Exploration of the Suitability of Bicyclic Guanidinates as Ligands in Catalytic Chemistry Mediated by Titanium[†]

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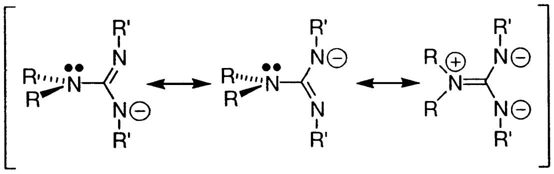
The synthesis, structure, and reactivity of titanium complexes supported by the bicyclic guanidinate ligand derived from 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) are described. In situ reaction between a THF solution of the lithium salt, $(\text{hppLi})_n$, and titanium chloride starting materials afforded the series of compounds $\text{Ti(hpp)}_n\text{Cl}_{4-n}(\text{THF})_x$ [$n = 1$, $x = 1$ (**1**); $n = 2$, $x = 0$ (**3**); $n = 3$, $x = 0$ (**4**)]. The dimeric, base-free complex $[\text{Ti(hpp)Cl}_2(\mu\text{-Cl})]_2$ (**2**) was synthesized from the reaction of the silylated ligand precursor, hppSiMe_3, with TiCl_4 in CH_2Cl_2. Preliminary olefin polymerization studies of **1**−**3** using MAO as activator indicated low activities. The reaction between **3** and 2 equiv of AlMe_3 resulted in formation of a novel trimetallic Ti(III) species, $\text{Ti}\{\text{AlMe}_2(\text{hpp})_2\}\text{Cl}(\mu\text{-Cl})\text{AlMe}_3$ (**5**), highlighting the noninnocent behavior of the ligands. The bis(benzyl) complex $\text{Ti(hpp)}_2(\text{CH}_2\text{Ph})_2$ (**6**) was synthesized from the alkane elimination reaction between the neutral ligand precursor, hppH, and $\text{Ti(CH}_2\text{Ph)}_4$. Attempted generation of the corresponding mono-benzyl cation through reaction with the neutral borane $\text{B(C}_6\text{F}_5)_3$ again afforded reduced species. The synthesis of titanium *tert*-butylimido compounds $[\text{Ti}(\mu\text{-N}^t\text{Bu})(\text{hpp})\text{Cl}]_2$ (**7**) and $[\text{Ti(N}^t\text{Bu)(hpp)}(\mu\text{-hpp})]_2$ (**8**) from the salt metathesis reaction of 1 and 2 equiv of $(\text{hppLi})_n$, respectively, with $\text{Ti(N}^t\text{Bu)Cl}_2(\text{py})_3$ is reported. The molecular structures of compounds **2** and **3** and **5**−**8** are reported, and the distribution of π-electron density throughout the guanidinate ligands is discussed in detail.

Introduction

Featured among the many classes of nitrogen-based ligands that have been investigated as alternatives to the cyclopentadienyl anion in early transition metal chemistry are the amidinates $[\text{RC}\{\text{NR}'\}_2]^-$ and guanidinates $[\text{R}_2\text{NC}\{\text{NR}'\}_2]^-$.[1] Tuning the properties of the former type of ligand to meet specific requirements has, to date, largely been restricted to investigations of the steric demands of the carbon[2] and nitrogen substituents.[3] An additional feature associated with the guanidinate anions that allows a certain degree of control to be exercised over the electron donor properties to a metal center is the presence of a third, "zwitterionic" resonance structure arising from delocalization of the N_{amide} lone-pair into the "CN_3" core of the ligands (**I**, Scheme 1). The extent to which this component is able to contribute to the overall bonding is dependent upon the angle (α) between the "$\text{R}_2\text{N}-$" and "NCN" moieties, with maximum contribution arising from a parallel arrangement (α = 0°), which generates the correct orbital alignment for π-overlap between the N lone-pair and the p-orbital of the sp^2-carbon atom.

Scheme 1. Principal Resonance Structures of the Generic Guanidinate Anion $[\text{R}_2\text{NC}\{\text{NR}'\}_2]^-$



(**I**)

To a varying degree, the steric demands of the nitrogen substituents have been shown to effect the angle α and, hence, influence the extent of delocalization from the amide nitrogen atom. For example, in the aluminum dichloro complexes $\text{Al}[\text{R}_2\text{NC}\{\text{N}^i\text{Pr}\}_2]\text{Cl}_2$,[4] when the R-substituent is a relatively bulky $-\text{SiMe}_3$ group, the α-value is relatively large (86.2°), while in the analogous $-\text{N}Me_2$ derivative, α = 28.4°. It has also been argued that an increase in the electron-withdrawing nature of the silyl group versus the methyl group contributes to the observed distribution of π-electron density within the guanidinate framework. Concurrent with this reduction in α, there is a pronounced shorten-

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[†] Part of this work, including the crystal structures of compounds **3** and **5**, has previously been communicated. See ref 6.

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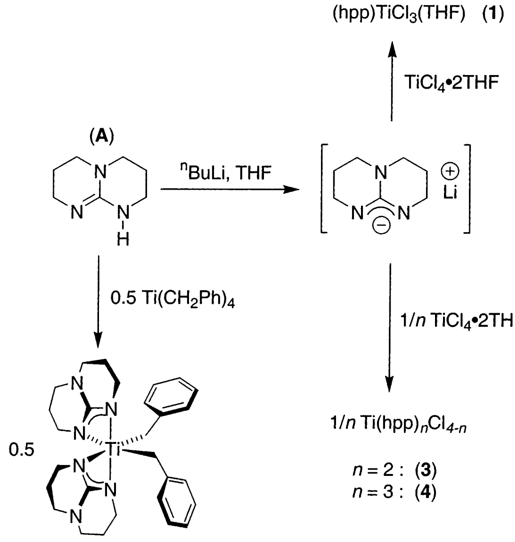
10.1021/om0341092 CCC: $25.00

Scheme 2



ing of the $R_2N{-}C$ distance from 1.400(4) Å in the silyl derivative to 1.343(5) Å in the methyl derivative, commensurate with increased delocalization into the carbon−nitrogen bond.

An alternative method to the incorporation of silyl substituents by which the π-overlap may be promoted is to constrain the two components of the ligand into a cyclic structure such that a conformation approaching coplanarity is enforced. To investigate the effect of this imposed geometry, we have initiated a program into the study of the commercially available bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH, **A**, Scheme 2), as a source of neutral[5] and anionic ligands[6] in transition metal chemistry. Previous work employing $[hpp]^-$ as a ligand has principally focused on its application as a bridging group between multiply bonded metal complexes,[7] although recent accounts of monomeric and dimeric main-group (Sn, Al) metal complexes containing bridging and chelating coordination modes have been reported.[4,8] A simple explanation for the observed tendency of the $[hpp]^-$ anion to bridge two metal centers has been offered, namely, that the incorporation of the $N_{amidine}$ substituents into the bicyclic framework of the ligand promotes a parallel projection of the donor orbitals. In contrast, steric interactions between substituents in acyclic analogues force the orbitals to point toward the "mouth" of the ligand, favoring a chelating coordination mode.

A number of group 4 metal complexes incorporating the $[hpp]^-$ anion have previously been presented in the patent literature and investigated as precatalysts for the polymerization of ethylene.[9] However, structural analyses of the complexes were not performed, and detailed discussion concerning the nature of the interaction between the $[hpp]^-$ anion and the metal center was not reported. We have previously communicated our initial studies of the $[hpp]^-$ anion as a ligand in titanium chemistry[6] and report here further studies into the synthesis of hpp complexes of titanium, presenting a detailed examination of the bonding within such complexes.

Experimental Section

General Experimental Procedures. All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agent and degassed prior to use. hppH (Fluka), ${}^nBuLi$ (2.5 M solution in hexanes, Acros), $TiCl_4$ (Aldrich), and $AlMe_3$ (2.0 M solution in hexanes, Aldrich) were purchased from commercial sources and used without further purification. $TiCl_4(THF)_2$,[10] $Ti(CH_2Ph)_4$,[11] and $Ti(N^tBu)Cl_2(py)_3$[12] were synthesized using published procedures. $hppSiMe_3$ was synthesized from the reaction of $(hppLi)_n$ and $SiMe_3Cl$[13] and used without further purification. Elemental analyses were performed by S. Boyer at London Metropolitan University. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300 (^1H) and 75 ($^{13}C\{^1H\}$) MHz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances. Coupling constants, *J*, are quoted in Hz.

$Ti(hpp)Cl_3(THF)$ (1). A solution of hppH (0.50 g, 3.6 mmol) in THF was cooled to 0 °C, and 1 equiv of ${}^nBuLi$ (2.5 M solution in hexanes) was added. The solution was allowed to warm to room temperature and stirred for 1 h. The resulting mixture was added to a solution of $TiCl_4(THF)_2$ (1.20 g, 3.6 mmol) in THF at −78 °C, during which time a color change from yellow to red was observed. After stirring at ambient temperature for 15 h, the volatile components were removed and the product was extracted with CH_2Cl_2. Removal of the solvent afforded 1.11 g of **1** (85%) as a red solid. Analytically pure samples were obtained from slow cooling of a warm (60 °C) saturated toluene solution to room temperature.

