *tert*-butyl sites. Based upon the activation parameters, a transition state that involves substantial η^1-pyrazolato ligand character can be ruled out. High level ab initio calculations on a model titanium pyrazolato complex demonstrated that η^2-pyrazolato ligand coordination is more stable than the η^1-pyrazolato mode by 20−25 kcal/mol.[9] If a η^1-pyrazolato ligand was involved in the transition state, the enthalpy of activation ($\Delta H^\ddagger$) should approach 20−25 kcal/mol. Instead, the observed $\Delta H^\ddagger$ was 9.7 kcal/mol. We caution that the calculations affording the energy difference between the η^2- and η^1-pyrazolato ligand modes were carried out on the sterically unencumbered model complex trichloro-

Table 5. Rates of Reaction of **9** in Toluene-d_8

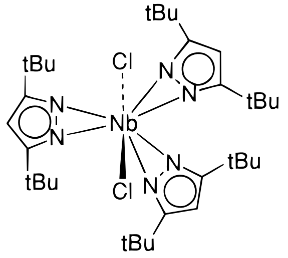
temp, K	k, s^{-1}	temp, K	k, s^{-1}
201	34	233	1110
208	58	246	3180
213	94	263	12 200
218	230	278	31 000
226	510		



9



13



14

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(18) *gNMR*, Version 4; Cherwell Scientific Publishing: Oxford, 1997.

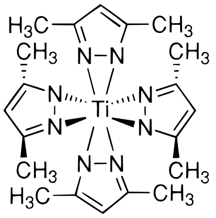
(19) For leading references to dynamic processes involving 5-coordinate transition metal complexes, see: Jesson, J. P.; Muetterties, E. L. In *Dynamic Nuclear Magnetic Resonance*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; pp 253−316. Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 89−171. Faller, J. W. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: Chichester, 1994; pp 3914−3933. Green, M. L. H.; Wong, L.-L.; Sella, A. *Organometallics* **1992**, *11*, 2660.

(20) For relevant comparisons, see: Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 8187. Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 782.

(3,5-dimethylpyrazolato)titanium.[9] Complex **9** possesses a more crowded coordination sphere, and it is possible that there is a smaller energy difference between the η^2 and η^1 modes in this molecule. However, if the transition state possesses significant η^1-pyrazolato ligand character, the entropy of activation ($\Delta S^{\ddagger}$) should be large and positive due to the increased disorder associated with motion from the η^2- to η^1-pyrazolato ligand mode. We propose, based upon the activation parameters, that the transition state leading to site interconversion retains substantial η^2-pyrazolato ligand character. The negative value of $\Delta S^{\ddagger}$ is consistent with a slight increase in order in the transition state due to motion of the *tert*-butyl groups about the crowded coordination sphere. The relatively small value of $\Delta H^{\ddagger}$ probably reflects the loss of optimum bonding between niobium and the nitrogen atoms as well as energy associated with steric interactions.

Discussion

A significant result of the present study pertains to increased documentation of η^2-pyrazolato ligand coordination among the d-block metals. The first example of such a coordination mode in a transition metal was reported by Erker in 1994 in the complex $[Cp_2Zr(C_3H_3N_2)(THF)]BPh_4{\cdot}(THF)_{0.5}$.[8] Initial reports from our laboratory have described the structures of **1** and **15**–**17**,[9–11] all of which contain η^2-pyrazolato ligands. Additionally, molecular orbital calculations on model titanium pyrazolato complexes suggest that η^2-pyrazolato ligand coordination is preferred over the η^1-coordination mode by 20–25 kcal/mol.[9] The precedent of Erker, coupled with our initial reports, suggested that η^2-pyrazolato ligand coordination might be a common coordination mode in high valent early transition metal complexes. The results of the present study are completely consistent with this prediction: the structurally characterized complexes **3**, **8**, and **9** possess only η^2-pyrazolato ligands in the solid state. Furthermore, analysis of the dynamic NMR processes that is observed for **9** suggests that the transition state retains η^2-pyrazolato ligation. The net implications are that η^2-pyrazolato ligands are strongly bonded to early transition metal centers and that this coordination mode is likely to be conserved at temperatures that are accessible in common organic solvents. Therefore, pyrazolato ligands should possess a predictable steric profile and this profile should be easily modified through choice of the substituents on the carbon atoms at the 3- and 5-positions of the pyrazolate ring.



