New Chiral Amide Ligands Derived from (±)-*trans*-1,2-Diaminocyclohexane. Applications in Titanium(IV) Chemistry

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Titanium(IV) hydrocarbyl compounds containing chiral bis(amide) ligands derived from (±)-*trans*-1,2-$(NHSiR_3)_2$-cyclohexanes (**6a**−**c**: SiR_3 = $SiMe_3$ (**a**), $SiMe_2Ph$ (**b**), $SiMePh_2$ (**c**) are described. The reaction of (±)-*trans*-1,2-diaminocyclohexane with SiR_3Cl and NEt_3 affords diamines **6a**−**c** in 60−80% yield. Double deprotonation of **6a**−**c** with 2 equiv of *n*-BuLi yields the dilithio salts Li_2[(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane] **(7a**−**c)** in 70−97% yield. The reaction of **7a**,**b** with $TiCl_4(THF)_2$ in toluene yields mixtures of {(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane}$TiCl_2$ (**8a**,**b**) and bis(ligand) complexes {*trans*-1,2-$(NSiR_3)_2$-cyclohexane}$_2$Ti (**9a**,**b**; mixture of diastereomers). The reaction of **7c** with $TiCl_4$ yields {(±)-*trans*-1,2-$(NSiMePh_2)_2$-cyclohexane}$TiCl_2$ (**8c**; 15% isolated yield). The reaction of **6a**,**b** and $Ti(CH_2Ph)_4$ yields {(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane}$Ti(CH_2Ph)_2$ (**10a**,**b**) cleanly, but these species are difficult to isolate due to their high solubility. Iodinolysis of **10a**,**b** with I_2 yields {(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane}TiI_2 (**11a**,**b**) in 60−80% isolated yield. **11a**,**b** can be prepared in 60−80% isolated yield (vs $Ti(CH_2Ph)_4$) in a "one-pot" reaction by treatment of $Ti(CH_2Ph)_4$ with **6a**,**b** followed by iodinolysis. The dimethyl and diphenyl derivatives {(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane}$TiMe_2$ (**12a**,**b**) and {(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane}$TiPh_2$ (**13a**,**b**) are prepared by the reaction of **11a**,**b** and RMgX reagents. X-ray crystallographic analyses establish that **10a** and **11a** have distorted tetrahedral structures with small N−Ti−N angles (ca. 92°) and large X−Ti−X angles (ca. 116°).

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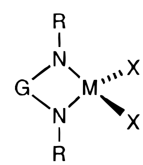
Introduction

Group 4 metal complexes of general type (RN−G−NR)MX_2 (**1**; G = linking group) containing bidentate bis(amide) ligands are promising systems for applications in catalysis because of their relationship to the well-studied metallocene analogues Cp_2MX_2 (**2**),[1] hybrid "half-metallocene" $(C_5R_4SiR_2NR)MX_2$ complexes (**3**),[2] and bis(amide) $(R_2N)_2MX_2$ compounds (**4**).[3] An attractive goal in this area is to design and develop chiral metal complexes which incorporate readily available chiral amides for exploitation in stereoselective catalysis. Here we describe the chemistry of new Ti hydrocarbyl complexes which contain bis(silylamide) ligands derived from (±)-*trans*-1,2-diaminocyclohexane (**5**, eq 1). Cloke recently described a Zr benzyl complex containing a chiral bis(amide) ligand derived from 2,2′-diamino-6,6′-dimethylbiphenyl,[4] and a variety of other *achiral*



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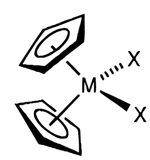

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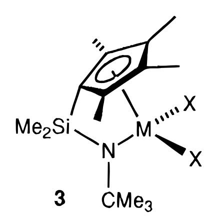

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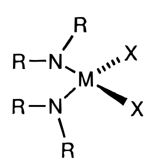

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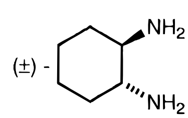

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⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1997.

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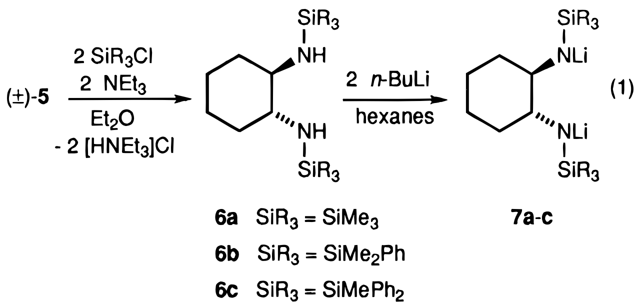
bidentate bis(amide) ligands have been used in group 4 metal chemistry.[5]

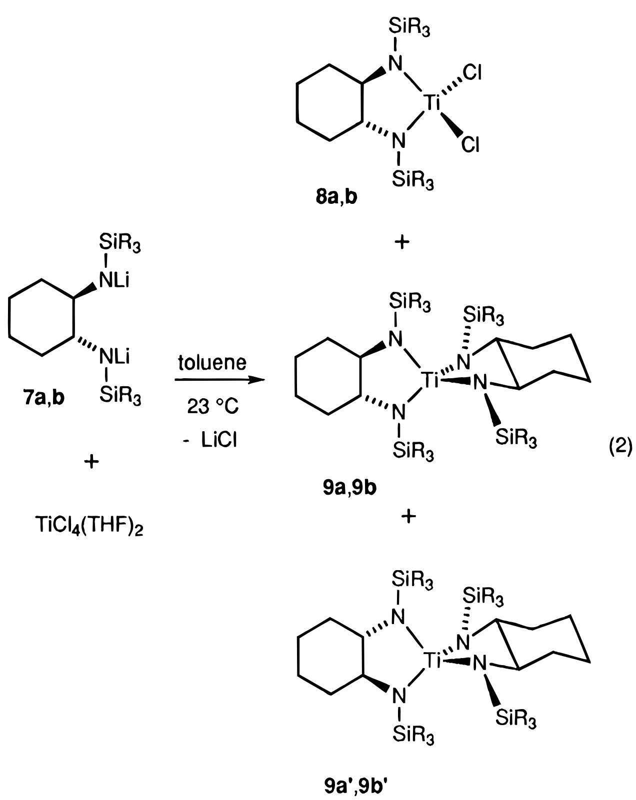
Results and Discussion

Synthesis of {(±)-*trans*-1,2-($NSiR_3$)$_2$-cyclohexane}-TiX_2 and {(±)-*trans*-1,2-($NSiR_3$)$_2$-cyclohexane}TiR_2 Complexes. The reaction of **5** with 2 equiv of SiR_3Cl (R_3 = Me_3, Me_2Ph, $MePh_2$) and 2 equiv of NEt_3 in Et_2O yields (±)-*trans*-1,2-($NHSiR_3$)$_2$-cyclohexanes **6a**−**c** and 2 equiv of [$HNEt_3$]Cl (eq 1). Bis(amines) **6a**−**c** are



isolated as viscous oils in 60−80% yield by vacuum distillation. Double deprotonation of **6a**−**c** with *n*-BuLi in hexanes yields dilithio salts **7a**−**c**, which are isolated as white solids (70−97%).

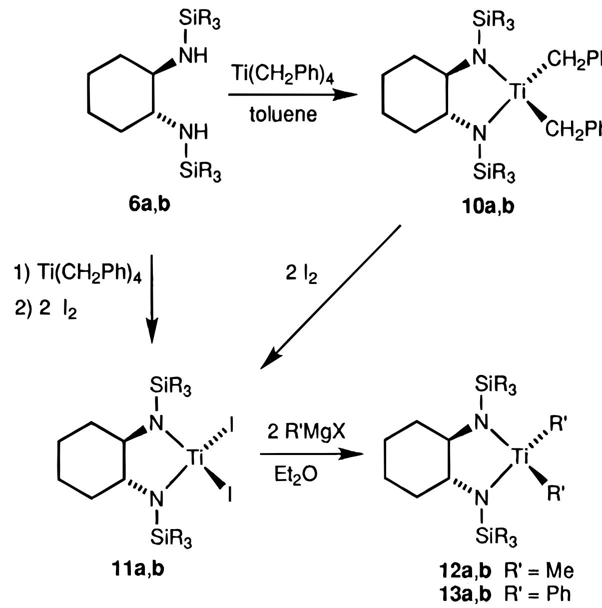
We initially investigated halide displacement routes to {(±)-*trans*-1,2-($NSiR_3$)$_2$-cyclohexane}TiX_2 complexes (eq 2). The reaction of **7a** with $TiCl_4(THF)_2$ in toluene



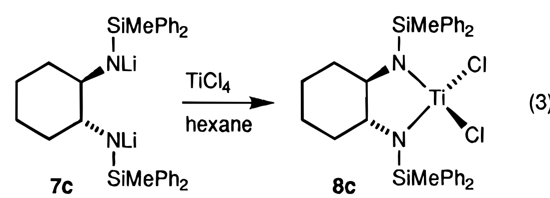
yields a 1/1 mixture of {(±)-*trans*-1,2-($NSiMe_3$)$_2$-cyclohexane}$TiCl_2$ (**8a**) and {*trans*-1,2-($NSiMe_3$)$_2$-cyclohexane}$_2$Ti (**9a**,**a′**). The latter species can be isolated in low yield from this reaction, but **8a** cannot. Similarly, the reaction of **7b** with $TiCl_4(THF)_2$ yields a 3/5 mixture

(4) Cloke, F. G. N.; Geldbach, T. J.; Hitchcock, P. B.; Love, J. B. *J. Organomet. Chem.* **1996**, *506*, 343.