Anal. Calcd for $C_{11}H_{20}Cl_3N_3OTi$: C, 36.2; H, 5.5; N, 11.5. Found: C, 36.0; H, 5.7; N, 11.6. ^1H NMR (C_6D_6, 298 K): δ 3.75 (m, 8H, CH_2 + *THF*), 2.10 (br m, 4H, CH_2), 1.36 (br m, 4H, CH_2), 1.10 (m, 4H, *THF*). ^{13}C NMR (C_6D_6, 298 K): δ 160.0 (CN_3), 70.3 (*THF*), 49.7 (CH_2), 45.4 (CH_2), 25.8 (*THF*), 21.7 (CH_2). MS (EI^+, *m*/*z*, ^{35}Cl): 291 $[M - THF]^+$, 255 $[M - THF - Cl]^+$.

$[Ti(hpp)Cl_2(\mu\text{-}Cl)]_2$ (2). A solution of $hppSiMe_3$ (1.43 g, 6.8 mmol) in CH_2Cl_2 was added dropwise to a solution of $TiCl_4$ (1.28 g, 6.8 mmol) in CH_2Cl_2 at room temperature. The reaction was stirred for 15 h, during which time formation of a red precipitate was observed. Filtration and drying under vacuum afforded 1.22 g of **2** as a microcrystalline solid (62%). Analytically pure samples were obtained from slow cooling of a warm (60 °C) saturated toluene solution to room temperature.

Anal. Calcd for $C_7H_{12}Cl_3N_3Ti$: C, 28.8; H, 4.1; N, 14.4. Found: C, 28.7; H, 4.2; N, 14.5. ^1H NMR (CD_2Cl_2, 298 K): δ 4.04 (t, $^3J_{HH}$ = 5.8, 4H, CH_2), 3.29 (t, $^3J_{HH}$ = 5.9, 4H, CH_2), 1.97 (m, 4H, CH_2). ^{13}C NMR (CD_2Cl_2, 298 K): δ 160.3 (CN_3), 50.1 (CH_2), 46.2 (CH_2), 22.2 (CH_2). MS (EI^+, *m*/*z*, ^{35}Cl): 292 $[M]^+$, 255 $[M - Cl]^+$ (where M = "$Ti(hpp)Cl_3$").

$Ti(hpp)_2Cl_2$ (3). This compound was prepared by the procedure outlined for **1**, using 1.00 g of hppH (7.2 mmol) and 1.20 g of $TiCl_4(THF)_2$ (3.6 mmol). Extraction with CH_2Cl_2 afforded 1.23 g of **3** (86%) as an orange solid. Crystals were

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obtained by the slow cooling of a warm (60 °C) toluene solution to 0 °C.

Anal. Calcd for $C_{14}H_{24}Cl_2N_6Ti$: C, 42.6; H, 6.1; N, 21.3. Found: C, 42.4; H, 6.2; N, 21.1. ^{1}H NMR (C_6D_6, 298 K): δ 3.86 (t, $^3J_{HH} = 5.7$, 8H, CH_2), 2.26 (t, $^3J_{HH} = 5.9$, 8H, CH_2), 1.34 (m, 8H, CH_2). ^{13}C NMR (C_6D_6, 298 K): δ 160.2 (CN_3), 47.1 (CH_2), 45.7 (CH_2), 22.6 (CH_2). MS (EI$^+$, *m/z*, ^{35}Cl): 394 [M]$^+$, 358 [M − Cl]$^+$, 256 [M − hpp]$^+$.

Ti(hpp)$_3$Cl (4). This compound was prepared by the procedure outlined for **1**, using 1.00 g of hppH (7.2 mmol) and 0.80 g of $TiCl_4(THF)_2$ (2.4 mmol). Extraction with CH_2Cl_2 and recrystallization from hot toluene afforded 0.35 g of **4** (29%) as an analytically pure orange solid.

Anal. Calcd for $C_{21}H_{36}ClN_9Ti$: C, 50.66; H, 7.29; N, 25.32. Found: C, 50.60; H, 7.29; N, 25.37. ^{1}H NMR (C_6D_6, 298 K): δ 3.82 (t, $^3J_{HH} = 5.7$, 4H, CH_2), 2.64 (t, $^3J_{HH} = 5.9$, 4H, CH_2), 1.67 (m, 2H, CH_2). ^{13}C NMR (C_6D_6, 298 K): δ 160.0 (CN_3), 46.7 (CH_2), 45.7 (CH_2), 23.8 (CH_2). MS (EI$^+$, *m/z*, ^{35}Cl): 497 [M]$^+$, 462 [M − Cl]$^+$, 358 [M − hpp]$^+$.

Ti{AlMe$_2$(hpp)$_2$}Cl(μ-Cl)AlMe$_3$ (5). A slurry of **3** (0.40 g, 1.0 mmol) in toluene was cooled to 0 °C, and 2 equiv of $AlMe_3$ (2.0 M solution in toluene) was added. The mixture was allowed to warm to room temperature and stirred for 15 h. Removal of the volatiles and extraction with toluene afforded a green solution, from which 0.15 g of **5** (29%) precipitated.

Anal. Calcd for $C_{19}H_{39}Al_2Cl_2N_6Ti$: C, 43.5; H, 7.5; N, 16.0. Found: C, 43.5; H, 7.7; N, 15.8. ESR (toluene, 298 K): $g_{iso} = 1.9617$ (width 8.3 G). MS (EI$^+$, *m/z*, ^{35}Cl): 303 [Al(hpp)$_2$]$^+$, 180 [Al(hpp)Me]$^+$.

Ti(hpp)$_2$(CH$_2$Ph)$_2$ (6). A solution of hppH (0.50 g, 3.6 mmol) in toluene was added dropwise to a solution of $Ti(CH_2Ph)_4$ (0.74 g, 1.8 mmol) that had been precooled −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. Removal of the volatile component afforded **6** as a red solid, which was crystallized by cooling a saturated Et_2O solution to −35 °C. Yield: 0.57 g, 63%.

^{1}H NMR (C_6D_6, 298 K): δ 7.26 (m, 8H, CH$_2$*Ph*), 6.91 (tt, $^3J_{HH} = 6.6$, $^4J_{HH} = 2.1$, 2H, Ph-H_{para}), 3.35 (t, $^3J_{HH} = 5.7$, 8H, CH_2), 2.85 (s, 4H, CH_2Ph), 2.47 (t, $^3J_{HH} = 7.0$, 8H, CH_2), 1.31 (quin, $^3J_{HH} = 5.8$, 8H, CH_2). ^{13}C NMR (C_6D_6, 298 K): δ 163.4 (CN_3), 153.3 (Ph-C_{ipso}), 127.7 (Ph-$C_{ortho/meta}$), 126.3 (Ph-$C_{ortho/meta}$), 119.5 (Ph-C_{para}), 84.0 (CH_2Ph), 45.3 (CH_2), 43.9 (CH_2), 22.7 (CH_2).

[Ti(μ-N^{t}Bu)(hpp)Cl]$_2$ (7). A solution of hppH (1.00 g, 7.2 mmol) in THF was cooled to 0 °C, and 1 equiv of ^{n}BuLi (2.5 M solution in hexanes) was added. The solution was allowed to warm to room temperature and stirred for 1 h. The resulting mixture was added dropwise to a solution of Ti(N^{t}Bu)Cl$_2$(py)$_3$ (3.05 g, 7.2 mmol) in THF that was precooled −78 °C. The resultant orange-red solution was allowed to warm slowly to room temperature and stirred for 18 h. The volatiles were removed under reduced pressure, affording a deep red solid, which was extracted from LiCl using toluene. The volatiles were then removed to afford pure **7**. Yield: 1.37 g, 65%.

Anal. Calcd for $C_{11}H_{21}N_4ClTi$: C, 45.2; H, 7.2; N, 19.2. Found: C, 45.0; H, 7.4; N, 19.2. ^{1}H NMR (C_6D_6, 298 K): δ 3.93 (br t, 4H, CH_2), 2.36 (t, $^3J_{HH} = 5.8$, 4H, CH_2), 1.45 (m, 4H, CH_2), 1.44 (s, 9H, NCMe_3); (CDCl$_3$, 298 K): δ 3.82 (br t, 4H, CH_2), 3.17 (t, $^3J_{HH} = 5.8$, 4H, CH_2), 1.92 (m, 4H, CH_2), 1.11 (s, 9H, NCMe_3). ^{13}C NMR (C_6D_6, 298 K): δ 161.7 (CN_3), 72.5 (CMe_3), 46.1 (CH_2), 44.8 (CH_2), 31.8 (CMe_3), 23.5 (CH_2); (CDCl$_3$, 298 K): δ 161.3 (CN_3), 72.6 (CMe_3), 46.4 (CH_2), 44.4 (CH_2), 31.3 (CMe_3), 23.4 (CH_2). MS (EI$^+$, *m/z*, ^{35}Cl): 584 [M]$^+$, 569 [M − Me]$^+$.

