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Dititanium Complexes of Preorganized Binucleating Bis(amidinates)

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Four different dianionic bis(amidinate) ligands ($^{iPr}L_{DBF}{}^{2-}$, $^{tBu,Et}L_{DBF}{}^{2-}$, $^{iPr}L_{Xan}{}^{2-}$, $^{tBu,Et}L_{Xan}{}^{2-}$) featuring rigid dibenzofuran (DBF) and 9,9-dimethylxanthene (Xan) backbones have been used to prepare several new dititanium complexes. Reaction of the free-base bis(amidines) (LH_2) with 2 equiv of $Ti(NMe_2)_4$ forms the hexaamido derivatives $^{iPr}L_{DBF}Ti_2(NMe_2)_6$ **(1)**, $^{tBu,Et}L_{DBF}Ti_2(NMe_2)_6$ **(2)**, $^{iPr}L_{Xan}Ti_2(NMe_2)_6$ **(3)**, and $^{tBu,Et}L_{Xan}Ti_2(NMe_2)_6$ **(4)** in good yields. Compound **4**, which features an unsymmetrically substituted bis(amidinate) ligand, was isolated as an 8:1 mixture of rotational diastereomers with C_2 and C_s symmetry, respectively. The two diastereomers interconvert upon heating, and at equilibrium the C_2 isomer is preferred thermodynamically by 0.2 kcal/mol. Compound **3** reacts with excess Me_3SiCl in toluene to form the mixed amido–chloride derivative $^{iPr}L_{Xan}Ti_2(NMe_2)_2Cl_4$ **(5)** in low-moderate yield. Alternatively, **5** is also prepared by reaction of $^{iPr}L_{Xan}H_2$ with 2 equiv of $Ti(NMe_2)_2Cl_2$ in good yield. Compound **3** reacts with CO_2 to form the red carbamate derivative $^{iPr}L_{Xan}Ti_2(NMe_2)_4(O_2CNMe_2)_2$ **(6)** in moderate yield. Infrared data for **6** indicates bidentate coordination of the carbamate ligands. Metathesis reaction of $^{iPr}L_{Xan}Li_2$ with 2 equiv of $CpTiCl_3$ affords $^{iPr}L_{Xan}Ti_2Cp_2Cl_4$ **(7)** in moderate yield. Reduction of **7** with 1% Na amalgam in toluene solution affords the paramagnetic dititanium(III) complex $^{iPr}L_{Xan}Ti_2Cp_2Cl_2$ **(8)** in good yield. Structural studies reveal that **8** features two bridging chloride ligands. Reaction of the free-base bis(amidines) with 2 equiv of $CpTiMe_3$ forms the red σ-alkyl derivatives $^{iPr}L_{DBF}Ti_2Cp_2Me_4$ **(9)**, $^{tBu,Et}L_{DBF}Ti_2Cp_2Me_4$ **(10)**, and $^{iPr}L_{Xan}Ti_2Cp_2Me_4$ **(11)** in good yields. Structural data are presented for compounds **4**, **5**, **8**, and **9**.

Introduction

Bimetallic complexes play important roles in numerous areas of chemistry including metalloprotein modeling, supramolecular chemistry, and catalysis.[1] To control the physical properties and chemical reactivities of this class of compounds, it is necessary that a broad range of well-defined binucleating ligands be developed.[2] Generally these ligands feature multiple donor groups that are linked together with some sort of unreactive spacer. When properly designed, these ligands can prevent unwanted processes such as fragmentation and oligomerization. Their design is also useful for tailoring reactivity. In this context, we have been developing new preorganized binucleating ligands that are suitable for the preparation of early transition metal bimetallics. Binucleating ligands suitable for these relatively large and Lewis acidic metals are limited. Indeed, the vast majority of reported group 4 bimetallics have been supported by a small set of related oligocyclopentadienyl ligands.[3,4] These complexes are of interest as olefin polymerization catalysts,[5−16] and recently reported complexes have demonstrated promis-

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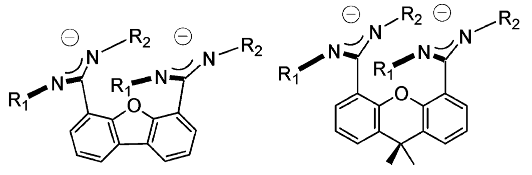
ing reactivity,[5−7] including increased branching in ethene homopolymerization and increased α-olefin incorporation in ethene/α-olefin copolymerization when compared to closely related mononuclear catalysts. In addition to their use in polymerizations, group 4 bimetallics have featured interesting structures and small-molecule reactivity. Notably, Petersen,[17−19] Cuenca,[20−22] and others[23−27] have explored insertion and redox chemistry of fulvalene and bridged bis(cyclopentadienyl) systems.

One direction for the further development of binuclear early metal chemistry involves the use of new binucleating ligands containing N- and O-donor atoms. Ligands using these donors have been widely used in mononuclear chemistry, often with dramatic effects on chemical reactivity.[28,29] However, this approach remains poorly developed in the context of early metal binuclear systems. Recent examples include rigid bis(amido),[30,31] bis(phenolate),[32] and bis(amidinate)[33−35] donors. To further develop this class of complexes, we are exploring several new preorganized binucleating ligands including bis(amidinates) supported by dibenzofuran and 9,9-dimethylxanthene backbones (Chart 1). These bis(amidinate) ligands have many desirable properties from a synthetic standpoint, including control over key structural features such as intermetal separation and sterics.

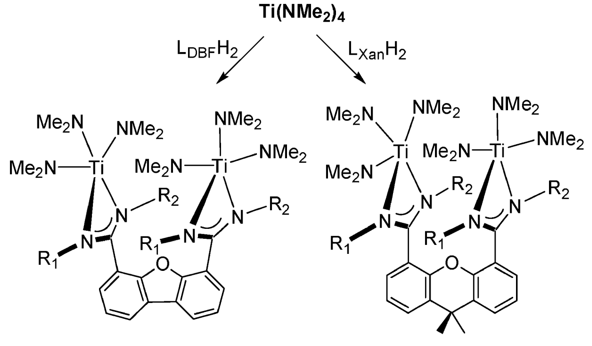
Chart 1



	R1	R2
$^{iPr}L_{DBF}$	^{i}Pr	^{i}Pr
$^{tBu,Et}L_{DBF}$	^{t}Bu	Et

	R1	R2
$^{iPr}L_{Xan}$	^{i}Pr	^{i}Pr
$^{tBu,Et}L_{Xan}$	^{t}Bu	Et

Scheme 1



	R1	R2
1	^{i}Pr	^{i}Pr
2	^{t}Bu	Et

	R1	R2
3	^{i}Pr	^{i}Pr
4	^{t}Bu	Et

Additionally, amidinates are known to form isolable complexes with a wide range of transition and main-group metals.[36,37] In this report we describe the preparation and characterization of several new dititanium complexes supported by these bis(amidinate) ligands.

