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Bulky-Hindrance-Controlled Ligand Transformation from Linked Bis(amidinate) to Linked Imido-Amidinate Promoted by a Mono(cyclopentadienyl)titanium Group

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A novel class of silyl-linked bis(amidinate) ligands [$SiMe_2$-{$NC(Ph)N(2,6-R_2Ph)Li$}$_2$] [**L¹** (R = H), **L²** (R = Me), and **L³** (R = *i*Pr)] reacted with $TiCl_3(C_5H_5)$ to produce the half-sandwich titanium complexes **1**, **2**, and **3**. The molecular structures of **1**–**3** were confirmed successfully by X-ray crystallography. An unprecedented intramolecular ligand transformation from the linked bis(amidinate) configuration to the linked imido-amidinate configuration took place in the cases of **L¹** and **L²**. It was found that the rearrangement process was related to the steric hindrance of the terminal substituents.

Introduction

Both cyclopentadienyl and amidinate ligands have been extensively studied for decades because of their high adaptability to a wide variety of metals in coordination chemistry. The corresponding metal complexes have shown remarkable utility as homogeneous catalysts for olefin polymerization.[1,2] As a further step, systematic investigations on the metal compounds with a mixed-ligand environment containing these two types of ancillary ligands have been carried out in the past few years, involving the new generation of Ziegler–Natta catalysts, carbon mono- or dioxide reactants, and Kharasch reaction catalysts.[3–9] These merits have made the chemistry of half-sandwich compounds an attractive research field. On the other hand, much attention has recently been paid to metal compounds incorporated with the linked bis(amidinate) ligands, as these unique dianionic ligands have the advantage of affording dinuclear complexes or mononuclear complexes analogous to "ansa-metallocenes", leading to valuable geometric structures and properties. Nevertheless, there have been few reports on linked bis(amidinate) half-sandwich compounds.[4a,9]

A novel class of linked bis(amidinate) ligands (**L¹**, **L²**, and **L³**) were developed in our laboratory. They displayed close contact between the two amidinate moieties; that is in contrast to other common examples reported in the literature.[10] We next attempted the preparation of the half-sandwich derivatives from the reactions of ligands with $TiCl_3(C_5H_5)$. It was found, to our surprise, that in the cases of the substituents attached to the terminal nitrogen atoms, which were less bulky, the N–C–N–Si–N–C–N backbone of these dianionic ligands could be transformed to a new class of linked imido-amidinate ligands. We believe that the metal center of mono(cyclopentadienyl)titanium complexes promoted the rearrangement reaction.

Result and Discussion

Synthesis and Structural Characterization

The analogous silyl-linked bis(amidinate) ligands **L¹**, **L²**, and **L³** were prepared in our previous work. They demonstrated a trend of increasing steric hindrance by variation of the 2,6-substituents of the corresponding phenyl analogue. Treatment of **L¹** with 1 equiv. of $TiCl_3(C_5H_5)$ in thf gave, after extraction with CH_2Cl_2 and crystallization, compound **1** as red crystals in 82% yield. Complexes **2** and **3** were prepared under similar synthetic procedures in yields of 48% and 65%, respectively (Scheme 1). These half-sandwich titanium compounds were characterized by NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis.

The molecular structure of **1** is shown in Figure 1 and the key bonding parameters are listed in Table 1. The ligand coordinating to the titanium center does not keep the configuration in **L¹**. The original linked bis(amidinate) ligand was expected to coordinate to the metal center in a tetradentate mode. However, the ligand is tridentate in compound **1**. On both sides of the silyl bridge, the two amidinate moieties exhibit different coordination styles to the Ti ion. One is chelating and the other is monodentate. Moreover, the latter one adopts the opposite direction involving a phenyl migration from N4 to N3. It gives a new imido

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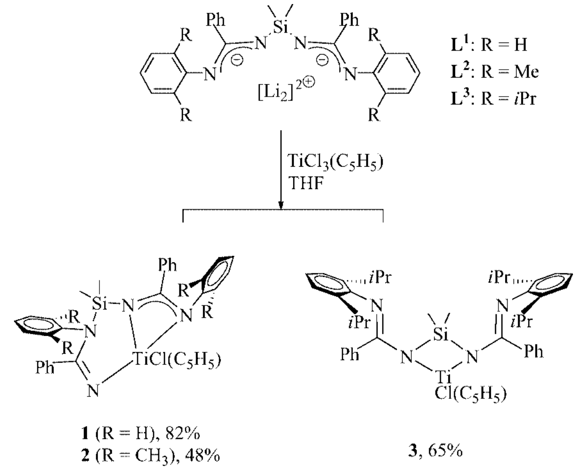