[Ti(N^{t}Bu)(hpp)(μ-hpp)]$_2$ (8). A solution of hppH (1.00 g, 7.2 mmol) in THF was cooled to 0 °C, and 1 equiv of ^{n}BuLi (2.5 M solution in hexanes) was added. The solution was allowed to warm to room temperature and stirred for 1 h. The resulting mixture was added dropwise to a solution of Ti(N^{t}Bu)Cl$_2$(py)$_3$ (1.52 g, 3.6 mmol) in THF at room temperature. The resultant orange-red solution was heated to 60 °C and stirred for 18 h. The mixture was allowed to cool to room temperature, and the volatiles were removed under reduced pressure to afford an orange-yellow solid, which was extracted from LiCl using toluene. Recrystallization from Et_2O afforded an intimate mixture of orange and yellow crystals, from which a single crystal of the yellow bis(guanidinate) complex **8** was separated mechanically and the X-ray diffraction study performed.

Polymerization Procedure. A solution of 0.02 mmol of the precatalyst was dissolved in toluene (200 mL) and added to a glass-walled reactor containing 13.3 mL of a toluene solution of MAO (1.5 M), to generate a Al:Ti ratio of 1000:1. The mixture was stirred, by means of an overhead mechanical stirrer, under an atomsphere of 9 bar of ethlyene for 1 h. The reaction was quenched, and the polymer was collected, washed with MeOH/H$^+$, and then water, and dried in a vacuum oven at 60 °C overnight. The yield was recorded and the activity calculated (g PE mmol^{-1} h^{-1} bar^{-1}) for the 1 h period.

Crystallography. Details of the crystal data, intensity collection, and refinement for complexes **2**, **3**, **5**, and **6** are listed in Table 1, and for complexes **7** and **8** in Table 6. Crystals were covered in oil, and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97.[14] Additional features are described below.

[Ti(hpp)Cl$_3$]$_2$ (2). C(3) is disordered [0.69:0.31] over two positions, corresponding to different ring conformations. The highest occupancy structure is shown in Figure 1.

Ti{AlMe$_2$(hpp)$_2$}Cl(μ-Cl)AlMe$_3$ (5). C(3) is disordered [0.47:0.53] over two positions, corresponding to different ring conformations. The highest occupancy structure is illustrated in Figure 3.

Ti(hpp)$_2$(CH$_2$Ph)$_2$ (6). The absolute structure was defined by refinement of the Flack parameter in the least squares.

[Ti(μ-N^{t}Bu)(hpp)Cl]$_2$ (7b). The dimer lies on a crystallographic inversion center. C(3) is disordered [0.89:0.11] over two positions, corresponding to different ring conformations. The highest occupancy structure is illustrated in Figure 5.

Crystal structure data for compounds **3** and **5** have been previously deposited at the CCDC, reference numbers 160792 and 160793.

Results and Discussion

Deprotonation of the neutral bicyclic guanidine, hppH, to the corresponding guanidinate anion, [hpp]$^-$, was readily achieved in THF at 0 °C, using ^{n}BuLi. Although the Li salt can be isolated as the base-free species (hppLi)$_n$,[15] for the sake of convenience we opted to use the salt in situ as the THF solution. Accordingly, the reaction with 1 equiv of $TiCl_4(THF)_2$ proceeded smoothly to afford the mono-ligand compound Ti(hpp)Cl$_3$(THF) (**1**, Scheme 2). Although the molecular structure of **1** was not solved, NMR and elemental analysis revealed that one molecule of THF was retained in the coordination sphere of the metal, as previously observed in the amidinate complexes Ti(p-MeC$_6$H$_4$-C{NMe}$_2$)Cl$_3$(THF)[16] and Ti(PhC{NSiMe$_3$}{NR*})Cl$_3$(THF) (R* = myrtanyl).[17] In contrast to the former complex where the N*Me* substituents were inequivalent in solution, assigned as *cis* and *trans* positions with respect to the position of the THF molecule, the ^{1}H and ^{13}C NMR data for **1** show

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Table 1. Crystal Structure and Refinement Data for 2, 3, 5, and 6

	2	**3**	**5**	**6**
formula	$C_{14}H_{24}Cl_6N_6Ti_2$	$C_{14}H_{24}Cl_2N_6Ti\cdot(C_7H_8)$	$C_{19}H_{39}Al_2Cl_2N_6Ti$	$C_{28}H_{38}N_6Ti$
fw	584.89	487.33	524.32	506.54
temperature (K)	173(2)	173(2)	173(2)	173(3)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst size (mm)	0.40 × 0.20 × 0.05	0.20 × 0.20 × 0.05	0.20 × 0.20 × 0.05	0.20 × 0.10 × 0.10
cryst syst	monoclinic	monoclinic	monoclinic	tetragonal
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P4_1$ (No. 76)
a (Å)	9.2379(6)	12.4604(6)	32.1612(12)	9.3107(3)
b (Å)	11.3740(8)	8.4351(6)	8.7247(6)	9.3107(3)
c (Å)	10.6759(8)	22.9507(15)	22.3495(11)	30.4556(11)
β (deg)	90.799(4)	104.261(4)	120.135(3)	90
V (Å^3)	1121.6(1)	2337.9(3)	5423.6(5)	2640.2(2)
Z	2	4	8	4
D_{calc} (Mg/m^3)	1.73	1.39	1.28	1.27
abs coeff (mm^{-1})	1.44	0.62	0.60	0.35
θ range for data collection (deg)	3.82 to 23.55	3.73 to 22.97	3.74 to 25.04	4.00 to 22.98
no. of reflns collected	7000	10 686	12 618	6295
no. of indep reflns	1655 [$R_{int} = 0.086$]	3230 [$R_{int} = 0.070$]	4783 [$R_{int} = 0.060$]	3234 [$R_{int} = 0.040$]
no. of reflns with $I > 2\sigma(I)$	1408	2507	3406	2970
no. of data/restraints/params	1655/0/137	3230/0/399	4783/0/281	3234/1/316
goodness-of-fit on F^2	1.035	1.006	1.021	0.669
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.036$, $wR_2 = 0.077$	$R_1 = 0.041$, $wR_2 = 0.083$	$R_1 = 0.046$, $wR_2 = 0.093$	$R_1 = 0.039$, $wR_2 = 0.107$
R indices (all data)	$R_1 = 0.047$, $wR_2 = 0.082$	$R_1 = 0.062$, $wR_2 = 0.091$	$R_1 = 0.0792$, $wR_2 = 0.1058$	$R_1 = 0.044$, $wR_2 = 0.112$
largest diff peak and hole (e Å^{-3})	0.44 and −0.38	0.22 and −0.28	0.32 and −0.33	0.20 and −0.18

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Ti(hpp)Cl$_2$(μ-Cl)]$_2$ (2)[a]

Ti−N(1)	2.003(3)	Ti−N(2)	1.963(3)
Ti−Cl(1)	2.602(1)	Ti−Cl(2)	2.294(1)
Ti−Cl(3)	2.266(1)	Ti−Cl(1′)	2.423(1)
C(1)−N(1)	1.353(4)	C(1)−N(2)	1.356(5)
C(1)−N(3)	1.318(4)	Δ_{CN}	0.003
Δ'_{CN}	0.037		
N(1)−Ti−N(2)	66.99(12)	N(2)−Ti−Cl(3)	104.61(9)
N(1)−Ti−Cl(3)	97.32(8)	N(2)−Ti−Cl(2)	90.00(9)
N(1)−Ti−Cl(1′)	94.60(8)	Cl(3)−Ti−Cl(2)	94.78(4)
Cl(3)−Ti−Cl(1′)	90.01(3)	Cl(2)−Ti−Cl(1′)	106.00(4)
N(2)−Ti−Cl(1)	86.89(8)	N(1)−Ti−Cl(1)	86.42(8)
Cl(2)−Ti−Cl(1)	85.78(4)	Cl(1′)−Ti−Cl(1)	78.81(3)
N(1)−C(1)−N(2)	107.8(3)	N(1)−C(1)−N(3)	126.3(3)
N(2)−C(1)−N(3)	125.8(3)	C(1)−N(3)−C(4)	119.5(3)
C(1)−N(3)−C(5)	119.7(3)	C(4)−N(3)−C(5)	120.8(3)

[a] Symmetry transformations used to generate equivalent atoms: ′ $-x$, $-y+2$, $-z$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Ti(hpp)$_2$Cl$_2$ (3)