Results and Discussion

Shown in Chart 1 are the four amidinate ligands used in this paper. As shown in Scheme 1, their neutral free-base forms, the bis(amidines), reacted with 2 equiv of $Ti(NMe_2)_4$ at 50 °C to form hexaamido derivatives **1**−**4**. These complexes were isolated as orange crystalline solids from Et_2O solutions in good yields, and they have been characterized by a combination of NMR spectroscopy and single-crystal X-ray diffraction. The ^{1}H NMR spectrum of **1** in C_6D_6 solution reveals a sharp singlet at δ 3.48 ppm (36H) for all 12 methyls of the 6 amido ligands. The bis(amidinate) ligand also features a characteristic septet at δ 3.30 ppm (4H) for the four methine protons of the isopropyl groups. These data indicate a highly symmetric structure which we attribute to rapid fluxionality in solution. Analogous Zr complexes have likewise displayed fluxional NMR spectra in solution.[38] To gain additional insight into the solution dynamics of these compounds we have also examined the NMR spectra of complexes featuring unsymmetrically substituted amidinate ligands. As shown in Scheme 2, compound **4** can exist as two diastereomers that are related by the 180° rotation of an amidinate group. ^{1}H NMR spectra of freshly prepared

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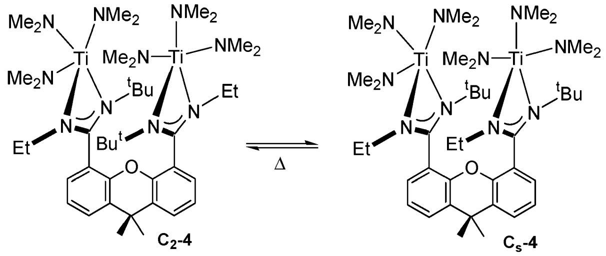
Table 1. Crystallographic Data and Collection Parameters

param	**4**	**5**	**8**	**9**
formula	$C_{41}H_{76}N_{10}OTi_2$	$C_{33}H_{52}N_6OCl_4Ti_2$	$C_{39}H_{50}Cl_2N_4OTi_2$	$C_{40}H_{56}N_4OTi_2$
fw	820.84	786.35	757.53	704.63
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	*Pnma* (No. 62)
temp (°C)	−122	−140	−132	−130
a (Å)	17.9840(8)	13.1241(6)	10.9048(3)	24.6997(10)
b (Å)	14.0692(6)	17.5798(8)	24.8225(6)	12.1194(5)
c (Å)	19.3685(8)	19.5927(8)	13.9014(3)	12.8143(5)
α (deg)	90	74.6940(1)	90	90
β (deg)	101.9340(1)	77.7090(1)	92.7880(10)	90
γ (deg)	90	79.2640(1)	90	90
Z	4	4	4	4
V ($Å^3$)	4794.7(4)	4219.4(3)	3758.4(2)	3835.9(3)
d_{calc} (g/cm^3)	1.137	1.299	1.339	1.220
θ range (deg)	2.02−25.03	2.09−27.48	2.04−25.03	2.29−25.03
μ (mm^{-1})	0.373	0.666	0.603	0.451
cryst size (mm)	0.5 × 0.4 × 0.3	0.5 × 0.3 × 0.2	0.2 × 0.2 × 0.15	0.3 × 0.3 × 0.2
reflcns collcd	37 384	32 256	21 861	29 725
data/restraints/params	11 006/0/510	19 132/7/907	6636/0/443	4595/41/437
R1 (for $F_o > 4\sigma(F_o)$)	0.0533	0.0691	0.0403	0.0524
R1, wR2 (all data)	0.0644, 0.1544	0.1079, 0.2004	0.0591, 0.1054	0.0935, 0.1453
GOF	1.066	1.026	1.024	0.954
largest peak, hole (e/Å^3)	0.59, −0.44	1.49, −0.79	0.54, −0.35	0.64, −0.44

Scheme 2



solutions of **4** in C_6D_6 revealed an 8:1 ratio for C_2-**4** and C_s-**4**, respectively. This ratio remained unchanged after several hours at room temperature. Heating the solution to 68 °C overnight, however, caused the ratio to change to 2:1. Further heating did not affect the ratio but led to slow decomposition to unidentified products. Thus, the initial 8:1 ratio is attributed to kinetic factors, and the equilibrium shown in Scheme 2 is close to thermoneutral with a calculated Δ*G* of 0.2 kcal/mol.

A sample of **4** was dissolved in Et_2O and cooled to 0 °C to afford crystals suitable for X-ray diffraction studies. These studies confirmed the general formulation, and a thermal ellipsoid plot of the solid-state structure is shown in Figure 1. Information related to data collection and refinement is shown in Table 1, and selected bond lengths and angles are found in Table 2. Not surprisingly, the molecule is the C_2-symmetric diastereomer that is preferentially formed during the synthesis. The molecule, however, does not reside on a crystallographic C_2-axis. The two Ti centers are quite similar with each featuring an asymmetric bidentate amidinate donor (e.g. Ti1−N1, 2.261(2), Ti1−N2, 2.071(2) Å) and three dimethylamido ligands. The geometry at each Ti center is intermediate to square pyramidal and trigonal bipyramidal. This is consistent with the calculated values of *τ* (Ti1, 0.57; Ti2, 0.51). The two Ti centers do not interact with each other, and the intermetal separation is 6.4792(6) Å. Bond lengths are typical when compared to reported values in related mononuclear complexes.[39,40]

The amido complexes **1**−**4** are useful precursors to many other derivatives. For example, **3** reacts with excess Me_3SiCl in toluene to form the mixed amido−chloride derivative **5**, which was isolated as a red solid in moderate yield (Scheme 3). Compound **5** can be conveniently prepared in higher yield by reaction of $^{iPr}L_{Xan}H_2$ with 2 equiv of $Ti(NMe_2)_2Cl_2$ in toluene solution. The ^1H NMR spectrum of **5** in $CDCl_3$ features a single resonance at *δ* 3.89 ppm (12H) for the two equivalent amido groups. There is also a septet at *δ* 3.35 ppm (4H) for the methine protons of the four ^iPr groups. These data are consistent with C_{2v} symmetry