Scheme 1



of mono- and bis(ligand) complexes **8b** and **9b**,**b′**. Bis(ligand) complexes **9a**,**a′** and **9b**,**9b′** are formed as mixtures of diastereomers which differ in the relative stereochemistry of the two bis(amide) ligands and can be distinguished but not structurally assigned by NMR spectroscopy.[6] In contrast, the reaction of the bulkier reagent **7c** with $TiCl_4$ in hexanes yields {(±)-*trans*-1,2-($NSiMePh_2$)$_2$-cyclohexane}$TiCl_2$ (**8c**) cleanly, but this complex is isolated only with difficulty and in low yield (15%) due to its high solubility (eq 3).



Alkane elimination approaches to {(±)-*trans*-1,2-($NSiR_3$)$_2$-cyclohexane}TiR_2 and {(±)-*trans*-1,2-($NSiR_3$)$_2$-cyclohexane}TiX_2 compounds were investigated to avoid the difficulties encountered in the chloride substitution reactions (Scheme 1). The reaction of **6a**,**b** and Ti(CH_2-

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(6) The configuration of **9a**,**b** is *R*,*R*,*R*,*R*, and the point group symmetry is D_2. The configuration of the *meso* diastereomer **9a′**,**b′** is *S*,*S*,*R*,*R*, and the point group symmetry is S_4. Due to these symmetry properties, the NMR spectra of both isomers have the same number of resonances.

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Table 1. Summary of Crystallographic Data for {(±)-*trans*-1,2-($NSiMe_3$)$_2$-cyclohexane}Ti(CH_2Ph)$_2$ (10a) and {(±)-*trans*-1,2-($NSiMe_3$)$_2$-cyclohexane}TiI_2 (11a)

	10a	**11a**·C_6H_6
empirical formula	$C_{26}H_{42}N_2Si_2Ti$	$C_{18}H_{34}I_2N_2Si_2Ti$
fw	486.71	636.35
crystal size (mm)	0.18 × 0.30 × 0.67	0.24 × 0.32 × 0.44
color/shape	orange/plate	red/fragment
space group	*C*2/*c*	*Cmcm*
a (Å)	20.131(5)	8.637(1)
b (Å)	9.850(3)	20.295(2)
c (Å)	14.335(4)	15.807(2)
β (deg)	101.26(2)	90
V ($Å^3$)	2788(3)	2770.8(5)
Z	4	4
T (K)	210	295
diffractometer	Enraf-Nonius CAD4	Siemens P4
radiation, *λ* (Å)	Mo Kα, 0.7107	Mo Kα, 0.7107
2*θ* range (deg)	4−55	4.0−50.0
data collected: *h*; *k*; *l*	-25, 26; −12, 1; −18, 4	0, 10; 0, 24; 0, 18
no. of reflns	4760	1348
no. of unique reflns	3182	1348
R_{int}	0.012	
no. of obsd reflns ($I > 2\sigma(I)$)	2603	855
μ (cm^{-1})	4.02	26.3
transm range (%)	97−100	69.0−82.5
structure soln	direct methods	direct methods
refinement	FMLS on *F* non-H anisotropic H refined, isotropic	FMLS on F^2 non-H anisotropic H fixed, isotropic
GOF	1.018	1.031
R indices	$R = 0.030^a$ $R_w = 0.036^b$	R1 (all data) = 0.0838^c wR2 (all data) = 0.1350^d
max resid density (e/$Å^3$)	0.28	0.74

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$. [b] $R_w = \{[\Sigma(F_o - F_c)^2]/[\Sigma w(F_o)^2]\}^{1/2}$. [c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = [\Sigma w_i(F_o^2 - F_c^2)^2/\Sigma w_i(F_o^2)^2]^{1/2}$.

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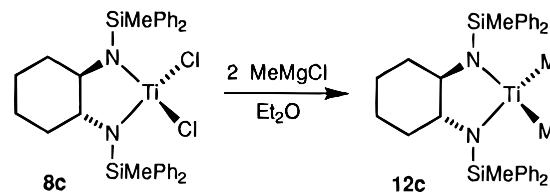
Ph)$_4$ in toluene affords the corresponding dibenzyl compounds **10a**,**b** with release of 2 equiv of toluene (NMR yield: **10a**, 100%; **10b**, 80%). **10a** forms cleanly after 48 h at room temperature and can be recrystallized as orange plates from pentane (10%). **10b** forms after 5 d at room temperature and is isolated as a red-brown solid by crystallization from toluene (45%). The low isolated yields again reflect the high solubility of these compounds. No bis(ligand) side products are seen in either case. However, **6c** does not react with Ti(CH_2Ph)$_4$ at room temperature in toluene, presumably due to excessive steric hindrance. At higher temperatures, Ti(CH_2Ph)$_4$ decomposes.

The reaction of **10a**,**b** with 2 equiv of I_2 yields diiodide complexes **11a**,**b**, which are isolated as crystalline solids in 80% yield by recrystallization from pentane (Scheme 1). Benzyl iodide is the sole benzyl-containing product of these reactions.[7] Complexes **11a**,**b** can be prepared in high yield from Ti(CH_2Ph)$_4$ in "one-pot" reactions. Thus, *in situ* generation of **10a**,**b** (from **6a**,**b** and Ti(CH_2Ph)$_4$; Scheme 1) followed by iodinolysis affords **11a**,**b** in 80% and 63% isolated yields, respectively (based on Ti(CH_2Ph)$_4$). This approach avoids the difficulty of isolating highly soluble **10a**,**b**. Diiodides **11a**,**b** are converted to the dimethyl derivatives **12a**,**b** by reaction with MeMgI and to the diphenyl derivatives **13a**,**b** by reaction with PhMgBr (Scheme 1). Similarly, the reaction of **8c** with MeMgCl yields {(±)-*trans*-1,2-($NSiMePh_2$)$_2$-cyclohexane}$TiMe_2$ (**12c**, eq 4).



(4)

Characterization of {(±)-*trans*-1,2-($NSiR_3$)$_2$-cyclohexane}TiX_2 and {(±)-*trans*-1,2-($NSiR_3$)$_2$-cyclohexane}TiR_2 Complexes. The new {(±)-*trans*-1,2-($NSiR_3$)$_2$-cyclohexane}TiX_2 and {(±)-*trans*-1,2-($NSiR_3$)$_2$-cyclohexane}TiR_2 complexes **8** and **10**−**13** have been characterized by NMR spectroscopy and elemental analysis. The NMR spectra are consistent with the expected C_2-symmetric structures. In all cases, the methine C*H*N ^{1}H NMR resonance shifts downfield by 3−4 ppm to δ 4−5 from the corresponding resonances in **6a**−**c** and **7a**−**c**. The J_{HH} and J_{CH} values for the $TiCH_2Ph$ groups in **10a**,**b** are in the range observed for normal η^1-benzyl complexes; i.e., there is no evidence for Ti···Ph (η^n-benzyl) interactions in these systems.[8]

The molecular structures of **10a** and **11a** have been determined by X-ray diffraction. Crystallographic details and selected bond distances and angles are listed in Tables 1−3.

The molecular structure of **10a** is shown in Figure 1. **10a** is located on a crystallographic 2-fold axis, which passes through the Ti atom and the centers of the C1−C1′ and C3−C3′ bonds, and therefore has rigorous C_2 symmetry. The cyclohexane ring of **10a** adopts a chair

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(8) For leading references relating to characterization of metal−benzyl bonding, see refs 1a and 1c and: (a) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897. (b) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (c) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902.