Ti−N(1)	2.014(3)	Ti−N(2)	2.066(3)
Ti−N(4)	2.028(3)	Ti−N(5)	2.043(2)
Ti−Cl(1)	2.3455(9)	Ti−Cl(2)	2.3414(10)
C(1)−N(1)	1.347(4)	C(1)−N(2)	1.340(4)
C(1)−N(3)	1.340(4)	C(8)−N(4)	1.344(4)
C(8)−N(5)	1.338(4)	C(8)−N(6)	1.339(4)
$\Delta_{CN}(1)$	0.007	$\Delta_{CN}(2)$	0.006
$\Delta'_{CN}(1)$	0.004	$\Delta'_{CN}(2)$	0.002
N(1)−Ti−N(2)	65.04(11)	N(4)−Ti−N(5)	65.06(10)
N(1)−Ti−N(5)	94.68(11)	N(2)−Ti−N(4)	96.74(11)
N(1)−Ti−Cl(1)	109.53(8)	N(4)−Ti−Cl(1)	89.36(7)
N(2)−Ti−Cl(1)	89.44(8)	N(4)−Ti−Cl(2)	110.05(8)
N(1)−Ti−Cl(2)	89.13(8)	N(5)−Ti−Cl(2)	95.93(8)
Cl(1)−Ti−Cl(2)	92.65(4)	N(1)−C(1)−N(2)	109.5(3)
N(1)−C(1)−N(3)	124.6(3)	N(2)−C(1)−N(3)	125.7(3)
C(1)−N(3)−C(4)	120.5(3)	C(1)−N(3)−C(5)	120.5(3)
C(4)−N(3)−C(5)	118.7(3)	N(4)−C(8)−N(5)	109.4(3)
N(4)−C(8)−N(6)	125.3(3)	N(5)−C(8)−N(6)	125.3(3)
C(8)−N(6)−C(11)	120.3(3)	C(8)−N(6)−C(12)	120.5(3)
C(11)−N(6)−C(12)	119.1(3)		

only three resonances for the methylene groups of [hpp]$^-$, consistent with an octahedral geometry with the THF *trans* to chloride (i.e., a *fac*-arrangement of chloride ligands), or the existence of a fluxional process whereby the two halves of the guanidinate are rendered equivalent.

To generate the base-free metal complex, the silylated ligand precursor hppSiMe$_3$,[13] prepared from the reaction of (hppLi)$_n$ and SiMe$_3$Cl, was added to a solution of TiCl$_4$ in CH$_2$Cl$_2$ (Scheme 3). The product (**2**) was isolated as a red solid, which was purified by crystallization from a warm toluene solution. As for **1**, the ^{1}H and ^{13}C NMR spectra revealed only three resonances for the [hpp]$^-$ methylene units, consistent with a monomeric species in solution with an equatorially bound guanidinate, in agreement with the highest molecular fragment detected in the mass spectrum of 292 atomic mass units. It has previously been shown however that the analogous benzamidinate complex, [Ti(PhC{NSiMe$_3$}$_2$)Cl$_2$(μ-Cl)]$_2$, consists of a chloride-bridged dimer in the solid state.[18] To determine which structure was adopted by **2** in the solid state, an X-ray structural analysis was performed (Figure 1); crystal data are summarized in Table 1 and selected bond lengths and angles are collected in Table 2.

Compound **2** crystallizes from toluene as the chlorine-bridged dimer [Ti(hpp)Cl$_2$(μ-Cl)]$_2$, with a chelating guanidinate anion and two terminal chlorides, analogous to the benzamidinate complex.[18] The geometry at titanium is distorted octahedral, with bond angles in the range 66.99(12)−106.00(4)°, where the smallest value corresponds to the bite angle of the ligand. The [hpp]$^-$ ligand is positioned such that N(1) is *cis* to the chloro-bridges and N(2) is *trans*, and correspondingly different Ti−N bond lengths of 2.003(3) and 1.963(3) Å, respectively, are observed.

The distribution of electron density throughout the "CN$_3$" core of the guanidinate ligand is an important parameter when discussing the contribution of the

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[18] Fenske, D.; Hartmann, E.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43b*, 1611.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Ti{AlMe$_2$(hpp)$_2$}Cl(μ-Cl)AlMe$_3$ (5)

Ti–N(1)	2.069(2)	Ti–N(2)	2.227(2)
Ti–N(5)	2.055(3)	Ti–N(4)	2.250(3)
Ti–Cl(1)	2.350(1)	Ti–Cl(2)	2.460(1)
Cl(2)–Al(2)	2.382(1)	Al(2)–C(17)	1.966(4)
Al(2)–C(18)	1.968(4)	Al(2)–C(19)	1.978(3)
N(2)–Al(1)	1.957(3)	N(4)–Al(1)	1.959(2)
Al(1)–C(15)	1.955(3)	Al(1)–C(16)	1.958(4)
C(1)–N(1)	1.326(4)	C(1)–N(2)	1.379(4)
C(1)–N(3)	1.339(4)	C(8)–N(5)	1.328(4)
C(8)–N(4)	1.389(4)	C(8)–N(6)	1.320(4)
Δ_{CN}(1)	0.053	Δ_{CN}(2)	0.061
Δ'_{CN}(1)	0.014	Δ'_{CN}(2)	0.039
N(1)–Ti–N(2)	62.34(9)	N(4)–Ti–N(5)	62.22(9)
N(2)–Ti–N(4)	81.20(9)	N(2)–Al(1)–N(4)	96.14(11)
Cl(1)–Ti–Cl(2)	95.23(4)	N(1)–Ti–N(4)	93.39(10)
N(1)–Ti–Cl(1)	105.47(8)	N(1)–Ti–Cl(2)	92.13(7)
N(2)–Ti–N(5)	90.51(10)	N(2)–Ti–Cl(1)	98.10(7)
N(4)–Ti–Cl(2)	94.47(6)	N(5)–Ti–Cl(1)	96.26(7)
N(5)–Ti–Cl(2)	110.64(7)	Ti–Cl(2)–Al(2)	120.95(4)
C(15)–Al(1)–C(16)	118.53(18)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Ti(hpp)$_2$(CH$_2$Ph)$_2$ (6)

Ti–N(1)	2.105(3)	Ti–N(2)	2.080(3)
Ti–N(4)	2.064(3)	Ti–N(5)	2.095(3)
Ti–C(15)	2.185(4)	Ti–C(22)	2.181(4)
C(1)–N(1)	1.344(5)	C(1)–N(2)	1.330(5)
C(1)–N(3)	1.355(5)	C(8)–N(4)	1.341(5)
C(8)–N(5)	1.329(5)	C(8)–N(6)	1.349(5)
Δ_{CN}(1)	0.014	Δ_{CN}(2)	0.012
Δ'_{CN}(1)	−0.018	Δ'_{CN}(2)	−0.014
N(1)–Ti–N(2)	63.35(13)	N(4)–Ti–N(5)	63.50(13)
N(1)–Ti–N(5)	114.28(13)	N(2)–Ti–N(4)	107.67(13)
N(1)–Ti–C(15)	93.80(15)	N(5)–Ti–C(15)	81.16(15)
N(2)–Ti–C(15)	107.63(15)	N(4)–Ti–C(22)	95.32(15)
N(2)–Ti–C(22)	80.40(14)	N(5)–Ti–C(22)	102.37(15)
C(15)–Ti–C(22)	92.06(17)	Ti–C(15)–C(16)	114.0(3)
Ti–C(22)–C(23)	115.2(3)	N(1)–C(1)–N(2)	110.5(3)
N(1)–C(1)–N(3)	124.2(3)	N(2)–C(1)–N(3)	125.3(4)
C(1)–N(3)–C(4)	120.2(3)	C(1)–N(3)–C(5)	118.6(3)
C(4)–N(3)–C(5)	119.6(3)	N(4)–C(8)–N(5)	110.1(3)
N(4)–C(8)–N(6)	124.8(4)	N(5)–C(8)–N(6)	125.1(4)
C(8)–N(6)–C(11)	119.1(3)	C(8)–N(6)–C(12)	119.9(4)
C(11)–N(6)–C(12)	120.2(4)		

different resonance forms to the overall bonding. Previously the Δ_{CN} value,[19] defined as the difference in bond length between the C–N single and C═N double bonds, has been used as a *qualitative* indication of the delocalization within the amidine unit in metal amidinate complexes. This value is typically within the range 0 Å (for fully delocalized systems) to approximately 0.14 Å for isolated C–N$_{single}$ and C═N$_{double}$ bonds to an sp^2-carbon center,[20] although we have demonstrated that a certain degree of flexibility exists depending on crystallographic packing forces, as illustrated for a series of linked-bis(*N*,*N*′-dialkylamidine) compounds.[21] For comparative purposes, we also find it useful to define a Δ'_{CN} value as the difference between the average value of the C–N$_{amidine}$ bond lengths and the C–N$_{amide}$ distance, where the greater the contribution from resonance **I** (Scheme 1), the larger the value for Δ'_{CN}. Examination of the C–N distances in the guanidinate ligand of **2** indicates a symmetrical delocalization across the N(1)–C(1)–N(2) moiety [Δ_{CN} = 0 Å within the experimental limits of the data], with a significantly shorter C–N$_{amide}$ distance [Δ'_{CN} = 0.037 Å], which in combination with a small α-value between the "NR$_2$" (amide) and "CN$_2$" (amidine) ligand components [4.7°] signifies a large contribution from resonance **I** to the overall bonding. Therefore we predict an increased N→M electron donation due to localization of charge density at both N$_{amidine}$ atoms, realized in the observation that the titanium–nitrogen bond lengths are significantly shorter in **2** [1.963(3) and 2.003(3) Å] than in the corresponding benzamidinate complex [1.986(2) and 2.072(2) Å]. Caution must be exercised when comparing such values however, as there is a considerable difference in the steric demands of the two ligands, with the nitrogen methylene substituents in [hpp]$^-$ being effectively "tied-back", due to incorporation in the bicyclic framework.