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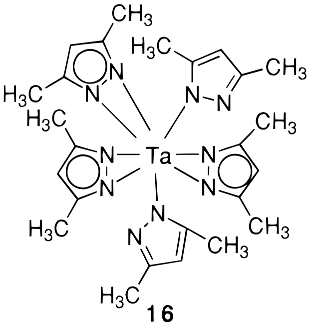

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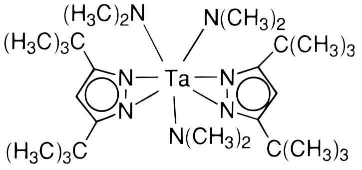
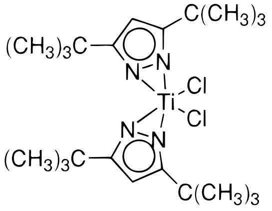
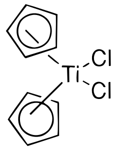


17

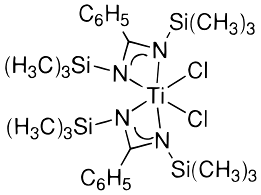
We suggest that there are structural and chemical similarities between the complexes prepared in the present study and well-known complexes in which cyclopentadienyl ligands have replaced the pyrazolato ligands. Comparison of **3** with cyclopentadienyltitanium trichloride provides an instructive example. Treatment of the N-silylated pyrazole **4** with titanium tetrachloride affords **3** as the exclusive product, in close analogy with the reaction of titanium tetrachloride with trimethylsilylcyclopentadiene to afford exclusively cyclopentadienyltitanium trichloride.[15] Like cyclopentadienyltitanium trichloride, **3** is inert toward elimination of chlorotrimethylsilane upon addition of excess reactive trimethylsilyl-based reagents. The bond lengths and angles found in the crystal structure of **3** (Ti–N, 1.955–1.963 Å; Ti–Cl, 2.1717–2.1901 Å; Cl–Ti–Cl, 103.95–108.37°) can be compared to the related values observed in cyclopentadienyltitanium trichloride[21] (Ti–Cp(centroid), 2.05 Å; Ti–Cl, 2.201–2.248 Å; Cl–Ti–Cl, 102.2–104.1°). The titanium–chlorine and titanium–nitrogen bond lengths in **3** are slightly shorter than the titanium–carbon and titanium–chlorine bond lengths found in cyclopentadienyltitanium trichloride. These data are consistent with the 3,5-di-*tert*-butylpyrazolato ligand being a poorer donor than the cyclopentadienyl ligand, which results in shorter bond lengths due to increased orbital overlap between the titanium atom and donor atoms. Of course, the lower coordination number of **3**, compared to cyclopentadienyltitanium trichloride, leads to shorter bond lengths due to increased electronic unsaturation with concomitant improvement of bonding interactions.



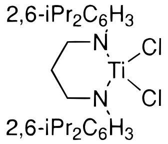
1
Ti-Cl 2.247(4), 2.251(3) Å
Cl-Ti-Cl 100.5(2)°



18
Ti-Cl 2.361(1), 2.367(2) Å
Cl-Ti-Cl 94.43(6)°



19
Ti-Cl 2.257(3) Å
Cl-Ti-Cl 98.6(1)°



20
Ti-Cl 2.257(2) Å
Cl-Ti-Cl 107.77(2)°

Comparison between the structures of **1**[11] and titanocene dichloride[22] (**18**) yields similar conclusions. Complex **1** exhibits shorter bond lengths (Ti–N, 1.972–1.986 Å; Ti–Cl, 2.247–2.251 Å) than the related values in **18** (Ti–Cp(centroid), 2.056–2.060 Å; Ti–Cl, 2.361–2.367 Å). Again, the shorter bond lengths associated with the pyrazolato complex compared to the analogous cyclopentadienyl complex are consistent with the pyrazolato ligand being a poorer donor ligand than cyclopentadienyl. Interestingly, the bond lengths and angles about the