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for {(±)-*trans*-1,2-($NSiMe_3)_2$-cyclohexane}Ti($CH_2Ph)_2$ (10a)[a]

Ti1−N1	1.879(1)	N1−C1	1.486(2)
Ti1−C10	2.143(2)	C1−C1′	1.543(3)
Si1−N1	1.749(1)	C1−C2	1.524(2)
C11−C12	1.392(3)	C2−C3	1.528(2)
Si1−C7	1.868(2)	C3−C3′	1.529(4)
Si1−C8	1.863(2)	C10−C11	1.486(3)
Si1−C9	1.869(2)		
N1−Ti1−N1′	91.97(8)	Ti1−N1−Si1	124.12(7)
N1−Ti1−C10	113.42(6)	Ti1−N1−C1	107.73(9)
N1−Ti1−C10′	108.67(7)	Si1−N1−C1	124.9(1)
C10−Ti1−C10′	117.8(1)	Ti1−C10−C11	113.7(1)

[a] Transformation used to generate equivalent atoms: (′) 2.0 − *x*, *y*, 1.5 − *z*.

Table 3. Bond Distances (Å) and Bond Angles (deg) for {(±)-*trans*-1,2-($NSiMe_3)_2$-cyclohexane}TiI_2 (11a)[a]

Ti−N	1.836(2)	Ti−I	2.6321(7)
Ti−C1	2.695(3)	Si−N	1.777(3)
Si−C4	1.830(3)	Si−C5	1.872(3)
N−C1	1.487(4)		
N−Ti−N′	93.0(2)	N−Ti−I″	111.57(3)
I−Ti−I″	115.45(3)	N−Si−C4	110.26(9)
N−Si−C5	107.6(2)	C4*−Si−C4	110.6(2)
C4−Si−C5	109.0(1)	C1−N−Si	123.7(2)
C1−N−Ti	107.9(2)	Si−N−Ti	127.4(1)
N−C1−C2	116.4(2)	N−C1−C1″	108.9(2)

[a] Symmetry transformations used to generate equivalent atoms: (′) *x*, *y*, −*z* + 3/2; (″) −*x*, *y*, −*z* + 3/2; (*) −*x*, *y*, *z*.

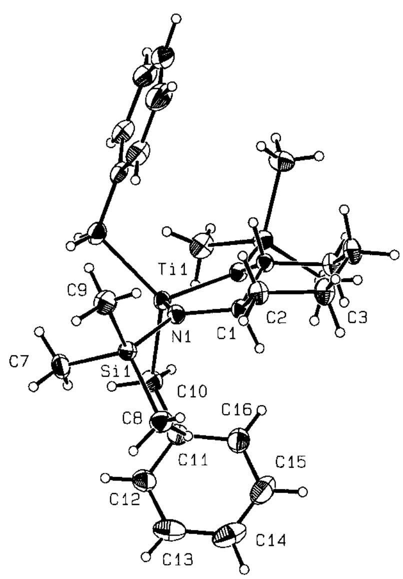

Figure 1. Molecular structure of {(±)-*trans*-1,2-($NSiMe_3)_2$-cyclohexane}Ti($CH_2Ph)_2$ (**10a**).

conformation with the −N(SiR_3)Ti groups in equatorial positions, and the five-membered Ti−N−C−C−N ring adopts an envelope conformation. The geometry around Ti is distorted tetrahedral; the N−Ti−N′ angle (91.97(8)°) is smaller than the ideal tetrahedral value due to the chelation, and the C10−Ti−C10′ angle is correspondingly larger (117.8(1)°). The benzyl ligands are bonded in a normal η^1-mode, and the amide nitrogens are sp^2-hybridized (sum of angles around N1 = 357°).

The molecular structure of **11a** is shown in Figure 2. The Ti atom lies on a 2-fold axis, and consequently **11a** has crystallographically-imposed C_2 symmetry. The structure of **11a** is very similar to that of **10a**; the chair

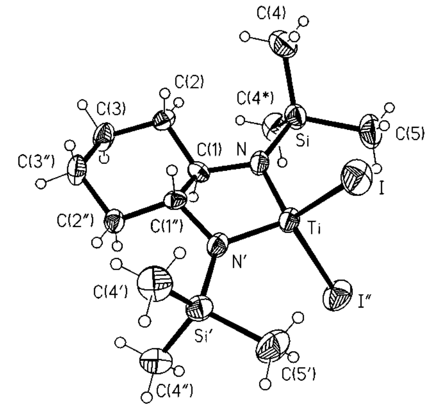

Figure 2. Molecular structure of {(±)-*trans*-1,2-($NSiMe_3)_2$-cyclohexane}TiI_2 (**11a**).

conformation of the cyclohexane ring, the distorted tetrahedral geometry around Ti, and the Ti−N distances are nearly identical for the two compounds.

The asymmetry of the (±)-*trans*-1,2-($NSiR_3)_2$-cyclohexane ligand appears not to be effectively transmitted to the Ti coordination sphere in **10a** and **11a**. In **10a**, the two $NSiMe_3$ groups, which are related by the crystallographically-imposed C_2 axis, are symmetrically placed above/below the Bn−Ti−Bn plane such that the Si1, N1, Ti1, N1′, and Si1′ atoms are essentially coplanar. The Si1 atom is displaced 0.070(4) Å from the N1′-Ti1-N1 plane, and the N1′-Ti1-N1-Si1 dihedral angle is −177.2(1)°. Similarly, in **11a**, the two $NSiMe_3$ units are related by a crystallographically-imposed mirror plane, and the Si, N, Ti, N′, and Si′ atoms are again coplanar. In contrast, the binding pocket created by the {2,2′-($NCH_2Ar)_2$-6,6′-Me_2-biphenyl}Zr core of Cloke's chiral system appears to have more pronounced C_2 character.[4]

Comparison of structural data for **10a**, **11a**, and related chelated bis(amide) Ti(IV) compounds of type **1** with data for complexes of types **2**−**4** reveals several significant trends. Key bond angles and distances for selected compounds are listed in Table 4. Linking the Cp and amide ligands in ($C_5Me_4SiMe_2N^tBu)TiCl_2$ (**14**) results in a 12−23° decrease in the L−Ti−L angle and corresponding 5−10° increase in the X−Ti−X angle versus the values observed for Cp_2TiX_2 (**15**) or ($R_2N)_2$-TiX_2 (**16**) complexes.[3g,9] Somewhat smaller L−Ti−L angles and larger X−Ti−X angles are observed for complexes of type **17**, which contain bis(amide) ligands joined by a three-carbon linker.[5j] In comparison, linking the amide ligands in a five-membered chelate ring in **10a**, **11a**, **18**, and **19** decreases the L−Ti−L angle by 15−18° and increases the X−Ti−X angle by 7−23° relative to the corresponding values for **14**.[5a,c] While steric interactions contribute to these differences to some degree, it is clear that the TiX_2 units in the latter set of compounds are much more sterically accessible than those in **14**−**16**. The commercially valuable performance features of **14** and analogous compounds in olefin polymerization, e.g. high comonomer incorporation in ethylene/α-olefin copolymerization and long-chain branching, have been ascribed to the open geom-

(9) (a) X-ray data for Cp_2TiCl_2: Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622. (b) X-ray data for Cp_2TiBn_2: Scholz, J.; Rehbaum, F.; Thiele, K. H.; Goddard, R.; Betz, P.; Krüger, C. *J. Organomet. Chem.* **1993**, *443*, 93.