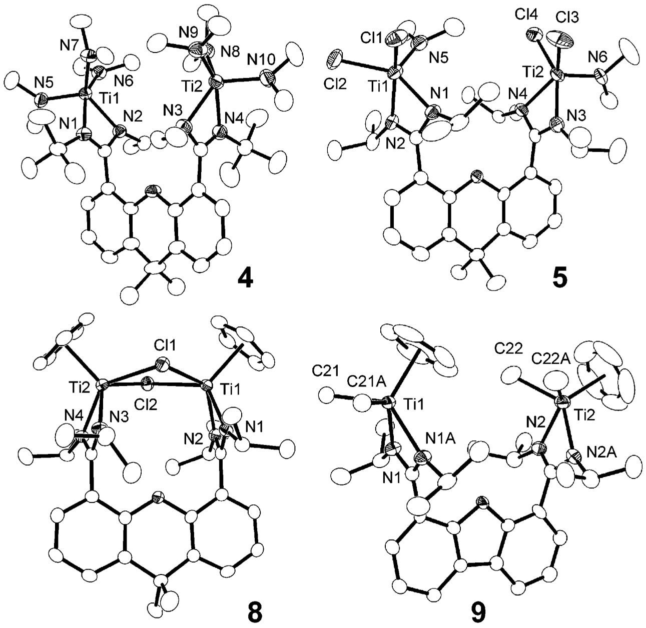


Figure 1. Molecular structures of **4**, **5**, **8**, and **9** drawn with 50% thermal ellipsoids. Hydrogens and cocrystallized solvent are not shown.

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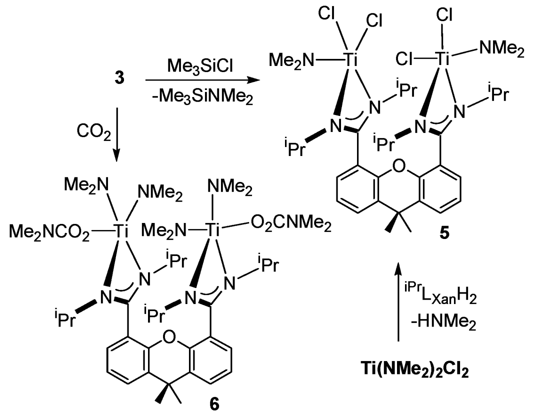
Table 2. Selected Bond Distances and Angles

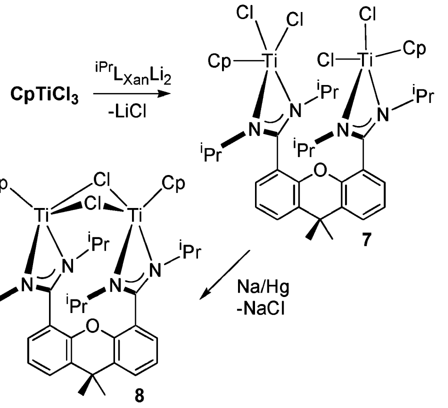
Compound **4**			
Ti1−N1	2.261(1)	Ti2−N8	1.912(2)
Ti1−N6	1.935(2)	Ti1−Ti2	6.4792(2)
Ti2−N4	2.258(2)	Ti1−N5	1.900(2)
Ti2−N10	1.895(2)	Ti2−N3	2.076(2)
Ti1−N2	2.071(1)	Ti2−N9	1.934(2)
Ti1−N7	1.909(2)		
N1−Ti1−N2	61.08(7)	N2−Ti1−N6	96.43(8)
N1−Ti1−N5	94.28(8)	N5−Ti1−N7	110.40(9)
N2−Ti1−N5	121.79(8)	N1−Ti1−N7	95.85(8)
N5−Ti1−N6	96.62(9)	N2−Ti1−N7	123.06(9)
N1−Ti1−N6	157.41(8)	N6−Ti1−N7	98.78(9)
Compound **5**			
Ti1−Cl1	2.291(1)	Ti2−N3	2.116(4)
Ti1−N2	2.066(3)	Ti1−Ti2	6.359(1)
Ti2−Cl4	2.319(1)	Ti1−N1	2.077(3)
Ti2−N6	1.842(3)	Ti2−Cl3	2.253(1)
Ti1−Cl2	2.292(1)	Ti2−N4	2.065(3)
Ti1−N5	1.846(3)		
Cl1−Ti1−Cl2	95.50(5)	Cl2−Ti1−N2	92.24(9)
Cl1−Ti1−N1	92.68(9)	N1−Ti1−N5	107.1(1)
Cl2−Ti1−N1	145.8(1)	Cl1−Ti1−N5	103.7(1)
N1−Ti1−N2	63.8(1)	Cl2−Ti1−N5	103.1(1)
Cl1−Ti1−N2	145.54(9)	N2−Ti1−N5	107.1(2)
Compound **8**			
Ti1−Cl1	2.4966(7)	Ti2−N3	2.067(2)
Ti1−N2	2.125(2)	Ti1−Ti2	3.7942(2)
Ti2−Cl2	2.4902(8)	Ti1−N1	2.086(2)
Ti2−$C_{Cp,ave}$	2.36	Ti2−Cl1	2.4978(8)
Ti1−Cl2	2.4886(8)	Ti2−N4	2.128(2)
Ti1−$C_{Cp,ave}$	2.37		
Cl1−Ti1−Cl2	78.19(2)	N1−Ti1−N2	63.56(8)
Cl1−Ti1−N1	89.82(6)	Cl1−Ti2−N4	133.33(6)
Cl2−Ti1−N2	86.66(6)	N3−Ti2−N4	63.34(8)
Cl1−Ti2−N3	84.56(6)	Cl2−Ti1−N1	125.09(6)
Cl2−Ti2−N4	91.20(6)	Cl1−Ti2−Cl2	78.14(2)
Ti1−Cl2−Ti2	99.29(3)	Cl2−Ti2−N3	122.72(7)
Cl1−Ti1−N2	133.19(6)	Ti1−Cl1−Ti2	98.87(3)
Compound **9**			
Ti1−N1	2.148(2)	N1−Ti1−N1A	62.0(1)
Ti2−N2	2.135(2)	Ti1−$C_{Cp,ave}$	2.36
Ti1−Ti2	6.8658(9)	Ti2−$C_{Cp,ave}$	2.35
Ti1−C21	2.132(3)	N1−Ti1−C21	87.10(9)
Ti2−C22	2.129(3)		
N1−Ti1−C21A	130.25(9)	N2−Ti2−C22A	130.1(1)
N2−Ti2−C22	86.9(1)	N2−Ti2−N2A	62.3(1)
C21−Ti1−C21A	85.1(2)	C22−Ti2−C22A	84.8(2)

Scheme 3



in solution on the time scale of the experiment. The coordination geometries at the Ti centers of **5** (Figure 1) are quite different from those of **4**. Compound **5** features symmetric amidinate ligands (Ti−N1, 2.077(3); Ti−N2, 2.066(3) Å) and distorted square pyramidal geometry at the two Ti centers, with τ values of 0.00 and 0.37 for Ti1 and Ti2, respectively. In d^0 square pyramidal complexes, the strongest donor is expected to occupy the apical position, and this is observed in **5**. Thus, the two amido donors occupy the pseudoapical positions, and the Ti−N_{amido} bonds (Ti1−N5, 1.846(3), Ti2−N6, 1.842(3) Å) are significantly shorter, by 0.07 Å on average, than the Ti−N_{amido} distances in compound **4**.