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coordination sphere in **1** are between the related values found in the bisamidinato complex **19**[23] (Ti−N, 2.066−2.106 Å; Ti−Cl, 2.257(3) Å; Cl−Ti−Cl, 98.6(1)°) and the chelating diamido complex **20** (Ti−N, 1.839−1.856 Å; Ti−Cl, 2.257(2) Å; Cl−Ti−Cl, 107.77(2)°).[24] These data support the idea of η^2-pyrazolato ligands acting as four-electron donors in a fashion similar to amidinato and amido ligands. The shorter titanium−nitrogen bond lengths in **1** compared to the analogous values for **18** and **19** imply that complexes containing η^2-pyrazolato ligands should possess more electrophilic metal centers than those found in structurally related cyclopentadienyl and amidinato complexes. Recently, cationic complexes derived from **20**[24] and bis(amidinato)titanium fragments[25] have been reported to be highly active olefin polymerization catalysts. Therefore, it is very likely that early transition metal pyrazolato chloride complexes can be employed in the development of new reactive complexes. The fact that the titanium−nitrogen bond lengths in **1** are significantly different than those of **19** and **20** argues that the η^2-pyrazolato ligand imparts unique electronic characteristics to the metal to which it is bonded. Resultant complexes may therefore have different reactivity characteristics than complexes bearing other nitrogen donors. Toward this end, we are exploring the chemistry of imido complexes derived from **1**[26] and are examining the use of bis(pyrazolato)metal complexes as precatalysts for olefin polymerization.[27] These studies will be published in due course.

Experimental Section

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane and toluene were freshly distilled from sodium. Diethyl ether and tetrahydrofuran were distilled from purple solutions of sodium benzophenone ketyl just prior to use. Dichloromethane was freshly distilled from calcium hydride. The metal chloride starting materials and chlorotrimethylsilane were used as received from Aldrich Chemical Co. Triethylamine (Aldrich Chemical Co.) was vacuum distilled from sodium before use. 3,5-Di-*tert*-butylpyrazole[28] and 3,5-di-*tert*-butylpyrazolatopotassium[12] were prepared according to literature procedures. Compound **4** exhibited a dynamic process at ambient temperature that led to broad peaks in the ^{1}H and ^{13}C(^{1}H} NMR spectra;[29] the spectra reported below were obtained at 85 °C to observe sharp resonances.

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

Preparation of Dichlorobis(3,5-di-*tert*-butylpyrazolato)titanium(IV) (1). A solution of 3,5-di-*tert*-butylpyrazole (3.99 g, 22.1 mmol) and triethylamine (3.01 mL, 22.1 mmol) in toluene (80 mL) was added by cannula to a solution of titanium tetrachloride (2.00 g, 10.5 mmol) in toluene (50 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 16 h. The resultant mixture was filtered through a 2-cm pad of Celite on a coarse glass frit and the volatile components were removed under reduced pressure to afford **1** as a spectroscopically pure yellow solid (4.68 g, 93%): mp 156 °C (lit. mp 157 °C[11]); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.68 (s, 2 H, ring C*H*), 1.29 (s, 36 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 161.08 (*C*C(CH$_3$)$_3$), 114.60 (ring *C*H), 32.53 (C*C*(CH$_3$)$_3$), 30.18 (CC(*C*H$_3$)$_3$).