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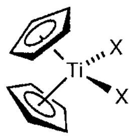
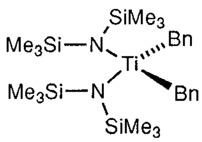
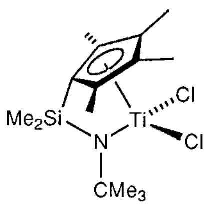
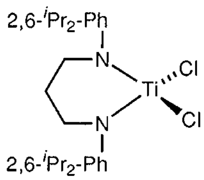
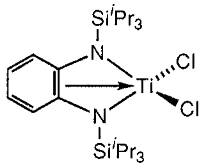
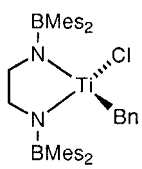
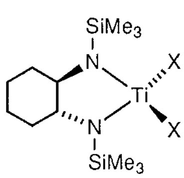
Table 4. Comparison of Key Structural Data for L_2TiX_2 Compounds

L_2TiX_2			L-Ti-L (deg)	X-Ti-X (deg)	Ti-X (Å)	Ti-N (Å)	Ref.
	**15**	X = Cl	130.89(5)	94.43(6)	2.367(2)		9a
		X = Bn	131.7	91.0(2)	2.239(6)		9b
	**16**		120.6(1)	98.4(2)	2.109(4)	1.931(3)	3g
	**14**		107.6	102.97(7)	2.263(1)	1.907(4)	2h
	**17**		99.2(2)	107.77(9)	2.257(2)	1.856(5)	5j
					2.240(2)	1.839(5)	
	**18**		92.6(2)	109.6(1)	2.251(2)	1.878(4)	5a
	**19**		89.2(2)	125.5(2)	2.325(3)	1.894(6)	5c
	**10a**	X = Bn	91.97(8)	117.8(1)	2.143(2)	1.879(1)	this work
	11a	X = I	93.0(2)	115.45(3)	2.6321(7)	1.836(2)	this work

etry imposed by the $[CpSiMe_2NR]^{2-}$ ligand, which facilitates coordination of the bulky (versus ethylene) α-olefin to the $(CpSiMe_2NR)TiR^+$ active species.[2] Additionally, the unusual living α-olefin polymerization behavior reported for catalysts derived from **17** may be related, at least in part, to the metal geometry imposed by the six-membered chelate ring.[5i] It will be interesting to probe how the more pronounced structural constraints caused by the bis(amide) ligands in the {(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane}TiX_2 complexes described here, and related complexes such as **18** and **19**, influence the reactivity of these systems.

Summary

C_2-symmetric {(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane}-TiX_2 and {(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane}TiR_2 complexes containing chiral bis(amide) ligands derived from (±)-*trans*-1,2-diaminocyclohexane are accessible by halide displacement or alkane elimination routes. The most efficient synthesis of the dialkyl derivatives is *in situ* generation of dibenzyl complexes **10a**,**b** by toluene elimination reactions of $Ti(CH_2Ph)_4$, iodinolysis to **11a**,**b**, and subsequent alkylation. These new {(±)-*trans*-1,2-$(NSiR_3)_2$-cyclohexane}TiX_2 complexes can be activated for olefin polymerization using standard approaches developed for metallocene catalysts, as will be discussed in a future report.

Experimental Section

General Procedures. All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum, Schlenk, or drybox techniques. Chlorotrimeth-

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ylsilane, (±)-*trans*-1,2-diaminocyclohexane, chlorodimethylphenylsilane, chloromethyldiphenylsilane, and triethylamine were distilled from CaH_2. Benzene-d_6, diethyl ether, tetrahydrofuran-d_8, toluene, pentane, and hexanes were distilled from Na/benzophenone ketyl. Commercial reagents MeMgCl, MeMgI, PhMgBr, $TiCl_4(THF)_2$, and *n*-BuLi were used as received. $Ti(CH_2Ph)_4$ was prepared by the literature method.[10] ^{1}H (360 MHz) and ^{13}C{^{1}H} (90 MHz) NMR spectra were recorded on a Bruker AMX-360 spectrometer at 23 °C. J_{CH} values were determined from ^{13}C gated-{^{1}H} spectra. Elemental analyses were performed by E&R Microanalytical Labs, Inc., Desert Analytics, or Galbraith Laboratories, Inc. Mass spectra were recorded on a VG Analytical ZAB-HF.

(±)-*trans*-1,2-(NHSiMe$_3$)$_2$-cyclohexane (6a). A solution of $SiMe_3Cl$ (4.04 g, 37.2 mmol) in Et_2O (5 mL) was cannula-transferred to a solution of (±)-*trans*-1,2-diaminocyclohexane (2.11 g, 18.4 mmol) in Et_2O (20 mL) at 23 °C. An exothermic reaction ensued, and a white solid formed. The reaction mixture was stirred for 1 h, and a solution of NEt_3 (3.98 g, 39.4 mmol) in Et_2O (45 mL) was added. The reaction mixture was stirred overnight and filtered, and the white precipitate was washed with Et_2O (50 mL). The filtrate and wash were combined and evaporated to dryness under vacuum. The product was isolated by short-path distillation (10^{-3} mm Hg, bp 92.9−96.0 °C) as a colorless oil (3.82 g, 80.3%). ^{1}H NMR (C_6D_6): δ 2.21 (m, 2H, CH), 1.87 (m, 2H, CH), 1.52 (m, 2H, CH), 1.15 (m, 2H, CH), 1.04 (m, 2H, CH), 0.66 (br s, 2H, NH), 0.13 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 59.2 (CN), 37.0 (NC*C*), 25.8 (NCC*C*), 1.1 (CSi). EI MS, *m/z*: M^+ calcd for $C_{12}H_{30}N_2Si_2$, 258.1948; found, 258.1966.

(±)-*trans*-1,2-(NHSiMe$_2$Ph)$_2$-cyclohexane (6b). A solution of $SiMe_2PhCl$ (26.29 g, 154.0 mmol) in Et_2O (15 mL) was added by cannula to a solution of (±)-*trans*-1,2-diaminocyclohexane (8.80 g, 77.1 mmol) in Et_2O (15 mL). Neat NEt_3 (22.0 mL, 158 mmol) was immediately added by syringe. An exothermic reaction ensued, and a white precipitate formed. The mixture was stirred for 2 d at 23 °C and filtered. The white solid was washed with Et_2O (50 mL), and the filtrate and wash were combined. The volatiles were removed under vacuum, and the product was isolated by short-path distillation (10^{-3} mm Hg, bp 160−170 °C) as a colorless oil (23.7 g, 80.4%). ^{1}H NMR (C_6D_6): δ 7.6 (m, 4H, *o*-H), 7.3−7.2 (m, 6H, *m*- and *p*-H), 2.29 (m, 2H, CH), 1.78 (m, 2H, CH), 1.38 (m, 2H, CH), 0.95 (m, 6H, CH, CH, and NH), 0.34 (s, 6H, CH_3), 0.33 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 141.0 (Ph *ipso*-C), 134.1 (Ph *o*-C), 129.3 (Ph *m*- or *p*-C), 128.1 (Ph *m*- or *p*-C), 59.0 (CN), 36.7 (NC*C*), 26.0 (NCC*C*), −0.01 (CH_3), −0.28 (CH_3). EI MS, *m/z*: M^+ calcd for $C_{22}H_{34}N_2Si_2$, 382.2260; found, 382.2240.

(±)-*trans*-1,2-(NHSiMePh$_2$)$_2$-cyclohexane (6c). Neat $SiMePh_2Cl$ (48.0 mL, 232.6 mmol) was added by syringe to a solution of (±)-*trans*-1,2-diaminocyclohexane (13.6 g, 119.1 mmol) in Et_2O (600 mL). A white precipitate formed. Neat NEt_3 (42.0 mL, 301.3 mmol) was immediately added by syringe. The reaction mixture was stirred for 2 d and filtered, and the white precipitate was washed with Et_2O (200 mL). The filtrate and wash were combined, and the volatiles were removed under vacuum. The product was isolated by short-path distillation (10^{-3} mm Hg, bp 210−225 °C) as a pale yellow viscous oil (38.1 g, 63.0%). ^{1}H NMR (C_6D_6): δ 7.7 (m, 8H, *o*-H), 7.2 (m, 12H, *m*- and *p*-H), 2.48 (m, 2H, CH), 1.83 (m, 2H, CH), 1.30 (m, 4H, CH), 0.94 (m, 4H, CH and NH), 0.62 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 139.0 (Ph *ipso*-C), 138.9 (Ph *ipso*-C), 135.1 (Ph *o*-C), 135.0 (Ph *o*-C), 129.6 (Ph *p*-C), 128.2 (Ph *m*-C), 128.1 (Ph *m*-C), 59.2 (CN), 36.4 (NC*C*), 25.6 (NCC*C*), −1.30 (CH_3). EI MS, *m/z*: M^+ calcd for $C_{32}H_{38}N_2Si_2$, 506.2574; found, 506.2603.