Changing the stoichiometry of (hppLi)$_n$:TiCl$_4$(THF)$_2$ allowed access to the base-free, bis-guanidinate complex Ti(hpp)$_2$Cl$_2$ (**3**, Scheme 2). ^{1}H and ^{13}C NMR spectroscopic analysis of **3** indicated a symmetric environment for the [hpp]$^-$ anions, suggesting a structure with *trans*-chlorides. However, the molecular structure (vide infra) revealed *cis*-chlorides, indicating that a rapid fluxional process must be occurring at room temperature, as studied in detail for the acyclic guanidinate complex Ti(Me$_2$NC{N^{i}Pr}$_2$)$_2$Cl$_2$.[22] The molecular structure of **3** is illustrated in Figure 2, crystal data are summarized in Table 1, and selected bond lengths and angles are collected in Table 3.

Compound **3** exists as a monomer in the solid state, with two chelating guanidinate ligands and two terminal chlorides. The titanium is distorted octahedral [angles in the range 65.04(11)–110.05(8)°], with the main distortion again arising from the bite angle of the [hpp]$^-$ groups. The titanium–nitrogen distances follow trends similar to those observed in **2**, where the Ti–N bonds *trans* to a chloride ligand are slightly longer than those that are *cis*. Scheme 4 compares the titanium–nitrogen distances in **3** with those for the benzamidinate[23] and acyclic guanidinate analogues,[22,24] illustrating a decreased value in **3** commensurate with increased electron donation arising from the small values of α [3.8° and 2.9°]. However, the same steric arguments presented above for **2** must also be considered in this case. The Δ_{CN} values in **3** again indicate symmetry across the amidine moiety, although for this compound, a reduced contribution from resonance **I** is implied as indicated by a significant decrease in the Δ'_{CN} values (0.004 and 0.002 Å).

We can find no reports of conventional tris-guanidinate Ti(IV) complexes in the literature, although the closely related aminopyridinato species Ti{RN-2-C$_6$H$_4$N}$_3$-Cl (R = Me, Ph) have been synthesized,[25] demonstrating the possibility of a seven-coordinate titanium center using chelating ligands of this type. As [hpp]$^-$ may be considered a relatively sterically undemanding guanidi-

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Table 6. Crystal Structure and Refinement Data for 7a, 7b, and 8

	7a	7b	8
formula	$C_{22}H_{42}Cl_2N_8Ti_2{\cdot}C_7H_8$	$C_{22}H_{42}Cl_2N_8Ti_2$	$C_{36}H_{66}N_{14}Ti_2$
fw	677.47	585.34	790.83
temperature (K)	173(2)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst size (mm)	0.30 × 0.15 × 0.05	0.30 × 0.30 × 0.10	0.30 × 0.30 × 0.15
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$Pbca$ (No. 61)
a (Å)	10.8220(5)	17.8443(11)	10.7160(3)
b (Å)	10.4833(4)	9.1562(4)	15.3055(4)
c (Å)	15.3615(8)	19.2712(10)	24.9766(5)
β (deg)	102.882(2)	115.112(2)	90
V (Å^3)	1698.9(1)	2851.0(3)	4096.5(2)
Z	2	4	4
D_{calc} (Mg/m^3)	1.32	1.36	1.28
abs coeff (mm^{-1})	0.66	0.77	0.43
θ range for data collection (deg)	3.86 to 22.97	3.81 to 25.03	3.78 to 27.87
no. of reflns collected	12 813	9685	21 448
no. of indep reflns	2353 [$R_{\text{int}} = 0.121$]	2513 [$R_{\text{int}} = 0.062$]	4866 [$R_{\text{int}} = 0.066$]
no. of reflns with $I > 2\sigma(I)$	1770	2097	3509
no. of data/restraints/params	2353/0/190	2513/0/164	4866/0/235
goodness-of-fit on F^2	1.062	1.019	1.008
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.058$, $wR_2 = 0.106$	$R_1 = 0.033$, $wR_2 = 0.080$	$R_1 = 0.043$, $wR_2 = 0.099$
R indices (all data)	$R_1 = 0.089$, $wR_2 = 0.116$	$R_1 = 0.044$, $wR_2 = 0.085$	$R_1 = 0.070$, $wR_2 = 0.111$
largest diff peak and hole (e Å^{-3})	0.30 and −0.40	0.30 and −0.30	0.28 and −0.30

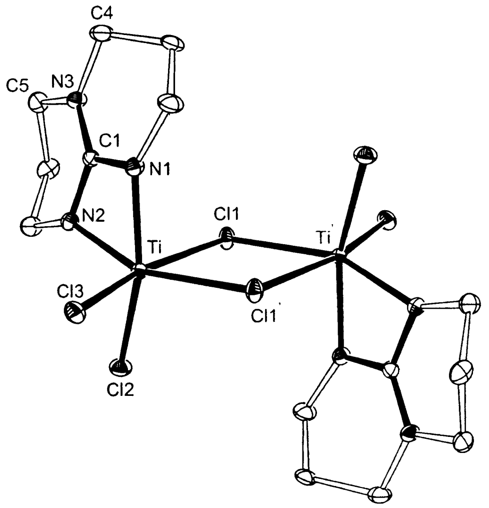

Figure 1. Molecular structure of [Ti(hpp)Cl_2(μ-Cl)]$_2$ (**2**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

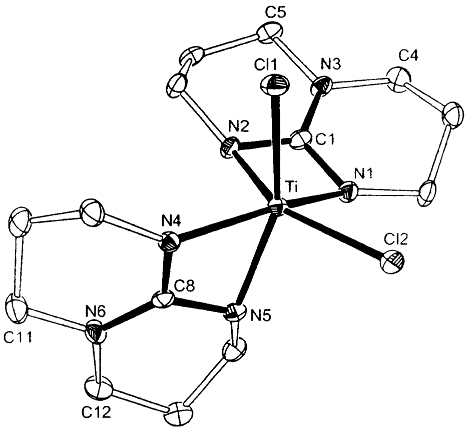

Figure 2. Molecular structure of Ti(hpp)$_2$$Cl_2$ (**3**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

nate ligand due to the N_{amidine} methylene substituents being incorporated into the six-membered ring, we reasoned that it may be possible to coordinate three such ligands at titanium. Accordingly, the reaction between 3 equiv of (hppLi)$_n$ and $TiCl_4(THF)_2$ proceeded to afford the tris-ligand species Ti(hpp)$_3$Cl (**4**) as the base-free complex. Unfortunately, crystals suitable for an X-ray analysis were not forthcoming, precluding a study of the structure of **4**, although the formulation as the tris-ligand complex was confirmed by elemental analysis and the observation of the molecular ion (m/z 497) in the mass spectrum.

Preliminary ethylene polymerization studies using compounds **1**−**3** as precatalyst and MAO as activator were performed to gauge the catalytic potential of titanium complexes supported by [hpp]$^-$ anions. Solutions of **1** and **2** (0.02 mmol) in toluene (200 mL) in the presence of excess MAO (Al/Ti = 1000) show low[26] polymerization activities at room temperature (9 bar, activity = 7.4 (**1**) and 7.1 (**2**) gPE mmol^{-1} h^{-1} bar^{-1}). The low activity may be due in part to the titanium procatalyst retaining THF (**1**) or adopting a dimeric structure (**2**), thus hindering activation by MAO and/or approach of an incoming monomer to the active catalyst species. It is generally accepted that the active species in group 4 metal olefin polymerization catalysis consists of a cationic metal alkyl complex, with a “vacant” coordination site *cis* to the M−C bond, supported by ancillary ligands. As such, we considered that upon activation by MAO, complex **3** would give rise to the best catalytic system, based on the crystal structure of the *cis*-dichloride precursor. Surprisingly however, even lower activity (2.2 g mmol^{-1} h^{-1} bar^{-1}) was observed for **3** compared with **1** and **2** under identical reaction conditions, suggesting that a facile deactivation pathway is present in these systems.