Scheme 4



Compound **3** reacts with CO$_2$ (10 psig) in C$_6$H$_6$ to form the mixed carbamate−amido derivative **6**, which was isolated in 36% yield as orange-red crystals. The composition of **6** is supported by a combination of NMR and IR spectroscopy and by combustion analysis. The IR spectrum of a mineral oil mull of **6** reveals a strong absorption at 1567 cm^{-1} which is consistent with bidentate coordination of the carbamate group.[41,42] It is unclear if the carbamates are each coordinated to a single Ti center or if they bridge the two metals. Both structural motifs have been reported.

Mixed Cp−amidinate complexes of Zr have been used to support reactive hydrido derivatives[38,43] as well as living catalysts for α-olefin polymerization.[44−46] Thus, we chose to explore the synthesis and reactivity of the related Ti-containing species. Entry to this class of compounds was achieved by the salt-metathesis reaction of $^{iPr}L_{Xan}Li_2$ with 2 equiv of CpTiCl$_3$ in toluene (Scheme 4). Dititanium **7** was isolated as a flocculent purple solid in moderate yield following extraction of the crude product into hot toluene and precipitation by the addition of hexanes. Solid **7** is highly susceptible to hydrolysis, and samples immediately turn yellow in the presence of water vapor. Unfortunately, we have been unable to determine the identity of the hydrolysis product due to its insolubility. The ^{1}H NMR spectrum of **7**

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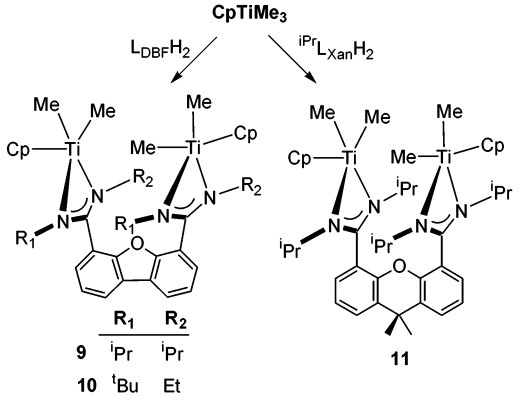
Scheme 5



(CDCl$_3$) is consistent with overall C_{2v} symmetry for the complex in solution. Reduction of **7** with an excess of 1% Na/Hg in toluene solution forms the paramagnetic dititanium(III) derivative **8**. Filtration of the solution, followed by the addition of HMDSO and cooling to −40 °C, afforded the product as orange-brown crystals in good yield. The ^{1}H NMR spectrum of **8** (C_6D_6) consists of four broad featureless resonances between 0 and 8 ppm, suggesting that the complex is paramagnetic. Using Evans' method, the solution magnetic moment was determined to be 2.3(1) μ_B. Thus, the pair of d^1 Ti centers is virtually uncoupled. The solid-state structure of **8** (Figure 1) reveals that the dititanium complex features a symmetric $Ti_2(\mu\text{-}Cl)_2$ core, with the four Ti−Cl bonds having lengths between 2.49 and 2.50 Å. The Ti−Cl−Ti angles are 98.87(3) and 99.29(3)°. The Cl−Ti−Cl angles are 78.19(2) and 78.14(2)°. Overall the structural features of the core are very similar to those reported for $[Ti_2Cl_2(Me_2ATI)_4]$[47] (Me_2ATI = *N,N′*-dimethylaminotroponiminate) and $[Cp_2TiCl]_2$.[48] Other dititanium(III) complexes, such as $\{[(Me_3SiNCH_2CH_2)_2NSiMe_3]TiCl\}_2$[49] and $[Ti(PMe_3)_2Cl_3]_2$,[50] have featured asymmetric $Ti_2(\mu\text{-}Cl)_2$ cores. As shown in Scheme 5, the bis(amidines) react with 2 equiv of $CpTiMe_3$ in toluene solution to afford dititanium σ-alkyl derivatives **9**−**11** in moderate-good yields. These products can also be synthesized by reaction of the bis(amidines) with $CpTiMe_3$, formed in-situ from $CpTiCl_3$ and MeLi in Et_2O at −30 °C. The advantage of this route is that the volatile and thermally sensitive $CpTiMe_3$ is never isolated. The molecular structure of **9** is shown in Figure 1. The molecule rests on a mirror plane of symmetry that passes through both Ti centers and the dibenzofuran backbone. The Ti−Me distances (Ti1−C21, 2.132(3), Ti2−C22, 2.129(3) Å) are similar to those of related Ti(IV) complexes.[40,51] Noticeably, the molecule features one Cp group directed inward while the other is directed outward. Despite this inequivalence of the Cp groups in the solid state, the ^{1}H NMR spectrum of **9** (C_6D_6) features sharp resonances consistent with overall C_{2v} symmetry for the bimetallic species. Thus, a singlet is observed at δ 6.49 ppm for the pair of equivalent Cp ligands. Another at δ 1.27 ppm is assigned to the four Ti−Me groups. ^{1}H NMR data for compound **11** indicate a similar symmetric structure in solution. ^{1}H NMR data for compound **10**, however, show that it is isolated as a 1:1 mixture of the C_2- and C_s-symmetric diastereomers.

In conclusion, we have demonstrated that preorganized bis(amidinate) ligands based on dibenzofuran and 9,9-dimethylxanthene backbones are well suited for the formation of a wide range of Ti bimetallics containing mixed-ligand systems. Reactivity studies with these complexes are ongoing.