1 (R = H), 82%
2 (R = CH$_3$), 48%

3, 65%

Scheme 1.

group [demonstrated by N3–C22 being 1.385(4) Å and N4–C22 being 1.288(4) Å]. On the other hand, the five-membered skeleton of N4–C22–N3–Si1–N2 displays analogous structural features, with an N2–Ti1–N4 angle of 84.70(13)°, as in some reported titanium β-diketiminates, such as [(Ar)NC(CH$_3$)CHC(CH$_3$)N(Ar)]Ti=NAr(OTf).[11] The Ti–N$_{imido}$ bond [1.847(3) Å] is much shorter than the Ti–N$_{amidinate}$ bonds [2.220(3) and 2.111(3) Å]. The "unsymmetrical" distribution of the two N–C–N moieties leads to a difference of 0.09 Å between the silyl bridge and the neighboring nitrogen atoms on either side.

Compound **2** was derived from **L^2**, which was more bulky than **L^1**, by introducing 2,6-dimethyl groups onto the terminal phenyl rings. Complex **2** is almost isostructural to **1** except for the presence of additional methyl groups. Structural analysis indicates that the increased steric bulk ascribed to the methyl groups plays no role in differentiating

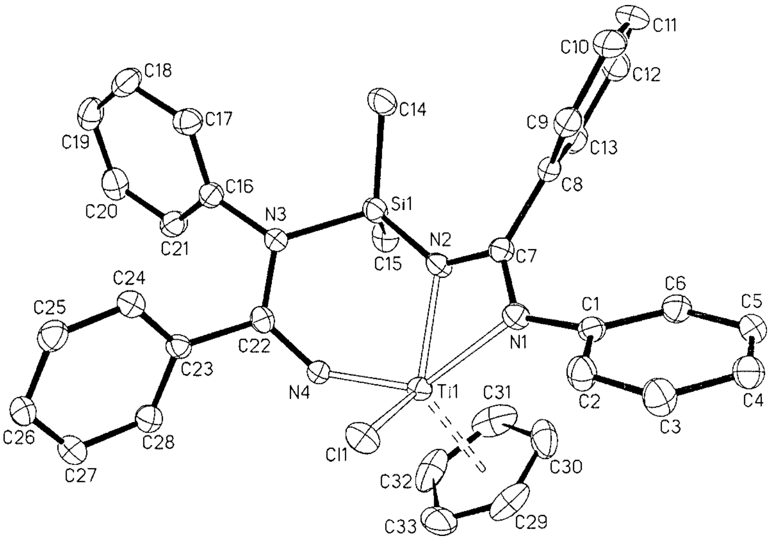


Figure 1. ORTEP drawing (30% probability level) of the molecular structure of compound **1**. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and bond angles [°] for compounds **1**, **2**, and **3**.

1		**2**		**3**	
Ti(1)–N(1)	2.220(3)	Ti(1)–N(1)	2.352(3)	Ti(1)–N(2)	1.900(3)
Ti(1)–N(2)	2.111(3)	Ti(1)–N(2)	2.061(3)	Ti(1)–N(3)	1.911(3)
Ti(1)–N(4)	1.847(3)	Ti(1)–N(4)	1.840(3)	Ti(1)–Cl(1)	2.2921(14)
Ti(1)–Cl(1)	2.362(3)	Ti(1)–Cl(1)	2.3392(11)	Ti(1)–Cp(centroid)	2.027
Ti(1)–Cp(centroid)	2.050	Ti(1)–Cp(centroid)	2.043	N(1)–C(13)	1.284(5)
N(1)–C(7)	1.313(4)	N(1)–C(9)	1.297(4)	N(2)–C(13)	1.397(4)
N(2)–C(7)	1.349(4)	N(2)–C(9)	1.344(4)	Si(1)–N(2)	1.790(3)
Si(1)–N(2)	1.709(3)	Si(1)–N(2)	1.709(3)	Si(1)–N(3)	1.791(3)
Si(1)–N(3)	1.799(3)	Si(1)–N(3)	1.794(3)	N(3)–C(22)	1.388(4)
N(3)–C(22)	1.385(4)	N(3)–C(26)	1.381(4)	N(4)–C(22)	1.278(5)
N(4)–C(22)	1.288(4)	N(4)–C(26)	1.282(4)	N(2)–Ti(1)–N(3)	83.26(13)
N(2)–Ti(1)–N(1)	60.91(12)	N(2)–Ti(1)–N(1)	59.54(10)	Cl(1)–Ti(1)–Cp(centroid)	116.4
N(4)–Ti(1)–N(2)	84.70(13)	N(4)–Ti(1)–N(2)	84.46(12)	C(21)–Si(1)–C(20)	116.9(2)
Cl(1)–Ti(1)–Cp(centroid)	116.6	Cl(1)–Ti(1)–Cp(centroid)	116.9	N(1)–C(13)–N(2)	116.8(3)
N(1)–C(7)–N(2)	111.2(3)	N(1)–C(9)–N(2)	113.3(3)	N(2)–Si(1)–N(3)	90.01(14)
N(2)–Si(1)–N(3)	105.97(15)	N(2)–Si(1)–N(3)	105.76(13)	N(4)–C(22)–N(3)	118.1(3)
N(4)–C(22)–N(3)	122.5(3)	N(4)–C(26)–N(3)	121.5(3)		
C(22)–N(4)–Ti(1)	137.0(2)	C(26)–N(4)–Ti(1)	143.7(3)		