To investigate possible explanations for the observed low activity and to gain insight into the stability of the

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[26] Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

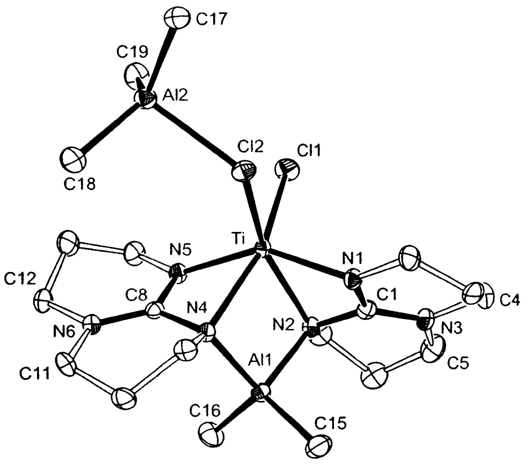


Figure 3. Molecular structure of Ti{AlMe$_2$(hpp)$_2$}Cl(μ-Cl)-AlMe$_3$ (**5**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

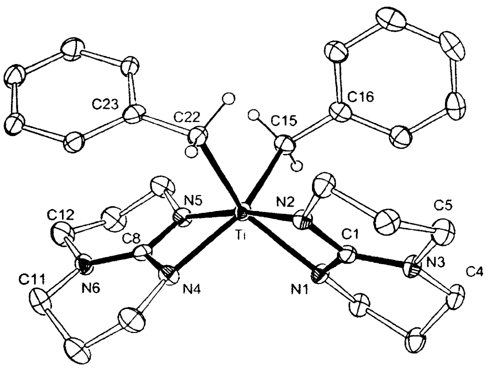


Figure 4. Molecular structure of Ti(hpp)$_2$(CH$_2$Ph)$_2$ (**6**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms except on the methylene unit of the benzyl group omitted for clarity.

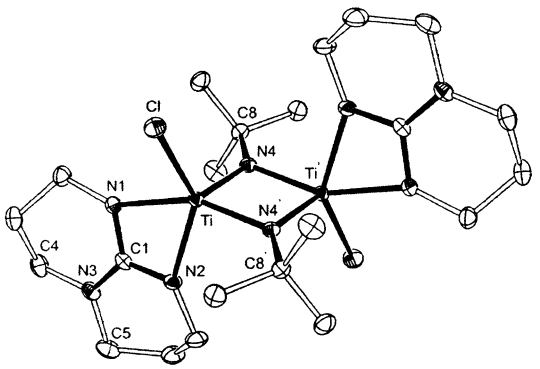
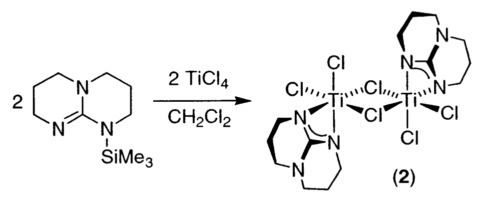


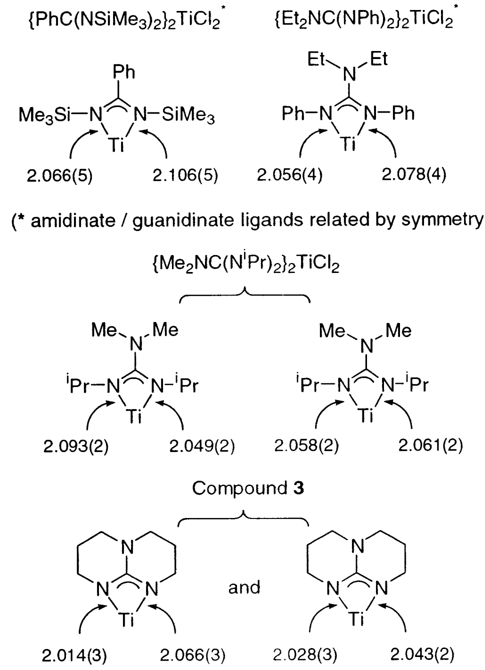
Figure 5. Molecular structure of [Ti(μ-N^{t}Bu)(hpp)Cl]$_2$ (**7b**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

[hpp]$^-$ ligands with respect to the alkyl aluminum component of MAO, the preparative scale reaction between **3** and AlMe$_3$ was explored (Scheme 5). Addition of a solution of AlMe$_3$ (2 equiv) to **3** gave an immediate color change from red-orange to green-red. Upon workup, green crystals (**5**) were isolated. The ^{1}H NMR spectrum indicated the presence of paramagnetic species, confirmed by the presence of an ESR signal at g_{iso} = 1.9617. The elemental analysis was consistent with the formula **3**·Al$_2$Me$_5$. The molecular structure of complex **5** was determined by a further X-ray diffraction analysis (Figure 3); crystal data are summarized in Table 1, and selected bond lengths and angles are collected in Table 4.

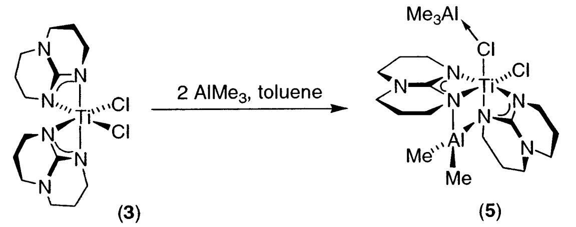
Scheme 3



Scheme 4. Comparison of Ti–N Bond Distances (Å) in Ti(amidinate)$_2$Cl$_2$ and Ti(guanidinate)$_2$Cl$_2$ Complexes



Scheme 5



Compound **5** consists of a novel trimetallic complex containing one titanium and two aluminum centers, linked through hpp and chloride bridges. The titanium(III) center exists in a distorted octahedral geometry, bound by two chelating hpp groups and two chloride atoms, one of which bridges to an AlMe$_3$ unit. In addition to coordinating to the titanium, the guanidinate anions are linked through one of the nitrogen atoms by an AlMe$_2$ moiety, resulting in a unit that may be considered as the η^4-monoanionic moiety, [Me$_2$Al(hpp)$_2$]$^-$. Inspection of the bond lengths and angles throughout this unit indicates that a redistribution of the π-electron density has occurred. The N(1) and N(5) atoms retain an approximately planar sp^2-hybridization [Σ_{angle} = 353.8° and 356.8°, respectively], with distances to titanium slightly longer than in **1** and **3** [2.069(3) and 2.055(3) Å, respectively]. The N(2) and N(4) atoms have however undergone rehybridization, with corresponding increased Ti−N bond distances of 2.227(3) and 2.250(3) Å, respectively. In addition, the π-system is no longer equally distributed throughout the CN_3 core of the ligand, with C(1)−N(2) and C(8)−N(4) bond lengths [1.379(4) and 1.389(4) Å, respectively] longer than the remaining C−N distances [1.320−1.339 Å], reflected in the relatively large Δ_{CN} values [0.053 and 0.061 Å] and inconsistent Δ'_{CN} values [0.014 and 0.039 Å]. The Ti−(μ-Cl) distance [2.460(1) Å] is slightly longer than the terminal titanium chloride distance [2.350(1) Å] typical for a bridge between titanium and aluminum.[27]

With reference to the lower olefin polymerization activity observed for **3**, complex **5** serves to illustrate that the guanidinate ligands are not merely acting in a supporting role as an ancillary ligand set, but are able to interact with trimethylaluminum, a known component of MAO. While we are not able to definitively say that this exact process is occurring during the polymerization reaction, isolation of **5** does serve to illustrate the noninnocent nature of the $[hpp]^-$ groups. The bridging nature of the guanidinates between the Ti and Al centers may also be representative of an intermediate in a ligand abstraction process, analogous to that proposed to occur during the polymerization of propylene by a zirconium benzamidinate/MAO system.[17] This hypothesis is further substantiated by mass spectral analysis of **5**, which shows peaks at m/z 303 and 180, corresponding to $[Al(hpp)_2]^+$ and $[Al(hpp)Me]^+$, respectively, where complete transfer of $[hpp]^-$ from titanium to aluminum has occurred.

Due to our limited success with the titanium chloride/MAO system, we decided to focus on the generation of well-defined alkyl cations, which may be accessed from the alkyl abstraction reaction of complexes of general type $Ti(hpp)_2R_2$ (R = methyl, benzyl) with $B(C_6F_5)_3$. To synthesize a suitable dialkyl precursor, 2 equiv of hppH was reacted with $Ti(CH_2Ph)_4$ at low temperature in toluene to afford the bis-benzyl complex $Ti(hpp)_2(CH_2Ph)_2$ (**6**, Scheme 2). Despite purification by crystallization from Et_2O, repeated attempts at obtaining accurate elemental analysis were unsuccessful, with values consistently low for the carbon content, suggesting possible formation of nonvolatile titanium carbide during combustion. The ^1H and ^{13}C NMR spectra of **6** show one environment for each of the hpp-methylene units, indicating a fluxional system in solution and rapid racemization of the C_2-symmetric structure (vide supra), with the benzyl methylene group appearing as a singlet at 2.85 ppm. This observation contrasts the recently reported acyclic analogue $Ti(Me_2NC\{N^iPr\}_2)_2(CH_2Ph)_2$, where a stereochemically rigid structure is maintained in solution, resulting in an AB splitting pattern for the methylene groups of the benzyl ligand.[28] The molecular structure of **6** is illustrated in Figure 4, crystal data are summarized in Table 1, and selected bond lengths and angles are collected in Table 5.

Compound **6** exists as the monomeric bis-ligand, dialkyl in the solid state, with the overall geometry at titanium best described as a distorted octahedron [ligand bite angles = 63.35(13)° and 63.50(13)°] and both alkyl groups present as η^1-benzyl groups. The titanium−nitrogen distances [range 2.064(3)−2.105(3) Å] are generally longer than in the chloride complexes **2** and **3**, reflecting the increase in electron density at titanium arising from the presence of the alkyl groups compared with chlorides. A slight localization of charge exists within the amidine moiety [Δ_{CN} = 0.014 and 0.012 Å], and negative values for Δ'_{CN} [−0.018 and −0.014 Å] indicate a reduced contribution from **I** to the more electron-rich titanium center, with α values of 5.1° and 3.4°.