Experimental Section

General Considerations. Standard Schlenk-line and glovebox techniques were used unless stated otherwise. Bis(amidines) $^{iPr}L_{DBF}H_2$, $^{tBu,Et}L_{DBF}H_2$, $^{iPr}L_{Xan}H_2$, and $^{tBu,Et}L_{Xan}H_2$ and their corresponding dilithium amidinate derivatives were prepared as previously described.[52] $Ti(NMe_2)_2Cl_2$ was prepared using a published method.[53] $CpTiMe_3$[54] was prepared from $CpTiCl_3$ and Me_2Mg in Et_2O solution and was sublimed (20 °C/10^{-2} mmHg) immediately prior to use. $Ti(NMe_2)_4$ and $CpTiCl_3$ were purchased from commercial sources. Hexanes, Et_2O, toluene, tetrahydrofuran (THF), and CH_2Cl_2 were passed through columns of activated alumina and sparged with N_2 prior to use. Hexamethyldisiloxane (HMDSO) was distilled from Na metal under nitrogen. C_6D_6 and toluene-d_8 were vacuum transferred from Na−benzophenone ketyl. $CDCl_3$ was vacuum transferred from CaH_2. Gaseous CO_2 (bone dry) was purchased from commercial sources and used as received. Chemical shifts (δ) for ^{1}H NMR spectra are given relative to residual protium in the deuterated solvent at 7.16, 7.24, and 2.10 ppm for C_6D_6, $CDCl_3$, and toluene-d_8, respectively. Infrared spectra were taken as mineral oil mulls between KBr plates unless stated otherwise. Solution magnetic moments were determined using Evans' method,[55] and diamagnetic corrections were applied using Pascal's constants.[56] Elemental analyses were determined by Desert Analytics. Analytical data are reported for one representative species for each series of closely related compounds. Melting points were determined in a N_2-filled drybox.

$^{iPr}L_{DBF}Ti_2(NMe_2)_6$ (1). $^{iPr}L_{DBF}H_2$ (1.28 g, 3.05 mmol) was dissolved in toluene (95 mL) to form a clear colorless solution. This solution was added to a stirring solution of $Ti(NMe_2)_4$ (1.37 g, 6.10 mmol) and toluene (5 mL). After 12 h at 50 °C the volatiles were removed under reduced pressure to afford an orange solid. The solid was dissolved in Et_2O (40 mL) and filtered. Cooling the solution to 0 °C afforded the product as orange crystals (1.8 g, 77%). Mp: 257 °C (dec). ^{1}H NMR (C_6D_6): δ 7.59 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.25 (dd, *J* = 7.4, 1.2 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 3.48 (s, 36 H, $-NMe_2$), 3.30 (sept, *J* = 6.4 Hz, 4H, $-NCMe_2H$), 1.10 (d, *J* = 6.4 Hz, 12H, $-NCHMeCH_3$), 1.04 (d, *J* = 6.4 Hz, 12H, $-NCHMeCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 172.3 (NCN), 153.1, 127.1, 125.3, 123.6, 121.4, 118.9, 50.4 ($-NCHMe_2$),

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47.1($-$N*Me*$_2$), 26.0 ($-$NCHMe*CH*$_3$), 25.5 ($-$NCHMe*CH*$_3$). IR: 2922 (s, br), 2853 (s, br), 2759 (vs, br), 1918 (w), 1858 (w), 1799 (w), 1523 (vs, br), 1461 (s, br), 1410 (vs, br), 1375 (s), 1334 (s), 1183 (s), 944 (s), 788 (m), 753 (w), 591 (m), 554 (m, br) cm^{-1}. Anal. Calcd (found) for $C_{38}H_{70}N_{10}OTi_2$: C, 58.61 (58.62); H, 9.06 (9.36); N, 17.99 (17.84).

$^{tBu,Et}L_{DBF}Ti_2(NMe_2)_6$ (2). The product was prepared in 76% yield from $^{tBu,Et}L_{DBF}H_2$ and $Ti(NMe_2)_4$ using a procedure analogous to that described for the preparation of **1**. ^{1}H NMR spectroscopic data of the isolated product (C_6D_6 solution) indicated a mixture of rotational diastereomers (C_2 and C_s symmetry) in an 11:1 ratio. The kinetic product is likely the C_2-symmetric form since it was observed in single-crystal X-ray diffraction studies. ^{1}H NMR spectroscopic data are given for both the C_2- and C_s-symmetric forms of compound **2**, but all other data are reported as observed for the product mixture as isolated. Mp: 236 °C (dec). ^{1}H NMR (C_6D_6) for C_2-**2**: δ 7.56 (dd, J = 7.7, 1.4 Hz, 2H), 7.25 (dd, J = 7.4, 1.2 Hz, 2H), 7.07 (t, J = 7.5 Hz, 2H), 3.47 (s, 36H, $-$N*Me*$_2$), 3.14 (m, 2H, $-$NC(H)*H*Me), 2.96 (m, 2H, $-$NC(H)*H*Me), 1.10 (s, 18H, $-$NC*(CH*$_3$*)*$_3$), 0.90 (t, J = 7.0 Hz, 6H, $-$NCH$_2$*CH*$_3$). ^{1}H NMR (C_6D_6) for C_s-**2**: δ 7.54 (dd, J = 7.7, 1.4 Hz, 2H), 7.28 (dd, J = 7.5, 1.4 Hz, 2H), 7.07 (t, J = 7.6 Hz, 2H), 3.45 (s, 36H, $-$N*Me*$_2$), 2.96 (m, 2H, $-$NC(H)*H*Me), 2.86 (m, 2H, $-$NC(H)*H*Me), 1.18 (s, 18H, $-$NC*(CH*$_3$*)*$_3$), 0.90 (t, J = 7.0 Hz, 6H, $-$NCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 172.5 ($-$N*C*N), 153.1, 128.3, 124.9, 123.1, 121.5, 120.8, 53.4 ($-$N*C*H$_2$Me), 46.5 ($-$N*Me*$_2$), 42.9, 32.7, 19.3. IR: 2955 (s, br), 2926 (vs, br), 2853 (vs, br), 2757 (m, br), 1921 (w), 1865 (w), 1809 (w), 1513 (m), 1458 (m, br), 1411 (m), 1239 (m), 963 (m), 945 (s), 784 (m), 753 (w), 591 (m), 566 (m, br) cm^{-1}.

$^{iPr}L_{Xan}Ti_2(NMe_2)_6$ (3). The product was prepared in 50% yield from $^{iPr}L_{Xan}H_2$ and $Ti(NMe_2)_4$ using a procedure analogous to that described for the preparation of **1**. Mp: 196 °C (dec). ^{1}H NMR (C_6D_6): δ 7.20 (d, J = 7.1 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 6.93 (t, J = 7.5 Hz, 2H), 3.44 (s, 36H, $-$N*Me*$_2$), 3.43 (sept, J = 6.5 Hz, 4H, $-$NC*H*Me$_2$), 1.43 (s, 6H, $-$C*Me*$_2$), 1.31 (d, J = 6.3 Hz, 12H, $-$NCHMe*CH*$_3$), 1.03 (d, J = 6.2 Hz, 12H, $-$NCHMe*CH*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 172.8, 147.8, 131.2, 128.6,, 127.2, 123.6, 123.2, 50.7 ($-$N*C*HMe$_2$), 47.6 ($-$N*Me*$_2$), 34.7 (-*C*Me$_2$), 33.5 ($-$C*Me*$_2$), 26.9 ($-$NCHMe*C*H$_3$), 25.3 ($-$NCHMe*C*H$_3$). IR: 2954 (s, br), 2924 (vs, br), 2853 (s), 2756 (m), 1489 (m), 1464 (m), 1422 (m), 1245 (m), 946 (s), 799 (w), 751 (w), 586 (w), 559 (w) cm^{-1}.