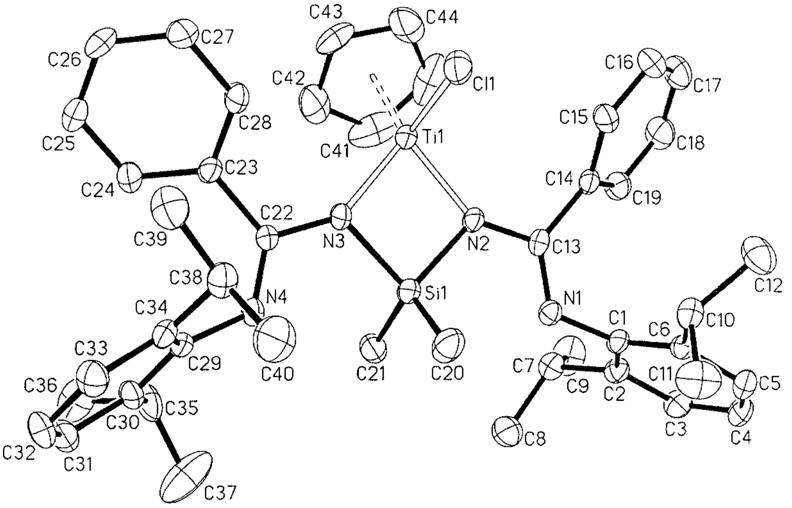


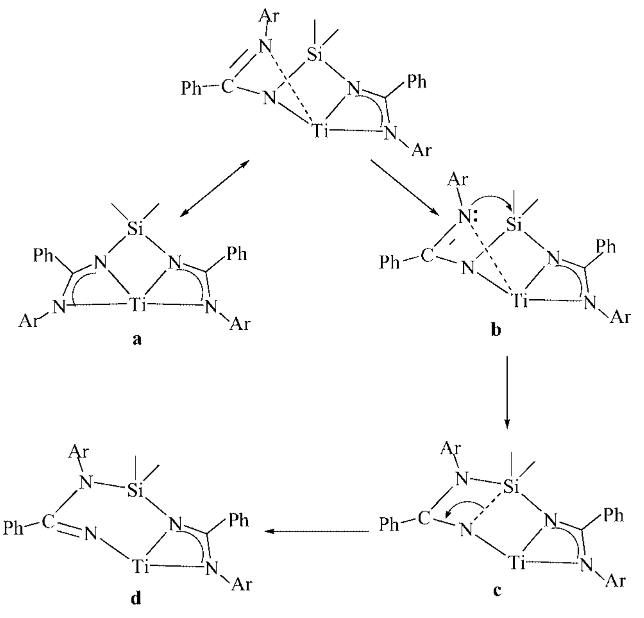
Figure 2. ORTEP drawing (30% probability level) of the molecular structure of compound **3**. Hydrogen atoms are omitted for clarity.

the configuration of **2** from that of **1**. However, the sterically more demanding isopropyl groups do make compound **3** saliently different from **1** and **2**. The ligand framework of **3** (Figure 2) is identical to that of ligand **L**^{3}. It should be pointed out that the ligand of **3** adopts the diamido configuration rather than the linked bis(amidinate) configuration. The Ti–N$_{\text{amido}}$ bonds in **3** are much shorter than the Ti–N$_{\text{amidinato}}$ bonds in **1** and **2**. The two terminal nitrogen atoms have no bonding contacts with the metal center and they are converted into imino groups. The resulting diamido ligand bites the titanium ion at a right angle and it exhibits a planar Ti–N–Si–N tetragonal core. The tetragonal square is perpendicular to another coincident plane composed of C20–Si1–C21 and Cl1–Ti1–Cp(centroid) (with a dihedral angle of 89.8°).