To ascertain the potential for **6** as a catalyst precursor in olefin polymerization, the NMR scale reaction with $B(C_6F_5)_3$ was performed in an attempt to characterize the cationic species formed during such a reaction. However, an instant color change from red to green took place on mixing a C_6D_6 solution of **6** with a stoichiometric amount of the borane activator, and an oily deposit formed on the walls of the NMR tube over a 1 min period. The ^1H NMR spectrum indicated that paramagnetic species had formed, again suggesting that the ligands are noninnocent with respect to cation formation. The precise nature of the product was not determined, and research into this area was not studied further.

Titanium Imido Complexes. In view of the apparent facile reduction of the metal center during the formation of cationic species for attempted olefin polymerization catalysis with both MAO and borane activators, and the resultant low activities of the complexes in the former system, we decided to investigate the synthesis of other potentially catalytically active titanium-based guanidinate species. Titanium-imido compounds are postulated as the intermediates in a number of organic transformations including hydroamination,[29] and a number of supporting ligands have recently been investigated, including the bis(cyclopentadienyl) framework[30] and pyrrolyl-supported systems.[31] Of particular relevance to our work, a recent report by Richeson and co-workers described an investigation of guanidinate-supported titanium-imido complexes as catalysts for the hydroamination of alkynes,[28] guanylation of amines, and transamination of guanidines.[32] We therefore initiated a study of the coordinating potential of the $[hpp]^-$ anion at titanium-imido centers, using Mountford's readily available *tert*-butylimido complex $Ti(N^tBu)Cl_2(py)_3$[12] as a convenient starting material.

The salt metathesis reaction between $(hppLi)_n$ and $Ti(N^tBu)Cl_2(py)_3$ proceeds to afford a dark red solution, from which base-free $[Ti(N^tBu)(hpp)Cl]$ (**7**) can be isolated (Scheme 6). In contrast to the ^1H and ^{13}C NMR data for the acetamidinate complexes $[Ti(\mu\text{-}N^tBu)(MeC\{NCy\}_2)X]_2$ (X = Cl[33] or Me[34]), where the two

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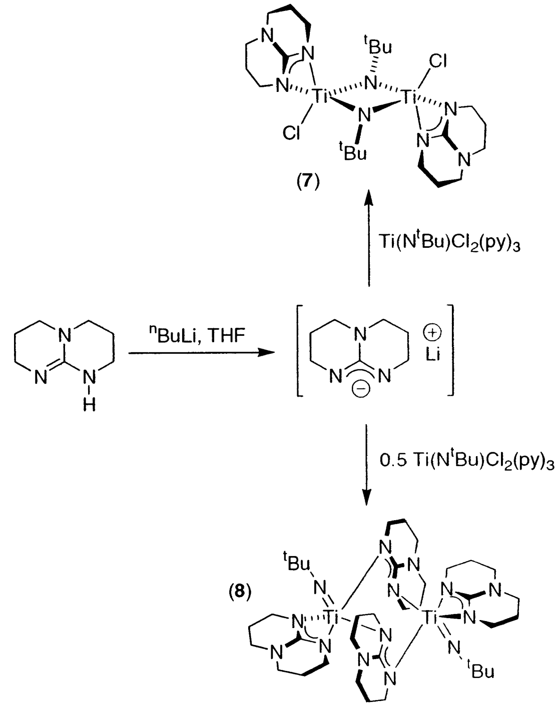
Scheme 6



cyclohexyl substituents are inequivalent in solution, the methylene units of the [hpp]$^-$ ligand appear as three signals in the NMR spectra, again suggesting a fluxional system in solution. Investigation of the difference in ^{13}C NMR shifts of the carbon atoms of the ^{t}Bu group ($\Delta\delta$ value) has been used as a measure of the electron density at the nitrogen atom in ^{t}Bu-imido compounds,[35] and we have recently applied this technique to titanium-imido complexes incorporating boron-substituted alkoxide ligands.[36] If the [hpp]$^-$ ion is truly acting as an electron-rich guanidinate through enhanced electron density due to contribution from **I**, we predict lower values for $\Delta\delta$ compared with conventional acyclic guanidinate complexes. The $\Delta\delta$ value for **7** ($CDCl_3$) of 41.3 ppm is slightly lower than the value for the analogous complex [Ti(μ-^{t}Bu)(MeC{NCy}$_2$)Cl]$_2$[33] in the same solvent ($\Delta\delta$ = 42.7), in agreement with the above argument. However, this argument appears counterintuitive when explaining the fluxionality observed in complex **7** but not in the acetamidinate species and may be owing to the preferred parallel orientation of the donor orbitals of [hpp]$^-$ (vide supra) facilitating a low-energy barrier to rotation via an N-bound η^1-intermediate, which equilibrates the methylene units of the [hpp]$^-$ ligand.

To try to gain a better understanding of the bonding within **7**, determination of the molecular structure by X-ray diffraction was performed (Figure 5). The complex crystallizes in the monoclinic crystal system as the toluene solvate (**7a**, space group $P2_1/c$) or as the solvate-free complex (**7b**, space group $C2/c$), with similar bond lengths and angles. Crystal data for each structure are summarized in Table 6, but for the purpose of comparing bond lengths and angles, only the latter structure **7b** is described (Table 7).[37]

Table 7. Selected Bond Lengths (Å) and Angles (deg) for [Ti(μ-N^{t}Bu)(hpp)Cl]$_2$ (7b)[a]

Ti(1)−N(4)	1.845(2)	Ti(1)−N(4′)	1.967(2)
Ti(1)−N(1)	2.078(2)	Ti(1)−N(2)	2.052(2)
Ti(1)−Cl	2.3301(7)	C(1)−N(1)	1.343(3)
C(1)−N(2)	1.335(3)	C(1)−N(3)	1.344(3)
Δ_{CN}	0.008	Δ'_{CN}	−0.005
N(4)−Ti(1)−N(4′)	85.25(8)	N(2)−Ti(1)−N(4)	109.44(7)
N(2)−Ti(1)−N(4′)	93.46(7)	N(1)−Ti(1)−N(4)	107.65(7)
N(1)−Ti(1)−N(2)	64.32(7)	N(1)−Ti(1)−N(4′)	156.80(7)
N(4)−Ti(1)−Cl	112.44(6)	N(4′)−Ti(1)-Cl	101.44(5)
N(2)−Ti(1)−Cl	136.39(6)	N(1)−Ti(1)−Cl	91.51(6)
N(1)−C(1)−N(2)	110.31(18)	N(1)−C(1)−N(3)	124.6(2)
N(2)−C(1)−N(3)	125.1(2)	C(1)−N(3)−C(4)	120.0(2)
C(1)−N(3)−C(5)	119.09(19)	C(4)−N(3)−C(5)	120.88(19)

[a] Symmetry transformations used to generate equivalent atoms: ′ −x, −y, −z.

In contrast to the benzamidinate species Ti(N^{t}Bu)(PhC{NSiMe$_3$}$_2$)Cl(py)$_2$, compound **7** exists as the dimeric, base-free species [Ti(μ-N^{t}Bu)(hpp)Cl]$_2$, with each titanium atom bound by terminal [hpp]$^-$ and chloride ligands and bridged by imido groups. The geometry at the metal is distorted toward tetragonal (τ = 0.34),[38] where N(4) defines the apical position and the remaining atoms form the base of the pyramid, with angles in the range 64.32(7)−101.44°. Similar arrangements of ligands are found in the acetamidinate complexes [Ti(μ-^{t}Bu)(MeC{NCy}$_2$)Cl]$_2$[33] and the methyl analogue [Ti(μ-^{t}Bu)(MeC{NCy}$_2$)Me]$_2$,[34] although more pronounced distortion toward C_{4v}-symmetric structures are evident in these cases (τ = 0.15 and 0.21, respectively). The Ti−N$_{imido}$ bond lengths exhibit significant asymmetry, [Ti(1)−N(4′) = 1.967(2) Å; Ti(1)−N(4) = 1.845(2) Å], which may be rationalized using purely geometrical arguments, given that N(4) is present in an apical site, while N(4′) may be considered as basal. An alternative explanation based on simple Hückel calculations that has been used to describe a similar difference within [M$_2$(μ-imido)] bond lengths for the group 6 metal complexes [M(μ-N^{t}Bu)(N^{t}Bu)(NMe$_2$)$_2$]$_2$ (M = Mo, W) attributes the cause to second-order Jahn−Teller distortions.[39] The Δ_{CN} and Δ'_{CN} values of 0.008 Å and −0.005 Å, respectively, indicate approximately equal delocalization throughout the CN$_3$ core of the guanidinate ligand, with an α-value of 3.0°. Once again the Ti−N$_{guanidinate}$ distances [Ti(1)−N(1) = 2.078(2) Å; Ti(1)−N(2) = 2.052(2) Å] are shorter than in the corresponding amidinate complex [2.112(3) and 2.076(3) Å], commensurate with contribution from **I** to the overall bonding situation.