Preparation of Chlorotris(3,5-di-*tert*-butylpyrazolato)titanium(IV) (2). A solution of 3,5-di-*tert*-butylpyrazole (1.47 g, 8.17 mmol) and triethylamine (1.47 mL, 10.54 mmol) in toluene (50 mL) was added by cannula to a solution of titanium tetrachloride (0.50 g, 2.64 mmol) in toluene (50 mL) at 0 °C. The mixture was stirred at ambient temperature for 10 days. The resultant mixture was filtered through a 2-cm pad of Celite on a coarse glass frit, and the volatile components were removed under reduced pressure to afford **2** as a yellow powder (1.53 g, 91%): mp 165 °C (lit. mp 169 °C[12]); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.43 (s, 3 H, ring C*H*), 1.16 (s, 54 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 158.55 (*C*C(CH$_3$)$_3$), 110.63 (ring *C*H), 32.33 (C*C*(CH$_3$)$_3$), 30.57 (CC(*C*H$_3$)$_3$).

Preparation of Trichloro(3,5-di-*tert*-butylpyrazolato)titanium(IV) (3). A solution of **4** (2.80 g, 11.09 mmol) in toluene (35 mL) was added by cannula to a solution of titanium tetrachloride (1.89 g, 9.98 mmol) in toluene (50 mL) at 0 °C. The yellow suspension was allowed to warm to room temperature and was stirred for 16 h. The resultant yellow solution was filtered through a 2-cm pad of Celite on a coarse glass frit and the volatile components were removed under reduced pressure to afford a yellow powder. The yellow powder was washed with cold hexane (20 mL) and was then dried under vacuum to yield **4** (3.10 g, 93%). The compound was obtained as large yellow crystals by crystallization from hexane at −20 °C: mp 105 °C; IR (Nujol, cm^{-1}) 1509 (m), 1251 (m), 1237 (m), 1094 (m), 1016 (w), 962 (m), 844 (w), 801 (s); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.99 (s, 1 H, ring C*H*), 1.42 (s, 18 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 164.01 (*C*C(CH$_3$)$_3$), 117.54 (ring *C*H), 33.17 (C*C*(CH$_3$)$_3$), 30.12 (CC(*C*H$_3$)$_3$). Anal. Calcd for $C_{11}H_{19}N_2Cl_3Ti$: C, 39.61; H, 5.74; N, 8.40. Found: C, 39.57; H, 5.84; N, 8.47.

Preparation of 1-Trimethylsilyl-3,5-di-*tert*-butylpyrazole (4). Chlorotrimethysilane (0.70 mL, 5.52 mmol) was added dropwise at ambient temperature to a solution of potassium 3,5-di-*tert*-butylpyrazolate (1.21 g, 5.54 mmol) in tetrahydrofuran (50 mL). The white suspension was stirred at ambient temperature for 24 h. Filtration through a 2-cm pad of Celite on a coarse glass frit, followed by removal of the solvent under reduced pressure, afforded **3** as a colorless liquid (1.13 g, 81%): IR (neat, cm^{-1}) 2963 (s), 1559 (w), 1540 (m), 1507 (w), 1457 (w), 1419 (w), 1362 (m), 1306 (m), 1260 (s), 1201 (w), 1087 (vs), 1019 (vs), 846 (m), 799 (vs); ^{1}H NMR ($C_6D_5CD_3$, 85 °C, δ) 6.00 (s, 1 H, ring C*H*), 1.30 (s, 18 H, C(C*H*$_3$)$_3$), 0.46 (s, 9 H, Si(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, 85 °C, ppm) 162.13 (s, *C*-C(CH$_3$)$_3$), 101.88 (s, ring *C*H), 32.32 (s, *C*(CH$_3$)$_3$), 31.29 (s, C(*C*H$_3$)$_3$), 3.14 (s, Si(*C*H$_3$)$_3$). HRMS Calcd for $C_{14}H_{28}N_2Si$, 252.20218. Found, 252.2022. MS (20 eV) *m*/*e* (assignment, rel int. (%)) 252 (M$^+$, 19), 237 (M$^+$ − CH$_3$, 100), 73 (Si(CH$_3$)$_3$$^+$, 50). Anal. Calcd for $C_{14}H_{28}N_2Si$: C, 66.60; H, 11.18; N, 11.10. Found: C, 64.17; H, 10.91; N, 11.07.