Li$_2$[(±)-*trans*-1,2-(NSiMe$_3$)$_2$-cyclohexane] (7a). A solution of **6a** (2.22 g, 8.60 mmol) in hexanes (50 mL) was cooled to −78 °C, and *n*-BuLi (6.5 mL, 2.73 M in hexanes, 17.7 mmol) was added by syringe. The reaction mixture was warmed to room temperature slowly and stirred for 9 h. The volatiles were removed under vacuum, leaving a white solid (2.24 g, 96.5%). ^{1}H NMR (C_6D_6): δ 2.61 (m, 2H, CH), 2.32 (m, 2H, CH), 1.60 (m, 2H, CH), 1.24 (m, 4H, CH), 0.21 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 67.1 (CN), 39.6 (NC*C*), 26.5 (NCC*C*), 3.1 (CH_3). Anal. Calcd for $C_{12}H_{28}Li_2N_2Si_2$: C, 53.29; H, 10.46; N, 10.36. Found: C, 53.23; H, 10.51; N, 10.16.

Li$_2$[(±)-*trans*-1,2-(NSiMe$_2$Ph)$_2$-cyclohexane] (7b). A solution of **6b** (2.14 g, 5.59 mmol) in hexanes (40 mL) was cooled to −78 °C, and *n*-BuLi (4.2 mL, 2.73 M in hexanes, 11.5 mmol) was added by syringe. A white precipitate formed. The mixture was warmed to room temperature, stirred for 9 h, and filtered, yielding a white solid, which was dried under vacuum overnight (2.04 g, 92.4%). ^{1}H NMR (C_6D_6): δ 7.92 (d, J = 6.92 Hz, 4H, *o*-H), 7.26 (m, 6H, *m*- and *p*-H), 2.07 (m, 2H, CH), 1.54 (m, 2H, CH), 0.99 (m, 4H, CH), 0.64 (m, 2H, CH), 0.49 (s, 3H, CH_3), 0.46 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (C_6D_6): δ 139.7 (Ph *ipso*-C), 136.3 (Ph *o*-C), 136.1 (Ph *o*-C), 130.4 (Ph *p*-C), 129.6 (Ph *m*-C), 64.8 (CN), 39.3 (NC*C*), 26.7 (NCC*C*), 6.7 (CH_3), 1.6 (CH_3).

Li$_2$[(±)-*trans*-1,2-(NSiMePh$_2$)$_2$-cyclohexane] (7c). A solution of **6c** (11.5 g, 22.7 mmol) in hexanes (50 mL) was cooled to 0 °C, and *n*-BuLi (28.0 mL, 2.14 M in hexanes, 59.9 mmol) was added by syringe. A white precipitate formed. The mixture was stirred at 23 °C for 24 h and filtered, yielding a white solid, which was dried under vacuum (8.59 g, 72.8%). ^{1}H NMR (THF-d_8): δ 7.57 (dd, J = 7.45, 1.55 Hz, 4H, *o*-H), 7.50 (dd, J = 5.98, 1.80 Hz, 4H, *o*-H), 7.18 (m, 12H, *m*- and *p*-H), 2.88 (br s, 2H, CH), 2.05 (m, 2H, CH), 1.46 (br s, 2H, CH), 1.20 (m, 4H, CH), 0.39 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (THF-d_8): δ 148.5 (Ph *ipso*-C), 148.0 (Ph *ipso*-C), 135.3 (Ph *o*-C), 135.2 (Ph *o*-C), 127.7 (Ph *p*-C), 127.6 (Ph *p*-C), 127.5 (Ph *m*-C), 127.4 (Ph *m*-C), 68.4 (CN), 41.0 (NC*C*), 27.8 (NCC*C*), 2.5 (CH_3).

Generation of {(±)-*trans*-1,2-(NSiMe$_3$)$_2$-cyclohexane}-TiCl$_2$ (8a) and {*trans*-1,2-(NSiMe$_3$)$_2$-cyclohexane}$_2$Ti (9a). Li$_2$[(±)-*trans*-1,2-(NSiMe$_3$)$_2$-cyclohexane] (0.51 g, 1.9 mmol) was added in portions to a slurry of $TiCl_4(THF)_2$ (0.63 g, 1.9 mmol) in toluene (60 mL) at 23 °C over 50 min. The mixture was stirred overnight, during which it turned from yellow to black. ^{1}H NMR analysis of an aliquot revealed the presence of **8a** and **9a** in a 53/47 molar ratio based on Ti. The mixture was filtered through Celite, yielding a brown precipitate and a dark orange filtrate. The filtrate was concentrated to ca. 20 mL and cooled to −20 °C for 2 d. Yellow crystals of **9a** (diastereomer ratio = 7/3) deposited from solution and were collected by filtration (0.060 g, 5.0%). The filtrate was taken to dryness under vacuum, yielding an orange solid which was determined to be a 5/1 mixture of **8a**/**9a**. The identity of **9a** was confirmed by independent NMR-scale synthesis: A mixture of **7a** (0.032 g, 0.12 mmol) and $TiCl_4(THF)_2$ (0.018 g, 0.054 mmol) in C_6D_6 (ca. 0.6 mL) was shaken for 2 min and maintained at 23 °C overnight. The ^{1}H NMR spectrum revealed complete conversion to **9a** (diastereomer ratio = 3/5). **8a** ^{1}H NMR (C_6D_6): δ 4.73 (m, 2H, methine H), 1.25 (m, 4H, CH), 1.13 (m, 2H, CH), 0.94 (m, 2H, CH), 0.25 (s, 18H, CH_3). **8a** ^{13}C{^{1}H} NMR (C_6D_6): δ 71.1 (CN), 33.3 (NC*C*), 24.9 (NCC*C*), 0.7 (CH_3). **9a** ^{1}H NMR (C_6D_6): 4.24 (m, 4H, methine H), 1.80 (m, 4H, CH), 1.52 (m, 4H, CH), 1.40 (m, 4H, CH), 1.22 (m, 4H, CH), 0.36 and 0.35 (s, CH_3, major isomer, and s, CH_3, minor isomer; total 18H). **9a** ^{13}C{^{1}H} NMR (C_6D_6): δ 67.7 (CN, major isomer), 67.0 (CN, minor isomer), 35.8 (NC*C*, minor isomer), 35.6 (NC*C*, major isomer), 25.7 (NCC*C*; both isomers), 3.0 (CH_3, major isomer), 2.6 (CH_3, minor isomer). Anal. Calcd for $C_{24}H_{56}N_4Si_4Ti$: C, 51.37; H, 10.08; N, 9.99. Found: C, 51.27; H, 10.08; N, 9.97.

Generation of {(±)-*trans*-1,2-(NSiMe$_2$Ph)$_2$-cyclohexane}-TiCl$_2$ (8b) and {*trans*-1,2-(NSiMe$_2$Ph)$_2$-cyclohexane}$_2$Ti (9b). An NMR tube was charged with Li$_2$[(±)-*trans*-1,2-(NSiMe$_2$Ph)$_2$-cyclohexane] (0.022 g, 0.060 mmol) and TiCl$_4$-(THF)$_2$ (0.019 g, 0.060 mmol). Benzene-d_6 (ca. 1.2 mL) was added by vacuum transfer at −78 °C, and the tube was sealed

(10) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

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and allowed to warm to room temperature. The mixture turned dark orange, and a brown precipitate formed. The ^{1}H NMR spectrum established that a 3/5 mixture of **8b**/**9b** was present. The identity of **9b** was confirmed by alternate synthesis: A mixture of **7b** (0.027 g, 0.069 mmol) and $TiCl_4(THF)_2$ (0.011 g, 0.033 mmol) in C_6D_6 (ca. 0.6 mL) was shaken for 2 min and maintained at 23 °C for 24 h. The ^{1}H NMR spectrum revealed complete conversion to **9b** (1/2 mixture of diastereomers). **8b** ^{1}H NMR (C_6D_6): δ 7.67 (m, 4H, *o*-H), ca. 7.2 (*m*- and *p*-H, obscured), 4.90 (m, 2H, methine H), cyclohexane CH's obscured, 0.64 (s, 6H, CH_3), 0.59 (s, 6H, CH_3). **8b** $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.7 (Ph *ipso*-C), 133.5 (Ph *o*-C), 130.3 (Ph *p*-C), 128.5 (Ph *m*-C), 72.0 (CN), 33.4 (NC*C*), 5.4 (NCC*C*), 1.8 (CH_3), −0.4 (CH_3). **9b** ^{1}H NMR: δ 7.78 (m, 8H, *o*-H), 7.20 (m, 12H, *m*- and *p*-H), 4.38 (m, 4H, methine H), 1.74 (m, 4H, CH), 1.25 (br m, 12H, CH), 0.85 and 0.82 (s, CH_3 minor isomer, and s, CH_3 major isomer; total 24H). **9b** $^{13}C\{^1H\}$ NMR: δ 142.3 (Ph *ipso*-C, minor), 142.1 (Ph *ipso*-C, major), 134.2 (Ph *o*-C, minor), 134.1 (Ph *o*-C, major), 129.2 (Ph *p*-C), 128.1 (Ph *m*-C), 67.9 (CN, minor), 67.4 (CN, major), 36.0 (NC*C*, minor), 35.7 (NC*C*, major), 25.4 (NCC*C*), 3.3 (CH_3, major and minor), 1.75 (CH_3, major), 0.44 (CH_3, minor).

