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# Coordination chemistry of group 4 metal compounds with mixed-ligand, silyl-linked bis(amidinate) ligand and cyclopentadienyl

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ABSTRACT

The synthesis and characterization of a class of group 4 metal derivatives based on the silyl-linked bis(amidinate) ligands $[SiMe_2\{NC(Ph)N(2,6\text{-}R_2Ph)Li\}_2]$ [$\mathbf{L^1}$ (R = H) and $\mathbf{L^2}$ (R = Me)] are described. The metal salts coordinated with cyclopentadienyl were used in order to increase the steric hindrance and lower the Lewis acidity of metal centers, which could prevent the N-ligands from rearranging. The tetradentate ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ reacted with $TiCl_2(C_5H_5)_2$ to give compounds **1** and **2** in tridentate and bidentate bonding modes, respectively. Treatment of the ligand $\mathbf{L^1}$ with $ZrCl_3(C_5H_5)$ produced the half-sandwich zirconium complex **3**. Reactions of the ligands with $ZrCl_2(C_5H_5)_2$ afforded zirconium compounds **4** and **5**, demonstrating the same geometry as **1**. Comparing these analogous molecular structures, it suggests that the coordination modes of the N-ligands are variable according to the properties of the metal centers as well as the bulky hindrance of the terminal groups on the seven-membered N–C–N–Si–N–C–N backbone.

## 1. Introduction

The monoanionic amidinate ligands, $[RC(NR')_2]^-$, are versatile through variation of R and R′ groups. They have proven to be able to support a wide range of metal centres across the periodic table [1,2]. Recently, there has been growing interest in the metal compounds incorporated with the dianionic linked bis(amidinate) ligands, which displayed various interesting geometry due to the nature of the linking unit [3]. In efforts to extend the range of the unique N-donor ligand array, a class of silyl-linked bis(amidinate) ligands displaying close contact between the two amidinate moieties were developed in our laboratory [4]. On the other hand, systematic investigations for the metal compounds with a mixed-ligand environment containing cyclopentadienyl and amidinate ligands were carried out in recent years [5–11]. A host of important discoveries involving the new generation of Ziegler–Natta catalysts, carbon mono- or dioxide reactants and Kharasch reaction catalysts were provided, resulting in an attractive research field. Nevertheless, only a few examples containing the linked bis(amidinate) ligands were reported in the cyclopentadienyl and amidinate mixed-ligand system [3k,11].

We are interested in utilizing the silyl-linked bis(amidinate) ligands to synthesize group 4 metal compounds. In the previous research, we found the ligands were labile to rearrangement when the tetrachlorides were used as metal salts. Especially for the titanium species, the ligands were found to be broken. It was supposed to be owing to the effect of the high Lewis acidity of metal chlorides, which made the Si–N bond more polar to be easily attacked by the nucleophilic reagent. Then the metal salts coordinated with cyclopentadienyl in advance were taken into account, since the electron-rich ligand could lower the Lewis acidity on a large scale. In addition, the goal of mixed-ligand environment composed of cyclopentadienyl and silyl-linked bis(amidinate) ligand could be reached readily through this way. Herein, we report the synthesis of a series of group 4 metal derivatives with the mixed-ligand environment and describe the variable coordination behaviors of the silyl-linked bis(amidinate) ligands in different conditions.

## 2. Experimental

### 2.1. General procedures

All reactions were carried out under nitrogen in flame-dried Schlenk-type glassware on a dual manifold Schlenk line. Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone under nitrogen. Dichloromethane was distilled from $CaH_2$ under nitrogen. The ligand transfer reagents $\mathbf{L^1}$ and $\mathbf{L^2}$ were prepared according to the reported methods [4]. The compounds of $TiCl_2(C_5H_5)_2$, $ZrCl_3(C_5H_5)$ and $ZrCl_2(C_5H_5)_2$ were purchased from Alfa Aesar corporation and used as received. $^1H$ 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.

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### 2.2. Preparation of [$SiMe_2\{NC(Ph)N(Ph)\}_2$]$Ti(\eta^5$-$C_5H_5)_2$ (**1**)

Compounds **1**, **2**, **4** and **5** were prepared in the same manner. The preparation of **1** was described as a typical run. A solution of **L$^1$** (2.00 mmol) in thf (15 mL) was added into a stirred slurry of $TiCl_2(C_5H_5)_2$ (0.50 g, 2.00 mmol) in $Et_2O$ (15 mL) at 0 °C. The reaction mixture was warmed to room temperature and kept stirring for 12 h. It was dried in vacuum to remove all volatiles and the residue was extracted with $CH_2Cl_2$ (25 mL). Concentration of the filtrate under reduced pressure and standing it gave orange crystals of compound **1**. Yield: 0.85 g (60%); m.p. 239–240 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.27$–$6.72$ (m, 20H; phenyl), 6.38 (s, 10H; Cp), −0.09 (s, 6H; Si*Me*$_2$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 167.1$ (N–*C*–N), 153.7–123.1 (phenyl), 117.1 (Cp), 6.4 (Si*Me*$_2$) ppm. *Anal.* Calc. for $C_{38}H_{36}N_4SiTi$ (624.67): C, 73.06; H, 5.81; N, 8.97. Found: C, 72.68; H, 5.83; N, 8.96%.