Preparation of Tetrakis(3,5-di-*tert*-butylpyrazolato)zirconium(IV) (5). A 100-mL Schlenk flask was charged with zirconium tetrachloride (0.24 g, 1.03 mmol), potassium 3,5-di-*tert*-butylpyrazolate (1.00 g, 4.58 mmol), and toluene (60 mL). The mixture was stirred for 16 h at ambient temperature. The reaction mixture was filtered through a 2-cm pad of Celite on a coarse glass frit to give a colorless solution. The volatile components were removed under reduced pressure to afford **5** as a colorless solid (0.75 g, 90%): dec pt 226 °C (lit. dec pt. 226 °C[16]); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.14 (s, 4 H, ring C*H*), 1.03 (s, 72 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 158.67 (*C*C(CH$_3$)$_3$), 105.37 (ring *C*H), 31.93 (C*C*(CH$_3$)$_3$), 30.47 (CC(*C*H$_3$)$_3$).

Preparation of Tetrakis(3,5-di-*tert*-butylpyrazolato)hafnium(IV) (6). In a fashion similar to the preparation of **5**, hafnium tetrachloride (0.33 g, 1.03 mmol) and potassium 3,5-di-*tert*-butylpyrazolate (1.00 g, 4.58 mmol) were reacted to afford **6** as a colorless solid (0.63 g, 68%): dec pt. 202 °C; IR (Nujol, cm^{-1}) 1524 (w), 1509 (m), 1363

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(m), 1304 (w), 1260 (s), 1230 (m), 1205 (w), 1095 (s), 1025 (s), 994 (m), 865 (w), 802 (s), 721 (w); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.27 (s, 4 H, ring C*H*), 1.02 (s, 72 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 158.58 (*C*C(CH$_3$)$_3$), 105.47 (ring *C*H), 31.91 (C*C*(CH$_3$)$_3$), 30.44 (CC(*C*H$_3$)$_3$). Anal. Calcd for $C_{44}H_{76}HfN_8$: C, 59.01; H, 8.55; N, 12.51. Found: C, 58.99; H, 8.63; N, 12.45.

Preparation of Chlorotris(3,5-di-*tert*-butylpyrazolato)zirconium(IV) (7). A 100-mL Schlenk flask was charged with **5** (0.40 g, 0.49 mmol), zirconium tetrachloride (0.050 g, 0.21 mmol), and dichloromethane (50 mL). The mixture was stirred for 16 h at ambient temperature. The volatile components were removed under reduced pressure and the resultant colorless solid was extracted with hexane (50 mL). After filtration through a 2-cm pad Celite on a coarse glass frit, the volatile components were removed under reduced pressure to afford **7** as a colorless solid (0.39 g, 89%): mp 146 °C; IR (Nujol, cm^{-1}) 1514 (s), 1484 (w), 1365 (s), 1299 (w), 1253 (s), 1233 (s), 1205 (w), 1120 (w), 1022 (m), 987 (s), 815 (s), 725 (m); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.35 (s, 3 H, ring C*H*), 1.13 (s, 54 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 160.02 (*C*C(CH$_3$)$_3$), 108.39 (ring *C*H), 32.12 (C*C*(CH$_3$)$_3$), 30.39 (CC(*C*H$_3$)$_3$). Anal. Calcd for $C_{33}H_{57}ClN_6Zr$: C, 59.65; H, 8.65; N, 12.65. Found: C, 58.77; H, 8.79; N, 12.85.