{(±)-*trans*-1,2-(NSiMePh$_2$)$_2$-cyclohexane}TiCl$_2$ (8c). A solution of **6c** (1.20 g, 2.37 mmol) in hexanes (60 mL) was cooled to 0 °C, and *n*-BuLi (2.0 mL, 2.5 M in hexanes, 5.0 mmol) was added by syringe. A white precipitate formed immediately. The mixture was stirred for 10 min at 0 °C, after which it was cooled to −196 °C, and $TiCl_4$ (0.42 g, 2.21 mmol) was added by vacuum transfer. The reaction mixture was warmed to −78 °C, stirred for 5 h, and then warmed to room temperature and stirred overnight. The mixture was filtered, and the filtercake was washed with hexanes (40 mL). The combined filtrate and wash were taken to dryness under reduced pressure to give an orange solid, which was recrystallized from toluene/hexanes (1/2 by volume) at −20 °C (3 d) to yield orange crystals (0.22 g, 15%). ^{1}H NMR (C_6D_6): δ 7.88 (m, 8H, *o*-H), 7.18 (m, 12H, *m*- and *p*-H), 5.24 (m, 2H, methine H), 1.35 (m, 2H, CH), 1.19 (m, 2H, CH), 0.97 (m, 2H, CH), 0.89 (s, 6H, CH_3), 0.68 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 135.9 (Ph *o*-C), 135.7 (Ph *o*-C), 135.1 (Ph *ipso*-C), 134.5 (Ph *ipso*-C), 130.8 (Ph *m*-C), 130.6 (Ph *m*-C), 128.6 (Ph *p*-C), 72.9 (CN), 34.1 (NC*C*), 24.9 (NCC*C*), −0.26 (CH_3).

{(±)-*trans*-1,2-(NSiMe$_3$)$_2$-cyclohexane}Ti(CH$_2$Ph)$_2$ (10a). NMR scale: An NMR tube was charged with $Ti(CH_2Ph)_4$ (0.23 g, 0.55 mmol) and **6a** (0.14 g, 0.54 mmol). C_6D_6 (2 mL) was added by vacuum transfer at −78 °C, and the tube was flame-sealed. The mixture was allowed to warm to room temperature, and a deep red solution formed. The tube was maintained at 23 °C for 48 h. A ^{1}H NMR spectrum was recorded and revealed complete conversion to **10a**. Prep scale: A solution of $Ti(CH_2Ph)_4$ (2.09 g, 5.06 mmol) and **6a** (1.33 g, 5.16 mmol) in toluene (20 mL) was stirred at room temperature for 48 h. The mixture was filtered, and the filtrate was evaporated under vacuum to yield a brown oil (71%). Recrystallization of the oil from pentane (2 mL, −40 °C, 4 d) gave orange plates (0.26 g, 10%). The extremely high solubility of this compound reduced the efficiency of the recrystallization. ^{1}H NMR (C_6D_6): δ 7.18 (t, J = 7.9 Hz, 4H, *m*-H), 7.05 (d, J = 7.1 Hz, 4H, *o*-H), 6.90 (t, J = 7.3 Hz, 2H, *p*-H), 3.88 (m, 2H, methine H), 2.68 (d, J = 10.7 Hz, 2H, CH_2Ph), 2.53 (d, J = 10.7 Hz, 2H, CH_2Ph), 1.53 (m, 2H, CH), 1.36 (m, 2H, CH), 1.13 (m, 2H, CH), 1.01 (m, 2H, CH), 0.21 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.5 (Ph *ipso*-C), 128.6 (Ph *o*-C), 127.4 (Ph *m*-C), 122.2 (Ph *p*-C), 75.2 (CH_2Ph, $^1J_{CH}$ = 117 Hz), 65.2 (CN), 34.2 (NC*C*), 25.3 (NCC*C*), 1.9 (CH_3). Anal. Calcd for $C_{26}H_{42}N_2Si_2Ti$: C, 64.15; H, 8.71; N, 5.76. Found: C, 63.25; H, 8.82; N, 5.23.

{(±)-*trans*-1,2-(NSiMe$_2$Ph)$_2$-cyclohexane}Ti(CH$_2$Ph)$_2$ (10b). NMR scale: An NMR tube was charged with $Ti(CH_2Ph)_4$ (0.14 g, 0.33 mmol) and **6b** (0.17 g, 0.44 mmol). C_6D_6 (1.2 mL) was added by vacuum transfer at −78 °C, and the tube was flame-sealed. The tube was warmed to and maintained at room temperature for 7 d. The ^{1}H NMR spectrum revealed that 80% conversion to **10b** had occurred. Preparative scale: A solution of $Ti(CH_2Ph)_4$ (7.39 g, 17.9 mmol) and **6b** (6.48 g, 16.9 mmol) in toluene (55 mL) was stirred at room temperature for 16 d. The solution was concentrated to 10 mL and cooled to −40 °C for 2 d. A red-brown solid precipitated (4.30 g, 45.3%). The ^{1}H NMR spectrum established that this material was 98% pure **10b**. ^{1}H NMR (C_6D_6): δ 7.47 (m, 4H, SiPh *o*-H), 7.23−7.20 (m, 10H, SiPh *m*- and *p*-H, benzyl *m*-H), 7.13 (m, 4H, benzyl *o*-H), 6.94 (d, J = 7.2 Hz, 2H, benzyl *p*-H), 4.12 (m, 2H, methine H), 2.80 (d, J = 10.8 Hz, 2H, CH_2Ph), 2.71 (d, J = 10.8 Hz, 2H, CH_2Ph), 1.43 (m, 2H, CH), 1.04 (m, 4H, CH), 0.73 (m, 2H, CH), 0.55 (s, 6H, CH_3), 0.50 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.6 (CH_2Ph *ipso*-C), 140.6 (SiPh *ipso*-C), 134.1 (SiPh *o*-C), 129.6 (SiPh *p*-C), 129.0 (SiPh *m*-C), 128.4 (CH_2Ph *o*-C), 127.3 (CH_2Ph *m*-C), 122.6 (CH_2Ph *p*-C), 77.0 (Ti*C*H$_2$Ph, $^1J_{CH}$ = 116.7 Hz), 65.8 (CN), 34.4 (NC*C*), 25.5 (NCC*C*), 1.4 ($SiCH_3$), −0.02 ($SiCH_3$). Anal. Calcd for $C_{36}H_{46}N_2Si_2Ti$: C, 70.77; H, 7.60; N, 4.59. Found: C, 70.84; H, 7.55; N, 4.60.

"One-Pot" Synthesis of {(±)-*trans*-1,2-(NSiMe$_3$)$_2$-cyclohexane}TiI$_2$ (11a). A flask was charged with $Ti(CH_2Ph)_4$ (11.86 g, 28.77 mmol) and **6a** (7.420 g, 28.72 mmol), and toluene (80 mL) was added at room temperature. The solution was stirred for 3 d, at which point the ^{1}H NMR spectrum of an aliquot (C_6D_6) revealed 94% conversion to **10a**. The solution of **10a** was cooled to −78 °C, and a solution of I_2 (13.70 g, 53.98 mmol) in toluene (70 mL) was added by cannula. The mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum to leave an oily brown solid. The crude material was taken up in pentane (125 mL), and the mixture was filtered to give an orange solid (10.66 g) and a brown filtrate. The filtrate was concentrated to 100 mL and cooled to −40 °C overnight to yield a second crop (1.346 g) of orange solid. Combined yield: 12.01 g, 79.52% based on $Ti(CH_2Ph)_4$.