$^{tBu,Et}L_{Xan}Ti_2(NMe_2)_6$ (4). The product was prepared in 80% yield from $^{tBu,Et}L_{Xan}H_2$ and $Ti(NMe_2)_4$ using a procedure analogous to that described for the preparation of **1**. ^{1}H NMR spectroscopic data of the isolated product (C_6D_6 solution) indicated a mixture of rotational diastereomers in an 8:1 ratio for the C_2- and C_s-symmetric forms, respectively. ^{1}H NMR spectroscopic data are given for both the C_2- and C_s-symmetric forms of compound **4**, but all other data are reported as observed for the product mixture as isolated. Mp: 195$-$197 °C. ^{1}H NMR (C_6D_6) C_2-**4**: δ 7.18 (dd, J = 7.3, 1.4 Hz, 2H), 7.12 (dd, J = 7.7, 1.6 Hz, 2H), 6.86 (t, J = 7.5 Hz, 2H), 3.42 (s, 36H, $-$N*Me*$_2$), 3.46 (m, 2H, $-$NC(H)*H*Me), 3.05 (m, 2H, $-$NC(H)*H*Me), 1.43 (s, 6H, $-$C*Me*$_2$), 1.21 (s, 18H, $-$NC*(CH*$_3$*)*$_3$), 0.92 (t, J = 6.9 Hz, 6H, $-$NCH$_2$*CH*$_3$). ^{1}H NMR (C_6D_6) for C_s-**4**: δ 7.24 (dd, J = 7.5, 1.6 Hz, 2H), 7.15 (dd, J = 7.5, 1.6 Hz, 2H), 6.89 (t, J = 7.6 Hz, 2H), 3.42 (s, 36H, $-$N*Me*$_2$), 3.38 (m, 2H, $-$NC(H)*H*Me), 2.88 (m, 2H, $-$NC(H)*H*Me), 1.51 (s, 3H, $-$C(Me)*Me*), 1.51 (s, 3H, $-$C(Me)*Me*), 1.27 (s, 18H, $-$NC*(CH*$_3$*)*$_3$), 0.87 (t, J = 7.2 Hz, 6H, $-$NCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 172.5, 147.1, 130.5, 129.8, 127.7, 124.8, 122.9, 54.1 (N*C*Me$_3$), 47.0 (N*Me*$_2$), 43.7 (N*C*H$_2$Me), 34.6, 34.4, 32.8 (NC*Me*$_3$), 18.6 (NCH$_2$*Me*). IR: 2921 (vs, br), 2854 (vs, br), 2806 (m), 2759 (m), 1499 (w), 1456 (s, br), 1424 (s), 1413 (m), 1378 (m), 1249 (m), 964 (w), 948 (s), 750 (w), 588 (w) cm^{-1}.

$^{iPr}L_{Xan}Ti_2(NMe_2)_2Cl_4$ (5). Method A. Toluene (20 mL) was added to **3** (0.208 g, 0.254 mmol) to form a clear orange solution. Me_3SiCl (0.592 mL, 4.68 mmol) was added, and the mixture was heated to 85 °C to form a clear red solution. After 6 h, the volatiles were removed under reduced pressure, and the resulting red solid was washed with hexanes (2 × 10 mL) and Et_2O (2 × 10 mL) to give **5** (0.071 g, 36%).

Method B. $^{iPr}L_{Xan}H_2$ (2.78 g, 6.60 mmol) was dissolved in toluene (30 mL) to form a clear colorless solution. This solution was added to a stirring solution of $Ti(NMe_2)_2Cl_2$ (2.73 g, 13.2 mmol) in toluene (50 mL). After 2 h the volatiles were removed under reduced pressure to give a red solid. The solid was washed with Et_2O (2 × 40 mL) and then dissolved in warm benzene (30 mL). Cooling the solution to 5 °C yielded the product as red crystals (3.83 g, 78%). An analytically pure sample was obtained by recrystallization from Et_2O. Mp: 223$-$224 °C. ^{1}H NMR ($CDCl_3$): δ 7.61 (dd, J = 7.9, 1.7 Hz, 2H), 7.26 (t, J = 7.7 Hz, 2H), 7.09 (dd, J = 7.4, 1.7 Hz, 2H), 3.89 (s, 12H, $-$N*Me*$_2$), 3.35 (sept, J = 6.5 Hz, 4H, $-$NCMe$_2$*H*), 1.71 (s, 6H, $-$C*Me*$_2$), 1.37 (d, J = 6.6 Hz, 12H, $-$NCHMe*CH*$_3$), 1.17 (d, J = 6.5 Hz, 12H, $-$NCHMe*CH*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 173.8, 146.3, 131.0, 128.8, 128.5, 123.9, 118.0, 52.6, 49.9, 34.5 (-*C*Me$_2$), 33.4 ($-$C*Me*$_2$), 25.0 ($-$NCHMe*C*H$_3$), 23.8 ($-$NCHMe*C*H$_3$). IR: 2956 (vs), 2925 (vs), 2869 (vs), 2854 (vs), 2778 (w), 1617 (w), 1593 (w), 1453 (s), 1422 (vs), 1380 (m), 1342 (m), 1245 (m), 1210 (m), 1134 (m), 1042 (m), 940 (s), 878 (w), 801 (s), 753 (w), 687 (s), 596 (m) cm^{-1}. Anal. Calcd (found) for $C_{37}H_{62}Cl_4N_6O_2Ti_2$ (**5**·Et_2O): C, 51.65 (51.80); H, 7.26 (7.30); N, 9.77 (9.51).