Preparation of Chlorotris(3,5-di-*tert*-butylpyrazolato)hafnium(IV) (8). In a fashion similar to the preparation of **7**, **6** (0.55 g, 0.61 mmol) and hafnium tetrachloride (0.10 g, 0.31 mmol) were reacted to afford **8** as a colorless solid (0.59 g, 97%): mp 149 °C; IR (Nujol, cm^{-1}) 1513 (m), 1365 (s), 1299 (w), 1261 (s), 1235 (w), 1206 (w), 1096 (s), 1023 (s), 987 (m), 807 (s), 723 (m); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.47 (s, 3 H, ring C*H*), 1.13 (s, 54 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 159.80 (*C*C(CH$_3$)$_3$), 108.35 (ring *C*H), 32.10 (C*C*(CH$_3$)$_3$), 30.35 (CC(*C*H$_3$)$_3$). Anal. Calcd for $C_{33}H_{57}ClHfN_6$: C, 52.72; H, 7.64; N, 11.18. Found: C, 52.64, H, 7.79: N, 11.17.

Preparation of Dichlorotris(3,5-di-*tert*-butylpyrazolato)niobium(V) (9). In a fashion similar to the preparation of **5**, niobium pentachloride (1.00 g, 3.70 mmol) and potassium 3,5-di-*tert*-butylpyrazolate (2.67 g, 12.2 mmol) were reacted to afford **9** as an orange crystalline solid (2.55 g, 98%): mp 214 °C; IR (Nujol, cm^{-1}) 1518 (m), 1363 (s), 1257 (s), 1235 (m), 1198 (w), 1092 (m), 1020 (m), 983 (w), 800 (s), 722 (w); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.64 (s, 3 H, ring C*H*), 1.29 (s, 54 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 156.81 (*C*C(CH$_3$)$_3$), 116.15 (ring *C*H), 32.10 (C*C*(CH$_3$)$_3$), 30.57 (CC(*C*H$_3$)$_3$). Anal. Calcd for $C_{33}H_{57}Cl_2N_6Nb$: C, 56.49; H, 8.19; N, 11.98. Found: C, 56.22; H, 7.99; N, 11.81.

Preparation of Dichlorotris(3,5-di-*tert*-butylpyrazolato)tantalum(V) (10). In a fashion similar to the preparation of **9**, tantalum pentachloride (0.30 g, 0.84 mmol) and potassium 3,5-di-*tert*-butylpyrazolate (1.00 g, 4.58 mmol) were reacted to afford **10** as a colorless crystalline solid (0.55 g, 83%): mp 211 °C; IR (Nujol, cm^{-1}) 1520 (m), 1363 (s), 1256 (s), 1236 (s), 1201 (w), 1093 (m), 1034 (w), 984 (m), 819 (s), 800 (s), 715 (w); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.76 (s, 3H, pz ring C*H*), 1.29 (s, 54 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 156.84 (s, *C*C(CH$_3$)$_3$), 115.24 (s, pz ring *C*H), 32.07 (C*C*(CH$_3$)$_3$), 30.56 (CC(*C*H$_3$)$_3$). Anal. Calcd for $C_{33}H_{57}Cl_2N_6Ta$: C, 50.19; H, 7.28; N, 10.64. Found: C, 50.30; H, 7.39; N, 10.44.

Preparation of Trichlorobis(3,5-di-*tert*-butylpyrazolato)niobium(V) (11). In a fashion similar to the preparation of **7**, **9** (1.00 g, 1.43 mmol) and niobium pentachloride (0.190 g, 0.703 mmol) were reacted to afford **11** as an orange crystalline solid (1.07 g, 90%): mp 242−244 °C; IR (Nujol, cm^{-1}) 3130 (w), 1654 (w), 1540 (w), 1516 (s), 1484 (w), 1426 (s), 1367 (s), 1253 (s), 1236 (s), 1202 (w), 1093 (w), 1033 (w), 1019 (s), 969 (s), 838 (m), 831 (m), 800 (w), 722 (m); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.93 (s, 2 H, ring C*H*), 1.51 (s, 36 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 159.99 (*C*C(CH$_3$)$_3$), 120.86 (ring *C*H), 32.67 (C*C*(CH$_3$)$_3$), 30.06 (CC(*C*H$_3$)$_3$). Anal. Calcd for $C_{22}H_{38}Cl_3N_4Nb$: C, 47.37; H, 6.87; N, 10.04. Found: C, 47.20; H, 6.79; N, 10.25.