Intramolecular Rearrangement Reaction

The tetradentate bonding mode between the ligands and the Ti center is not preferred because the common electron count of the titanium ion is 12 or 14. Apparently, the steric bulk of the terminal group plays an important role in the determination of the resulting configuration of compounds **1**, **2**, and **3**. In the absence of sterically demanding substituents, such as in **L**^{1} and **L**^{2}, one amidinate moiety of the ligand tends to take the end-contact mode rather than the general chelating mode in order to obtain 14 outer electrons for the Ti ion. The initial terminal nitrogen atom is linked to a phenyl group, which decreases the electronegativity of that N atom and the bond strength of the corresponding N–Ti edge. Comparatively, N4 in **1** or **2** becomes an imido nitrogen atom after rearrangement and the new N–Ti bond is greatly reinforced. These factors in combination drive the ligand transformation process in **1** and **2**.

The proposed mechanism for the formation of **1** and **2** is outlined in Scheme 2. Combination of the linked bis(amidinate) ligands and titanium salt gives the expected compounds with the tetradentate coordination environment (**a**). Induced by the electronically deficient metal center, one amidinate moiety is polarized, and its C–N double bond is located at the outer position because of the electronic withdrawal from the aromatic group. The electronically rich imino nitrogen atom then attacks the silicon atom (**b**). It forms an N–C–N–Si four-membered ring and a notable five-coordinate silicon transition state. The original N–Si bond is then weakened (**c**). Rearrangement is completed after electron transfer to form an imido group (**d**). It should be pointed out that the N–C–N–Si–N–C–N fragment in



Scheme 2.

these ligands is quite flexible. The intramolecular N–Si coupling could be fulfilled without shielding from sterically demanding substituents. This is the crucial step for the transformation. On the contrary, the isopropyl groups in **L^3** are bulky enough to stop that terminal N atom from being bonded to the Ti center or approaching the silyl bridge. This gives compound **3** with the ligand remaining intact and the Ti center with 12 outer electrons.

Conclusions

A novel intramolecular rearrangement of linked bis(amidinate) ligands was demonstrated. It was promoted by the active titanium ion but could be tuned by the bulky hindrance of terminal substituents. We are currently exploring the reactions between the ligands and other metal salts so as to investigate the generalization of this type of chemical transformation.

Experimental Section

General Procedures: All reactions were carried out under nitrogen in flame-dried Schlenk-type glassware on a dual-manifold Schlenk line. Solvents were dried prior to use. The ligand transfer reagents **L^1**, **L^2**, and **L^3** were prepared according to the reported methods.[10] $TiCl_3(C_5H_5)$ was prepared according to literature procedures.[12] ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DRX-300 spectrometer. Elemental analyses were performed with a Vario EL-III instrument. Melting points were taken with a Sanyo Gallenkamp Variable Heater.

Preparation of 1: A solution of **L^1** (1.88 mmol) in thf (20 mL) was added to a solution of $TiCl_3(C_5H_5)$ (0.41 g, 1.88 mmol) in thf (10 mL) at 0 °C. The red solution was stirred at room temperature for 12 h and then concentrated under vacuum. The residue was extracted with CH_2Cl_2 (20 mL) and the solution filtered. The filtrate was concentrated to give compound **1** as red crystals. Yield: 1.05 g (82%); m.p. 171–172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–6.99 (m, 20 H, phenyl), 6.67, 6.50, 6.13 (t, 5 H, Cp), 0.57, –0.47 (d, 6 H, Si*Me$_2$*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 163.4 (N-*C*-N), 148.9–125.9 (phenyl), 120.5, 118.9, 116.7 (Cp), 4.7, 2.9 (Si*Me$_2$*) ppm. $C_{33}H_{31}ClN_4SiTi{\cdot}CH_2Cl_2$ (679.98): calcd. C 60.06, H 4.89, N 8.24; found C 59.82, H 4.90, N 8.18.