$^{iPr}L_{Xan}Ti_2(NMe_2)_4(O_2CNMe_2)_2$ (6). Compound **3** (0.698 g, 0.850 mmol) was dissolved in benzene (10 mL) to form a clear orange solution. The flask was briefly evacuated and backfilled with CO_2 (10 psig). Within 5 h a red solution had formed. The volatiles were removed under reduced pressure, and the crude product was dissolved in warm HMDSO (20 mL) and filtered. Concentration to 5 mL followed by cooling to -15 °C afforded the product as a red solid (0.28 g, 36%). Mp: 161 °C (dec). ^{1}H NMR (C_6D_6): δ 7.44 (dd, J = 7.4, 1.7 Hz, 2H), 7.12 (dd, J = 7.8, 1.8 Hz, 2H), 6.97 (t, J = 7.6 Hz, 2H), 3.69 (s, 24H, $-$N*Me*$_2$), 3.49 (br, 4H, $-$NCMe$_2$*H*), 2.75 (s, 12H, O$_2$CN*Me*$_2$), 1.39 (s, 6H, $-$C*Me*$_2$), 1.38 (br, 12H, $-$NCHMe*CH*$_3$), 1.16 (br, 12H, $-$NCHMe*CH*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 170.1, 166.7, 146.9, 130.0, 129.3, 126.1, 122.5, 121.8, 50.3, 48.0, 34.0, 33.6, 32.3, 23.6. IR: 2950 (vs), 2928 (vs), 2918 (vs), 2914 (vs), 2850 (vs) 2804 (w), 1567 (s, $\nu_{str}(O_2CN)$), 1461 (s), 1410 (m), 1377 (s), 1274 (w), 1238 (w), 956 (m), 796 (w), 653 (m) cm^{-1}. Anal. Calcd (found) for $C_{49}H_{94}N_{10}O_6Si_2Ti_2$ (**6**·HMDSO): C, 54.94 (54.64); H, 8.84 (8.73); N, 13.08 (13.37).

$^{iPr}L_{Xan}Ti_2Cp_2Cl_4$ (7). Toluene (100 mL) was added to $CpTiCl_3$ (3.40 g, 15.5 mmol) and $^{iPr}L_{Xan}Li_2$ (3.68 g, 7.74 mmol) to form a dark orange-brown solution. After being stirred overnight, the volatile materials were removed under reduced pressure to afford a dark solid which was washed with hexanes (2 × 60 mL) to afford a lavender solid. The solid was extracted with hot toluene (300 mL) and filtered through a pad of diatomaceous earth on a fritted disk. To the purple filtrate was added hexanes (300 mL) to cause the formation of flocculent lavender microcrystals. The solid was isolated and dried under reduced pressure (4.00 g, 57.6%). ^{1}H NMR spectroscopy and elemental analysis indicate that the product cocrystallizes with ca. 0.75 equiv of toluene. Mp: 230 °C (dec). ^{1}H NMR ($CDCl_3$): δ 7.57 (d, 2H, J = 7.6 Hz), 7.26$-$7.22

(m, 5H), 7.17−7.12 (m, 4H), 6.93 (br s, 10H, *Cp*), 3.49 (sept, 4H, $J = 6.4$ Hz, NC(*H*)Me$_2$), 2.34 (s, 3H, *toluene*), 1.66 (s, 6H, −C*Me*$_2$-), 1.23 (d, 12H, $J = 6.4$ Hz, NC(H)Me(C*H*$_3$)), 1.09 (br, 12H, NC(H)Me(C*H*$_3$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 146.3, 137.9, 129.0, 128.2, 128.0, 125.3, 123.7, 121.0 (br), 119.1, 52.9, 34.3, 32.8, 24.4 (br), 23.2, 21.5. Anal. Calcd (found) for $C_{44.25}H_{56}Cl_4N_4OTi_2$ (**7**·0.75toluene): C, 59.22 (58.91); H, 6.29 (6.20); N, 6.24 (6.06).

$^{iPr}L_{Xan}Ti_2Cp_2Cl_2$ (8). Toluene (40 mL) was added to **7** (0.35 g, 0.38 mmol) and 1% Na/Hg amalgam (0.12 g Na, 5.1 mmol) to form a burgundy colored solution over the amalgam. After being stirred overnight, the solution was filtered through a pad of diatomaceous earth on a fritted disk to afford a clear orange solution. The solution was concentrated to 15 mL and HMDSO (20 mL) was added. Cooling to −40 °C yielded the product as orange-brown crystals, which were isolated and dried under reduced pressure (0.20 g, 69%). μ_{eff} (298 K, C$_6$D$_6$): 2.3(1) μ_B. ^{1}H NMR (C$_6$D$_6$): δ 6.75 (br, $\omega_{1/2} = 90$ Hz), 6.09 (br, $\omega_{1/2} = 35$ Hz), 1.97 (br, $\omega_{1/2} = 280$ Hz), 1.63 (br, $\omega_{1/2} = 32$ Hz). Anal. Calcd (found) for $C_{39}H_{50}Cl_2N_4OTi_2$: C, 61.84 (61.47); H, 6.65 (6.46); N, 7.40 (7.21).

$^{iPr}L_{DBF}Ti_2Cp_2Me_4$ (9). The product was prepared in 60% yield from CpTiCl$_3$, MeLi, and $^{iPr}L_{DBF}H_2$ by a procedure analogous to method B for the synthesis of **11**. Mp: 136 °C (dec). ^{1}H NMR (C$_6$D$_6$): δ 7.57 (dd, $J = 7.7$, 1.2 Hz, 2H), 7.27 (d, $J = 7.1$ Hz, 2H), 7.13 (t, $J = 7.6$ Hz, 2H), 6.49 (s, 10H, *Cp*), 3.18 (sept, $J = 6.6$ Hz, 4H, −NCMe$_2$*H*), 1.27 (s, 12H, Ti-*Me*), 1.02 (d, $J = 6.5$ Hz, 12H, −NCHMe(C*H*$_3$)), 0.98 (d, $J = 6.6$ Hz, 12H, −NCHMe-(C*H*$_3$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 169.3 (N*C*N), 152.6, 127.5, 125.2, 123.9, 121.7, 117.5, 115.6, 69.5 (Ti−*Me*), 51.1(N*C*HMe$_2$). IR (KBr, mineral oil): 2920 (vs, br), 2925 (vs, br), 2929 (vs, br, mineral oil), 2866 (vs, br), 2728 (w), 1646 (w), 1627 (w), 1464 (vs, br, mineral oil), 1419 (m), 1376 (s, mineral oil), 1344 (m), 1186 (m), 1169 (w), 810 (s), 789 (m) cm^{-1}.