{(±)-*trans*-1,2-(NSiMe$_3$)$_2$-cyclohexane}TiI$_2$ (11a). A solution of I_2 (3.27 g, 12.9 mmol) in toluene (50 mL) was added by cannula to a cold (−78 °C) solution of **10a** (3.13 g, 6.43 mmol) in toluene (20 mL). The mixture was allowed to warm slowly to room temperature and was stirred overnight, and all volatiles were removed under vacuum. The red-brown oil was taken up in pentane (4 × 20 mL), and the mixture was filtered to yield 1.16 g of red-orange powder. ^{1}H NMR analysis established that the red-orange powder was pure **11a**. The dark brown filtrate was concentrated to 30 mL, cooled to −40 °C overnight, and filtered, yielding a red-orange powder, which was washed with cold pentane (−40 °C, 2 × 40 mL) and dried (1.62 g). ^{1}H NMR analysis revealed that this material was also pure **11a**. Combined yield: 2.78 g, 77.5%. ^{1}H NMR (C_6D_6): δ 4.44 (m, 2H, methine H), 1.26 (m, 4H, CH), 1.07 (m, 2H, CH), 0.87 (m, 2H, CH), 0.41 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 70.5 (CN), 33.1 (NC*C*), 24.9 (NCC*C*), 1.7 (CH_3). Anal. Calcd for $C_{12}H_{28}I_2N_2Si_2Ti$: C, 25.81; H, 5.06; N, 5.02; I, 45.46. Found: C, 26.10; H, 5.16; N, 4.92; I, 45.33.

"One-Pot" Synthesis of {(±)-*trans*-1,2-(NSiMe$_2$Ph)$_2$-cyclohexane}TiI$_2$ (11b). A flask was charged with $Ti(CH_2Ph)_4$ (11.25 g, 27.28 mmol) and **6b** (10.43 g, 27.24 mmol), and toluene (75 mL) was added at room temperature. The solution was stirred for 10 d at room temperature, at which point a ^{1}H NMR spectrum of an aliquot revealed complete consumption of $Ti(CH_2Ph)_4$ and 83% conversion to **10b**. The solution was cooled to −78 °C, and a solution of I_2 (12.11 g, 47.72 mmol) in toluene (60 mL) was added by cannula. The mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum to leave a brown oil. The crude material was extracted with pentane (3 × 100 mL), and the extracts were combined, concentrated to 65 mL, and cooled to −40 °C overnight. The orange powder which precipitated was collected by filtration (10.27 g, 63.06%).

{(±)-*trans*-1,2-(NSiMe$_2$Ph)$_2$-cyclohexane}TiI$_2$ (11b). A solution of I_2 (5.41 g, 21.3 mmol) in toluene (62 mL) was added

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by cannula to a cold (−78 °C) solution of **10b** (6.08 g, 9.96 mmol) in toluene (45 mL). The mixture was allowed to warm slowly to room temperature and was stirred overnight, and the volatiles were removed under vacuum. The red-brown oil was taken up in pentane (150 mL), and the mixture was filtered through a Celite pad. The dark brown filtrate was concentrated to 50 mL and cooled to −40 °C overnight. The red-orange crystals which formed were collected by filtration, washed with cold pentane (−40 °C, 10 mL), and dried under vacuum (5.74 g, 84.4%). NMR analysis of this material revealed that it consisted of **11b** and $PhCH_2I$ in a 9/1 ratio. This material was washed with pentane (3 × 50 mL) and dried under vacuum to remove the $PhCH_2I$ contaminant. ^{1}H NMR (C_6D_6): δ 7.73 (m, 4H, *o*-H), 7.17 (m, 6H, *m*- and *p*-H, obscured), 4.58 (m, 2H, methine H), 1.18 (m, 2H, CH), 0.94 (m, 4H, CH), 0.83 (s, 6H, CH_3), 0.82 (s, 6H, CH_3), 0.59 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.7 (Ph *ipso*-C), 134.3 (Ph *o*-C), 130.3 (Ph *p*-C), 128.5 (Ph *m*-C), 71.1 (CN), 33.3 (NC*C*), 24.8 (NCC*C*), 1.4 (CH_3), 0.2 (CH_3). Anal. Calcd for $C_{22}H_{32}I_2N_2Si_2Ti$: C, 38.72; H, 4.78; N, 4.11; I, 37.20. Found: C, 38.37; H, 4.76; N, 4.00; I, 37.00.

{(±)-*trans*-1,2-($NSiMe_3$)$_2$-cyclohexane}$TiMe_2$ (12a). A dark red-brown slurry of **11a** (2.15 g, 3.85 mmol) in Et_2O (65 mL) was cooled to −78 °C, and MeMgI (2.6 mL, 3.0 M in Et_2O, 7.8 mmol) was added by syringe. The slurry turned chocolate brown within 10 min, and the mixture was warmed to room temperature and stirred overnight to give a brown solution. Dioxane (1.4 mL, 16.4 mmol) was added by syringe to precipitate the MgI_2. The mixture was filtered, and the brown filtrate was concentrated to 4 mL and cooled at −78 °C for 5 h. The solution was filtered cold to yield pale brown crystals (0.26 g, 20.3%). ^{1}H NMR (C_6D_6): δ 4.02 (m, 2H, methine H), 1.58 (m, 2H, CH), 1.43 (m, 2H, CH), 1.19 (m, 2H, CH), 1.09 (m, 2H, CH), 0.80 (s, 6H, $TiCH_3$), 0.37 (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 65.5 (CN), 46.0 ($TiCH_3$), 34.4 (NC*C*), 25.4 (NCC*C*), 1.9 ($SiCH_3$). This compound decomposed at room temperature (days), which precluded elemental analyses.[11]

{(±)-*trans*-1,2-($NSiMe_2Ph$)$_2$-cyclohexane}$TiMe_2$ (12b). A red-brown slurry of **11b** (3.09 g, 4.53 mmol) in Et_2O (50 mL) was cooled to −78 °C, and MeMgI (3.2 mL, 3.0 M in Et_2O, 9.6 mmol) was added by syringe. The slurry immediately turned red. The mixture was warmed to room temperature overnight, the MgI_2 dissolved, and the bulk solution turned yellow. Dioxane (2.0 mL, 23.5 mmol) was added by syringe. The mixture was filtered, and the volatiles were removed under vacuum. The brown oil was taken up in pentane (2 mL), and the mixture was cooled to −78 °C for 2.5 h. The pale yellow-brown solid was isolated by removing the pentane by cannula-transfer and dried under vacuum overnight (1.26 g, 60.4%). ^{1}H NMR analysis established that this material was >99% pure **12b**. ^{1}H NMR (C_6D_6): δ 7.74 (dd, ^3J = 6.2 Hz, ^4J = 1.4 Hz, 4H, *o*-H), 7.21 (m, 6H, *m*- and *p*-H), 4.15 (m, 2H, methine H), 1.47 (m, 2H, CH), 1.10 (m, 4H, CH), 0.85 (s, 6H, $TiCH_3$), 0.81 (m, 2H, CH), 0.66 (s, 6H, $SiCH_3$), 0.63 (s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.1 (Ph *ipso*-C), 134.3 (Ph *o*-C), 129.8 (Ph *p*-C), 128.4 (Ph *m*-C), 66.2 (CN), 48.0 ($TiCH_3$), 34.5 (NC*C*), 25.2 (NCC*C*), 1.2 ($SiCH_3$), 0.4 ($SiCH_3$). This compound decomposed at room temperature (days), which precluded elemental analyses.

{(±)-*trans*-1,2-($NSiMePh_2$)$_2$-cyclohexane}$TiMe_2$ (12c). A solution of **8c** (0.11 g, 0.18 mmol) in Et_2O (25 mL) was cooled to −78 °C, and MeMgCl (0.13 mL, 3.0 M in THF, 0.39 mmol) was added by syringe. The mixture was allowed to warm to room temperature slowly and was stirred overnight and filtered. The orange filtrate was concentrated to 5 mL, and hexane (10 mL) was layered onto the Et_2O layer. Dark orange microcrystals formed after 1 d at room temperature and were collected by filtration and dried under vacuum (0.08 g, 75.1%). ^{1}H NMR (C_6D_6): δ 7.86 (m, 8H, *o*-H), 7.19 (m, 12H, *m*- and *p*-H), 4.42 (m, 2H, methine H), 1.58 (m, 2H, CH), 1.24 (m, 2H, CH), 1.12 (m, 2H, CH), 0.86 (s, 6H, $SiCH_3$), 0.81 (m, 2H, CH), 0.53 (s, 6H, $TiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.8 (2C, Ph *ipso*-C), 135.8 (Ph *o*-C), 135.5 (Ph *o*-C), 130.2 (Ph *m*-C), 130.1 (Ph *m*-C), 128.5 (Ph *p*-C), 128.4 (Ph *p*-C), 67.2 (CN), 52.0 ($TiCH_3$), 34.9 (NC*C*), 25.3 (NCC*C*), 0.18 ($SiCH_3$).