Preparation of 2: A solution of **L^2** (2.51 mmol) in thf (20 mL) was added to a solution of $TiCl_3(C_5H_5)$ (0.55 g, 2.51 mmol) in thf (10 mL) at 0 °C. The red solution was stirred at room temperature for 12 h and then concentrated under vacuum. The residue was extracted with CH_2Cl_2 (20 mL) and the solution filtered. The filtrate was concentrated to give compound **2** as red crystals. Yield: 0.79 g (48%); m.p. 179–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–6.68 (m, 16 H, phenyl), 6.55, 6.48 (d, 5 H, Cp), 2.74–2.04 (m, 12 H, methyl), 0.70, –0.24, –0.95 (t, 6 H, Si*Me$_2$*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.3, 17.6, 168.5 (N-*C*-N), 149.8–124.2 (phenyl), 120.6, 117.1 (Cp), 27.1–24.9 (methyl), 9.5, 4.5 (Si*Me$_2$*) ppm. $C_{37}H_{39}ClN_4SiTi{\cdot}(CH_2Cl_2)_{0.25}$ (672.37): calcd. C 66.54, H 5.92, N 8.33; found C 66.89, H 5.97, N 8.31.

Preparation of 3: A solution of **L^3** (1.55 mmol) in thf (20 mL) was added to a solution of $TiCl_3(C_5H_5)$ (0.34 g, 1.55 mmol) in thf (10 mL) at 0 °C. The red solution was stirred at room temperature for 12 h and then concentrated under vacuum. The residue was extracted with CH_2Cl_2 (20 mL) and the solution filtered. The filtrate was concentrated to give compound **3** as red crystals. Yield: 0.77 g (65%); m.p. 186–187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–6.87 (m, 16 H, phenyl), 6.44, 5.83 (d, 5 H, Cp), 3.49, 2.78 (d, 4 H, *CH* of *i*Pr), 1.36–0.86 (m, 24 H, methyl of *i*Pr), 0.56, 0.18, (d, 6 H, Si*Me$_2$*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.7 (N-*C*-N), 143.8–123.6 (phenyl), 117.5 (Cp), 28.6, 27.8, 25.1, 22.8 (*i*Pr on phenyl), 2.3, –0.6 (Si*Me$_2$*) ppm. $C_{45}H_{55}ClN_4SiTi$ (763.37): calcd. C 70.80, H 7.26, N 7.34; found C 70.41, H 7.25, N 7.27.

X-ray Crystallography: Single crystals of **1**, **2**, and **3** suitable for X-ray diffraction studies were obtained by crystallization from CH_2Cl_2. X-ray diffraction data were collected using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with a Bruker Smart Apex CCD diffractometer, equipped with an Oxford Cryosystems CRYOSTREAM device. The collected frames were processed with the proprietary software SAINT and an absorption correction was applied (SADABS) to the collected reflections.[13,14] The structures of these molecules were solved by direct methods and ex-

Table 2. Crystal data and refinement results for compounds **1**, **2**, and **3**.

	1	**2**	**3**
Empirical formula	$C_{34}H_{33}Cl_3N_4SiTi$	$C_{37}H_{39}ClN_4SiTi$	$C_{45}H_{55}ClN_4SiTi$
Formula mass	679.98	651.16	763.37
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a [Å]	11.000(9)	11.4269(19)	18.187(6)
b [Å]	15.650(19)	24.534(4)	9.818(3)
c [Å]	19.278(17)	12.329(2)	24.152(8)
β [°]	102.70(6)	103.438(2)	96.464(6)
V [Å^3]	3237(5)	3361.9(10)	4285(3)
Z	4	4	4
F(000)	1408	1368	1624
$D_{calcd.}$ [g cm^{-3}]	1.395	1.286	1.183
μ(Mo-K_α) [mm^{-1}]	0.580	0.402	0.325
Reflections collected	13119	13786	20142
Unique reflections	5696	5864	7544
Observed reflections	3774	4109	4490
Gof (for F^2)	0.951	1.030	1.029
R_1, wR_2 [$I > 2\sigma(I)$]	0.0580, 0.1090	0.0605, 0.1184	0.0645, 0.1415
R_1, wR_2 (all data)	0.0927, 0.1203	0.0913, 0.1296	0.1182, 0.1670
Largest diff. peak/hole [e Å^{-3}]	0.492/–0.344	0.465/–0.286	0.445/–0.281

panded by standard difference Fourier syntheses using the software SHELXTL.[15] Structure refinements were made on F^2 using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective parent atoms. Pertinent crystallographic data and other experimental details are summarized in Table 2. CCDC-295090 (for **1**), -295091 (for **2**), and -295092 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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