Preparation of Trichlorobis(3,5-di-*tert*-butylpyrazolato)tantalum(V) (12). In a fashion similar to the preparation of **11**, **10** (1.00 g, 1.27 mmol) and tantalum pentachloride (0.230 g, 0.642 mmol) were reacted to afford **12** as a pale yellow crystalline solid (1.03 g, 84%): mp 239 °C; IR (Nujol, cm^{-1}) 3134 (w), 1657 (w), 1544 (w), 1517 (s), 1485 (w), 1367 (s), 1254 (s), 1237 (s), 1205 (w), 1093 (m), 1034 (m), 1021 (m), 969 (s), 830 (m), 800 (s), 719 (m); ^{1}H NMR ($CDCl_3$, 22 °C, δ) 6.95 (s, 2 H, ring C*H*), 1.50 (s, 36 H, C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C, ppm) 156.65 (*C*C(CH$_3$)$_3$), 119.49 (ring *C*H), 32.64 (C*C*(CH$_3$)$_3$), 30.11 (CC(*C*H$_3$)$_3$). Anal. Calcd for $C_{22}H_{38}Cl_3N_4Ta$: C, 40.91; H, 5.93; N, 8.67. Found: C, 40.69; H, 5.88; N, 8.35.

X-ray Crystallography for 3, 8, and 9. All 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 was integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with the program SADABS and the structures were solved and refined using the programs of SHELXS-86 and SHELXL-93.[30]

For **3**, 17 168 total data were averaged to yield 3464 ($R_{\mathrm{int}} = 0.066$) independent reflections. The compound crystallizes as yellow irregular fragments. The asymmetric unit of the unit cell contains one 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. One of the two *tert*-butyl groups was severely disordered and was modeled with partial (occupancy = 0.5) carbon atoms, viz., C(9)−C(11).

For **8**, 20 341 total data were averaged to yield 8329 ($R_{\mathrm{int}} = 0.093$) independent reflections. The colorless crystals contain arrays of molecular complexes with no associated solvent or ions. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound. All atoms occupy general positions in the cell. Moderate disorder in the *tert*-butyl groups was observed and is reflected in the large thermal parameters associated with these atoms.

For **9**, 22 170 total data were averaged to yield 8140 ($R_{\mathrm{int}} = 0.072$) independent reflections. The yellow compound crystallizes as plates and rods containing molecular complexes with no associated solvent or ions. Hydrogen atoms were calculated and assigned to ride on the carbons to which they were bound. All atoms occupy general positions in the unit cells.

NMR Kinetic Measurements on 9. A 5-mm NMR tube was charged with **9** (0.015 g, 0.021 mmol) and toluene-*d*$_8$ (0.80 mL) and was fitted with a rubber septum. The tube was transferred to the NMR probe and the ^{1}H NMR spectra (500 MHz) were recorded between −85 and +22 °C. At −85 °C, three equal intensity *tert*-butyl resonances were observed at δ 1.64, 1.59, and 0.94. Upon warming, the *tert*-butyl resonances at δ 1.64 and 1.59 coalesced at −58.0 °C to give a broad peak at δ 1.60. The resultant 2:1 resonances at δ 1.60 and 0.94 coalesced at about −33 °C to afford a single resonance at δ 1.36. At 22 °C, a single sharp *tert*-butyl resonance was observed at δ 1.36. The same coalescence temperatures were observed in a sample of **9** (0.007 g, 0.010 mmol) in toluene-*d*$_8$ (0.80 mL) that was about half as concentrated. The dynamic process was modeled as an $A_2B_2C_2$ exchange using the program gNMR.[18] For data, see the text and Supporting Information. Errors in the kinetic data are reported at the 95% confidence level.

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Supporting Information Available: Tables listing kinetics data and analyses for the dynamic NMR processes observed for **9**. X-ray crystallographic files, in CIF format, for the structure determination of **3**, **8**, and **9** are available on the Internet only. This material is available free of charge via the Internet at http://pubs.acs.org.

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