Previous reports have been presented on the synthesis and isolation of arylimido titanium complexes supported by amidinate and guanidinate ligands. For example, Mountford was able to access the benzamidinate complex Ti(NAr)(PhC{NSiMe$_3$}$_2$)Cl(py)$_2$ (Ar = 2,6-Me$_2$C$_6$H$_3$; 2,6-^{i}Pr$_2$C$_6$H$_3$) either by a metathetical route using the lithium salt of the benzamidine and the (arylimido)titanium dichloride starting material or by an imido exchange reaction of the *tert*-butylimido derivative Ti(N^{t}Bu)(PhC{NSiMe$_3$}$_2$)Cl(py)$_2$ with the free aniline.[33] Attempted reactions between (hppLi)$_n$ and Ti(NAr)Cl$_2$-

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Table 8. Selected Bond Lengths (Å) and Angles (deg) for $[Ti(N^tBu)(hpp)(\mu\text{-}hpp)]_2$ (8)[a]

Ti−N(1)	1.7143(16)	Ti−N(2)	2.1475(16)
Ti−N(4)	2.1573(17)	Ti−N(5)	2.0715(16)
Ti−N(7′)	2.1506(16)	C(5)−N(2)	1.331(3)
C(5)−N(4)	1.331(2)	C(5)−N(3)	1.376(2)
C(12)−N(5)	1.325(2)	C(12)−N(7)	1.361(2)
C(12)−N(6)	1.355(2)	$\Delta_{CN}(1)$	0
$\Delta'_{CN}(1)$	−0.045	$\Delta_{CN}(2)$	0.036
$\Delta'_{CN}(2)$	−0.012		

N(1)−Ti−N(2)	103.52(7)	N(1)−Ti−N(4)	100.85(7)
N(1)−Ti−N(5)	99.75(7)	N(1)−Ti−N(7′)	101.50(7)
N(2)−Ti−N(4)	61.94(6)	N(2)−Ti−N(7′)	93.52(6)
N(2)−Ti−N(5)	151.09(7)	N(4)−Ti−N(5)	97.08(6)
N(4)−Ti−N(7′)	150.08(6)	N(5)−Ti−N(7′)	98.46(6)
N(2)−C(5)−N(4)	112.65(16)	N(2)−C(5)−N(3)	123.81(18)
N(4)−C(5)−N(3)	123.55(18)	C(5)−N(3)−C(8)	119.44(17)
C(5)−N(3)−C(9)	118.77(17)	C(8)−N(3)−C(9)	116.67(16)
N(5)−C(12)−N(7)	115.05(16)	N(5)−C(12)−N(6)	123.28(17)
N(7)−C(12)−N(6)	121.42(17)	C(12)−N(6)−C(15)	121.80(17)
C(12)−N(6)−C(16)	123.18(18)	C(15)−N(6)−C(16)	114.66(17)

[a] Symmetry transformations used to generate equivalent atoms: ′ −*x*, −*y*, −*z*.

$(py)_3$ under a variety of experimental conditions however afforded no clean product; similar observations were made employing the lithiated *N*,*N′*-bis(cyclohexyl)acetamidinate ligand.[33] In addition, attempted NMR scale reactions between **7** and $2,6\text{-}^iPr_2C_6H_3NH_2$ showed no exchange after 1 week at room temperature, and gentle heating of the reaction led to decomposition. A plausible explanation for the lack of reactivity in this case may be due to the inability of the aniline to initially coordinate at the metal center prior to "H" transfer,[40] due to retention of the dimeric structure in solution. In contrast, the $Ti(N^tBu)(PhC\{NSiMe_3\}_2)Cl(py)_2$ is able to readily lose a labile pyridine group, allowing coordination of the aniline to occur and the reaction to proceed.

It has been demonstrated that two amidinate or guanidinate ligands may be incorporated around the metal center in titanium(imido) complexes, affording monomeric species with terminal imido groups which are more closely related to the proposed active species in hydroamination catalysis. For example, the bis(benzamidinate) complex has been reported as both the base-free complex $Ti(N^tBu)(PhC\{NSiMe_3\}_2)_2$[41] and the pyridine adduct,[42] while recent reports of bis(guanidinate) species include the monomeric arylimido compounds $Ti(NAr)(Me_2NC\{N^iPr\}_2)_2$ (Ar = Ph[22] or $2,6\text{-}Me_2C_6H_3$[28]). We attempted therefore to generate the bis(hpp) complex by reacting 2 equiv of $(hppLi)_n$ with $Ti(N^tBu)Cl_2(py)_3$ in THF. Unfortunately, even under relatively forcing conditions (60 °C) we were unable to cleanly make the bis(guanidinate) complex, with the reaction always generating an intimate mixture of compounds (heating to higher temperature resulted in decomposition). However, a single crystal of the desired complex, $[Ti(N^tBu)(hpp)(\mu\text{-}hpp)]_2$ (**8**), was mechanically separated from the mixture and the molecular structure solved using X-ray diffraction. Crystal data are summarized in Table 6, and selected bond lengths and angles collected in Table 8. In contrast to the previously reported bis(amidinate) and bis(guanidinate) complexes of titanium-imido species, compound **8** exists as the dimeric complex $[Ti(N^tBu)(hpp)(\mu\text{-}hpp)]_2$, in which one of the $[hpp]^-$ groups chelates to titanium in the predicted fashion and the other bridges two metal centers, with the coordination sphere completed by a terminal imido ligand (Figure 6). Considering the imido group as the apex, the geometry at titanium approaches regular tetragonal with a τ value of 0.02, the main distortion again arising from the bite angle of the chelating guanidinate [61.94(6)°]. The core of the ligand consists of an eight-membered metallacycle present in a pronounced chair-type conformation, with a similar "out-of-the CN_3-plane" bridging coordination of the $[\mu\text{-}hpp]^-$ group to that previously observed in the dimeric tin and aluminum complexes $[Sn(\mu\text{-}hpp)Cl]_2$[8] and $[Al(\mu\text{-}hpp)Me_2]_2$.[4]

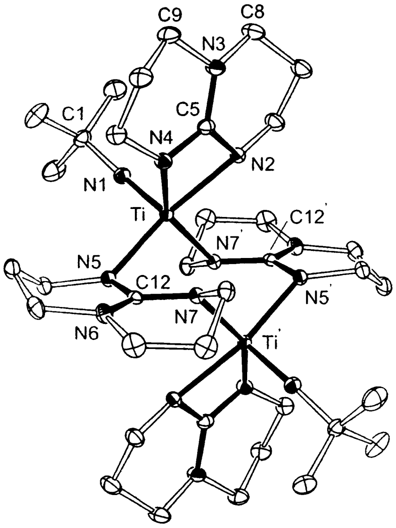

Figure 6. Molecular structure of $[Ti(N^tBu)(hpp)(\mu\text{-}hpp)]_2$ (**8**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

The bonding within the chelating guanidinate ligand is consistent with equal delocalization across the amidine unit (Δ_{CN} = 0 Å), with only a small contribution from the zwitterionic resonance structure (Δ'_{CN} = −0.045 Å) and a value of 8.0° for α. The bonding within the amidine unit is much more localized in the bridging guanidinate ligand [C(12)−N(5) = 1.325(2) Å; C(12)−N(7) =1.361(2) Å], with the corresponding Ti−N(5) and Ti−N(7′) distances of 2.0715(16) and 2.1506(16) Å, indicating a nonsymmetrical bonding situation for the $[\mu\text{-}hpp]^-$ group. The $Ti-N_{imido}$ bond length of 1.7143(16) Å is typical for a terminal *tert*-butylimido group, with the distance lying slightly toward the long end of the range normally quoted for such species (ca. 1.67−1.73 Å),[43] which may reflect a slight increase in electron density at the titanium. The angle at the imido nitrogen atom [169.67(15)°] is unremarkable.

In summary, we have synthesized a range of titanium complexes subtended by an anionic guanidinate ligand, derived from the bicyclic guanidine precursor, hppH. In solution the NMR analysis suggests a more fluxional system than reported for acyclic guanidinate complexes of titanium, provisionally attributed to the preferred parallel orientation of the donor orbitals facilitating a

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low-energy barrier to rotation. Investigation of the potential of several metal chloride species to serve as catalyst precursors for the polymerization of ethylene upon activation by MAO was performed with the observed low activities most probably arising from the facile reduction of the metal center and noninnocent nature of the supporting ligands. A similar reaction pathway was suggested from the reaction of the bis(benzyl) complex with the well-defined borane activator $B(C_6F_5)_3$. Extension to titanium-imido complexes resulted in formation of the mono-guanidinate complex containing a bridging imido unit in the solid state and the bis-guanidinate complex with a terminal imido unit and bridging $[\mu\text{-hpp}]^-$ anion.

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Supporting Information Available: Crystal structure data for **2** and **3** and **5**−**8**, including tables of atomic positional parameters, anisotropic thermal parameters, all bond distances and angles, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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