{(±)-*trans*-1,2-($NSiMe_3$)$_2$-cyclohexane}$TiPh_2$ (13a). A brown slurry of **11a** (2.94 g, 5.26 mmol) in Et_2O (55 mL) was cooled to −78 °C, and PhMgBr (3.6 mL, 3.0 M in Et_2O, 10.8 mmol) was added by syringe. The mixture was warmed and stirred overnight to give a dark brown solution. Dioxane (1.9 mL, 22 mmol) was added by syringe to precipitate MgBrI. The mixture was filtered, and the volatiles were removed under vacuum. The crude solid was dissolved in toluene (9 mL), and the solution was cooled to −40 °C (2 d). The lemon yellow crystals were isolated by filtration and washed with cold pentane (10 mL). Yield: 1.33 g, 56.4%. ^{1}H NMR (C_6D_6): δ 7.98 (dd, ^3J = 6.2 Hz, ^4J = 1.4 Hz, 4H, *o*-H), 7.24 (m, 6H, *m*- and *p*-H), 4.65 (m, 2H, methine H), 1.68 (m, 2H, CH), 1.52 (m, 2H, CH), 1.42 (m, 2H, CH), 1.21 (m, 2H, CH), 0.18 (s, 18H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 189.8 (Ph *ipso*-C), 133.7 (Ph *o*-C), 129.1 (Ph *p*-C), 127.4 (Ph *m*-C), 68.6 (CN), 34.4 (NC*C*), 25.4 (NCC*C*), 1.6 (CH_3). Duplicate analyses of a spectroscopically pure sample gave low carbon content values. Anal. Calcd for $C_{24}H_{38}N_2Si_2Ti$: C, 62.84; H, 8.37; N, 6.11. Found: C, 59.58; H, 8.48; N, 5.94.

{(±)-*trans*-1,2-($NSiMe_2Ph$)$_2$-cyclohexane}$TiPh_2$ (13b) A slurry of **11b** (3.45 g, 5.05 mmol) in Et_2O (50 mL) was cooled to −78 °C, and PhMgBr (3.40 mL, 3.0 M in Et_2O, 10.2 mmol) was added by syringe. The mixture was stirred and warmed overnight, and dioxane (1.8 mL, 21 mmol) was added by syringe to precipitate MgBrI. The mixture was stirred for 30 min and filtered, and the solution was concentrated to 35 mL and cooled to −78 °C for 2 d. The mixture was filtered to leave a dirty yellow solid (1.44 g, 48.98%) which was spectroscopically pure. The solid, dissolved in toluene (7 mL), was layered with hexanes (15 mL), and the mixture was cooled to −40 °C for 2 d to yield bright yellow crystals (0.60 g, 20.4%). ^{1}H NMR (C_6D_6): δ 7.98 (dd, ^3J = 5.8, ^4J = 1.6 Hz, 4H, TiPh *o*-H), 7.44 (m, 4H, SiPh *o*-H), 7.25 (m, 6H, SiPh *m*- and *p*-H), 7.15 (m, 6H, TiPh *m*- and *p*-H, obscured), 4.70 (m, 2H, methine H), 1.55 (m, 2H, CH), 1.25 (m, 4H, CH), 0.93 (m, 2H, CH), 0.47 (s, 6H, CH_3), 0.46 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 190.2 (TiPh *ipso*-C), 139.4 (SiPh *ipso*-C), 134.4 (SiPh *o*-C), 133.6 (TiPh *o*-C), 129.6 (SiPh *p*-C), 129.2 (TiPh *p*-C), 128.2 (SiPh *m*-C), 127.3 (TiPh *m*-C), 69.2 (CN), 34.5 (NC*C*), 25.2 (NCC*C*), 0.7 ($SiCH_3$), −0.01 ($SiCH_3$). Anal. Calcd for $C_{34}H_{42}N_2Si_2Ti$: C, 70.06; H, 7.28; N, 4.81. Found: C, 70.07; H, 7.41; N, 4.75.

X-ray Crystallography. Data collection, solution, and refinement procedures and parameters are summarized in Table 1. The structural analysis of **10a** was performed by D.C.S. and was routine. The structure of **11a** was determined by J.L.P. The observed systematic absences of *hkl*, $h + k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, are consistent with the noncentrosymmetric space group $Cmc2_1$ (C_{2v}^{12}, No. 36) and the centrosymmetric space group *Cmcm* (D_{2h}^{17}, No. 63). The distribution of normalized *E*(*hkl*)'s calculated from the structure factor amplitudes supported the latter as the space group of choice. The final lattice parameters and orientation matrix were calculated from a nonlinear least-squares fit of the orientation angles of 40 reflections (13° < 2θ < 25°) at 22 °C. The intensities of three standard reflections were measured after every 100 reflections and decreased by 13% during the course of the data collection. The raw data were corrected for Lorentz−polarization effects. ψ scans were measured for five reflections (χ ≈ ± 90°; 14° < 2θ < 33°) and indicated that an absorption correction was necessary. The resultant transmis-

(11) The thermal decomposition of **12a**,**b** was not studied in detail. Possible decomposition pathways include metalation of the Si−Me groups to yield metallacyclic products and α-H abstraction to yield Ti methylene species. For related chemistry, see: (a) Simpson, S. J.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3627. (b) Scoles, L.; Minhas, R.; Duchateau, R.; Jubb, J.; Gambarotta, S. *Organometallics* **1994**, *13*, 4978.

sion coefficients based on the ψ-scan data ranged from $T_{min} = 0.690$ to $T_{max} = 0.825$.

Initial coordinates for the unique non-hydrogen atoms were determined by a combination of direct methods and difference Fourier calculations performed with the algorithms provided in SHELXTL-IRIS operating on a Silicon Graphics Iris Indigo workstation. The Ti lies on the line of intersection between two crystallographic mirror planes: one that passes through the Ti and two mirror-related I atoms (I, I″) and a second that passes through the Ti, two mirror-related N atoms (N, N′), two mirror-related Si atoms (Si, Si′), and a methyl carbon atom (C5, C5′) of each mirror-related trimethylsilyl substituent, respectively. This situation requires that the puckered cyclohexane ring be disordered and reduces the number of independent carbon atoms within the ring from 6 to 3. These two crystallographic mirror planes further generate a 2-fold axis of rotation that bisects the N−Ti−N′ and I−Ti−I″ bond angles and passes through the midpoint of the C3−3″ bond and the C1−C1″ bond of the cyclohexane ring. Consequently, the molecular geometry of {(±)-*trans*-1,2-$(NSiMe_3)_2$-cyclohexane}-$TiI_2 \cdot C_6H_6$ rigorously conforms to C_2 symmetry. All of the non-hydrogen atoms were refined anisotropically with the C1−C2 and C2−C3 bond distances between the three crystallographically-independent carbon atoms (C1, C2, and C3) of the cyclohexane ring being restrained to 1.54 ± 0.02 Å. The hydrogen atom positions were idealized with isotropic temperature factors set at 1.2 times those of their respective carbons. The positions of the methyl hydrogens were optimized by a rigid-rotating-group refinement with idealized tetrahedral angles.

As the refinement progressed, it became apparent that the crystal lattice contains solvent molecules of benzene, which lie on a crystallographic mirror plane intersecting the *x* axis at 0.5000. A second mirror plane intersecting the *z* axis at ±0.2500 passes through opposite edges of each benzene ring. Due to the presence of substantial librational disorder, the structure of the benzene molecule is poorly resolved. However, reasonable positions for the three independent carbon atoms (C6, C7, and C8) were obtained by placing them at the corners of an equilateral triangle and restraining the three edge lengths at 2.41 ± 0.02 Å during the refinement. Full-matrix least-squares refinement with SHELXL-93,[12] based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$ with weighting given by the expression $w_i^{-1} = \sigma^2(F_o^2) + (0.0681P)^2 + 1.8747P$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, converged to give final discrepancy indices of R1 = 0.0455, wR2 = 0.1119 for the 855 reflections with $I > 2\sigma(I)$ and an overall GOF value of 1.031.

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Supporting Information Available: Description of the X-ray crystallographic analysis of **11a** and tables of crystal data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **10a** and **11a** (15 pages). Ordering information is given on any current masthead page.

OM960939M

(12) SHELXL-93 is a FORTRAN-77 program (Professor G. Sheldrick, Institut für Anorganische Chemie, University of Göttingen, D-37077 Göttingen, Germany) for single-crystal X-ray structural analyses.

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