$^{tBu,Et}L_{DBF}Ti_2Cp_2Me_4$ (10). The product was prepared in 40% yield from $^{tBu,Et}L_{DBF}H_2$ and CpTiMe$_3$ by a procedure analogous to method A for the synthesis of **11**. ^{1}H NMR spectroscopic data of the isolated product (C$_6$D$_6$ solution) indicated a mixture of rotational diastereomers (C_2 and C_s symmetry) in a 1:1 ratio. ^{1}H NMR (C$_6$D$_6$): δ 7.55 (dd, $J = 7.7$, 1.2 Hz, 2H), 7.54 (dd, 7.6, 1.2 Hz, 2H), 7.44 (br, 4H), 7.09 (t, $J = 7.5$ Hz, 2H), 7.08 (t, $J = 7.5$ Hz, 2H), 6.48 (s, 20H, *Cp*), 2.80 (m, 8H, NC*H*$_2$Me), 1.13 (s, 6H, Ti−*Me*), 1.12 (s, 6H, Ti−*Me*), 1.10 (s, 6H, Ti−*Me*), 1.09 (s, 6H, Ti−*Me*), 1.04 (s, 18H, NC*Me*$_3$), 1.02 (s, 18H, NC*Me*$_3$), 0.75 (t, $J = 7.2$ Hz, 6H, NCH$_2$*Me*), 0.72 (t, $J = 7.2$ Hz, 6H, NCH$_2$*Me*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 167.3, 167.1, 152.6, 152.5, 124.4, 124.4, 123.1, 123.0, 121.3, 121.3, 120.0, 120.0, 115.3, 115.3, 66.7, 66.3, 54.6, 54.6, 43.1, 43.0, 32.4, 32.3, 17.3, 17.2. IR: 2953 (s, br), 2924 (vs, br), 2854 (s, br), 1466 (m), 1456 (s, br), 1420 (w), 1190 (w), 807 (m), 784 (w), 755 (w) cm^{-1}.

$^{iPr}L_{Xan}Ti_2Cp_2Me_4$ (11). Method A. Toluene (80 mL) was added to CpTiMe$_3$ (2.88 g, 18.2 mmol) and $^{iPr}L_{Xan}H_2$ (4.22 g, 9.12 mmol) to form an orange-red solution with noticeable gas evolution. After being stirred overnight at 40 °C, the volatile materials were removed under reduced pressure. The resulting solid was extracted into warm hexanes (200 mL) and filtered. Cooling to −40 °C afforded the product as red crystals (5.0 g, 73%).

Method B. CpTiCl$_3$ (1.56 g, 7.12 mmol) was dissolved in Et$_2$O (80 mL) and cooled to −30 °C. An Et$_2$O solution of MeLi (13.2 mL, 21.4 mmol) was added dropwise to form a clear yellow solution. To this solution was added a toluene solution (30 mL) of $^{iPr}L_{Xan}H_2$ (1.65 g, 3.56 mmol), and the mixture was heated to 40 °C. After 12 h the volatiles were removed under reduced pressure to afford a red solid. This solid was dissolved in warm hexanes (150 mL) and filtered through diatomaceous earth on a glass frit. Concentration of the solution to 50 mL and cooling to −40 °C afforded the product as a deep red solid (1.6 g, 60%). An analytically pure sample was prepared by recrystallization from hexanes. Mp: 146−149 °C (dec). ^{1}H NMR (C$_6$D$_6$): δ 7.17 (m, 2H), 7.13 (dd, $J = 7.9$, 1.6 Hz, 2H), 6.92 (t, $J = 7.5$ Hz, 2H), 6.42 (s, 10H, *Cp*), 3.42 (sept, $J = 6.5$ Hz, 4H, −NCMe$_2$*H*), 1.37 (s, 6H, −C*Me*$_2$−), 1.21 (s, 12H, Ti-*Me*), 1.20 (d, $J = 6.5$ Hz, 12H, −NCHMe(C*H*$_3$)), 0.92 (d, $J = 6.3$ Hz, 12H, −NCHMe(C*H*$_3$)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 168.6 (N*C*N), 147.2, 130.8, 128.9, 127.1, 123.6, 121.8, 115.0 (*Cp*), 68.0 (Ti−*Me*), 50.8 (N*C*HMe$_2$), 34.3 (-*C*Me$_2$−), 32.8 (−C*Me*$_2$−), 26.1 (NCHMe(*Me*)), 24.5 (NCHMe(*Me*)). Anal. Calcd (found) for $C_{43}H_{62}N_4OTi_2$: C, 69.16 (68.65); H, 8.37 (8.26); N, 7.50 (7.37).

X-ray Crystallography. Table 1 lists a summary of crystal data and collection parameters for all crystallographically characterized compounds. Table 2 lists selected bond lengths and angles.

General Procedure. A crystal of appropriate size was mounted on a glass fiber using Paratone-N oil, transferred to a Siemens SMART diffractometer/CCD area detector, centered in the beam (Mo Kα; $\lambda = 0.710\,73$ Å; graphite monochromator), and cooled to by a nitrogen low-temperature apparatus. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A minimum of a hemisphere of data was collected using 0.3° ω scans. The raw data were integrated and the unit cell parameters refined using SAINT. Data analysis was performed using XPREP. Absorption correction was applied using SADABS. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Structure solutions and refinements were performed (SHELXTL-Plus V5.0) on F^2.[57]

Structure of $^{tBu,Et}L_{Xan}Ti_2(NMe_2)_6$ (4). Crystals suitable for X-ray diffraction studies were grown from Et$_2$O at 0 °C. Preliminary data indicated a primitive monoclinic cell. Systematic absences indicated space group $P2_1/c$ (No. 14) which was confirmed by the successful solution and refinement of the structure. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of $^{iPr}L_{Xan}Ti_2(NMe_2)_2Cl_4$ (5). Crystals suitable for X-ray diffraction studies were grown from C$_6$H$_6$ at 5 °C. Preliminary data indicated a primitive triclinic cell. The choice of the centric space group was confirmed by the successful solution and refinement of the structure. Carbon atoms associated with a disordered ^{i}Pr group were refined isotropically. All other non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of $^{iPr}L_{DBF}Ti_2Cp_2Cl_2$ (8). Crystals suitable for X-ray diffraction studies were grown from toluene-hexanes at 25 °C. Preliminary data indicated a primitive monoclinic cell. Systematic absences indicated space group $P2_1/n$ (No. 14). All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of $^{iPr}L_{DBF}Ti_2Cp_2Me_4$ (9). Crystals suitable for X-ray diffraction studies were grown from benzene at 5 °C. Preliminary data indicated a primitive orthorhombic cell. Analysis of all data indicated systematic absences consistent with space groups *Pnma*

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(57) Sheldrick, G. M. *SHELXTL: A Program for Crystal Structure Determination*, version 5.03; Siemens Analytical X-ray Instruments: Madison, WI, 1995.

and *Pna*2_1. The choice of *Pnma* (No. 62) was confirmed by the successful solution and refinement of the structure. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined. It was necessary to restrain the 1,2- and 1,3-bond lengths of both cyclopentadienyl anions.

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Supporting Information Available: Crystallographic information files (CIF) for compounds **2**−**5** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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