### 2.3. Preparation of [$SiMe_2\{NC(Ph)N(2,6$-$Me_2Ph)\}_2$]$Ti(\eta^5$-$C_5H_5)_2$ (**2**)

Compound **2** was obtained as dark red crystals in 65% yield. M.p. 260–261 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.09$–$6.58$ (m, 16H; phenyl), 6.86 (s, 10H; Cp), 2.29 (s, 12H; methyl), −0.35 (s, 6H; Si*Me*$_2$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 167.5$ (N—*C*—N), 153.2, 142.7 (*ipso*-C on phenyl), 131.5–123.1 (phenyl), 121.5 (Cp), 22.6 (methyl), 5.1 (Si*Me*$_2$) ppm. *Anal.* Calc. for $C_{42}H_{44}N_4SiTi$ (680.78): C, 74.10; H, 6.51; N, 8.23. Found: C, 73.86; H, 6.40; N, 8.01%.

### 2.4. Preparation of [$SiMe_2\{NC(Ph)N(Ph)\}_2$]$ZrCl(\eta^5$-$C_5H_5)(OC_4H_8)$ (**3**)

$ZrCl_3(C_5H_5)$ (0.48 g, 1.84 mmol) was added into the solution of **L$^1$** (1.84 mmol) in thf (20 mL) at 0 °C. The reaction mixture was warmed to room temperature and kept stirring for 12 h. It was dried in vacuum to remove all volatiles and the residue was extracted with $CH_2Cl_2$ (25 mL). Concentration of the filtrate under reduced pressure resulted in compound **3** as colorless crystals. Yield: 1.04 g (80%); m.p. 169–170 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$–$6.97$ (m, 20H; phenyl), 6.51–6.18 (m, 5H; Cp), 3.83 (t, 4H; O*CH*$_2$ of thf), 1.85 (m, 4H; 3,4-2*CH*$_2$ of thf), 0.70 to −0.41 (m, 6H; Si*Me*$_2$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 171.1$ (N–*C*–N), 150.1, 137.1 (*ipso*-C on phenyl), 133.1–124.1 (phenyl), 120.5–113.4 (Cp), 71.1 (O*CH*$_2$ of thf), 28.3 (3,4-2*CH*$_2$ of thf), 6.8, 3.8, 2.6 (Si*Me*$_2$) ppm. *Anal.* Calc. for $C_{33}H_{31}ClN_4SiZr \cdot$ (thf) (710.48): C, 62.55; H, 5.53; N, 7.89. Found: C, 62.75; H, 5.60; N, 7.95%.

### 2.5. Preparation of [$SiMe_2\{NC(Ph)N(Ph)\}_2$]$Zr(\eta^5$-$C_5H_5)_2$ (**4**)

Compound **4** was obtained as yellow crystals in 72% yield. M.p. 257–258 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.39$–$6.70$ (m, 20H; phenyl), 6.36 (s, 10H; Cp), −0.09 (s, 6H; Si*Me*$_2$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 168.6$ (N–*C*–N), 153.3–123.4 (phenyl), 114.2 (Cp), 6.0 (Si*Me*$_2$) ppm. *Anal.* Calc. for $C_{38}H_{36}N_4SiZr$ (668.03): C, 68.32; H, 5.43; N, 8.39. Found: C, 68.15; H, 5.44; N, 8.49%.

### 2.6. Preparation of [$SiMe_2\{NC(Ph)N(2,6$-$Me_2Ph)\}_2$]$Zr(\eta^5$-$C_5H_5)_2$ (**5**)

Compound **5** was obtained as yellow crystals in 70% yield. M.p. 297–299 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.11$–$6.71$ (m, 16H; phenyl), 6.43 (s, 10H; Cp), 2.35 (s, 12H; methyl), −0.07 (s, 6H; Si*Me*$_2$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 167.4$ (N–*C*–N), 149.3, 139.1 (*ipso*-C on phenyl), 130.6–121.7 (phenyl), 112.4 (Cp), 20.1 (methyl), 3.8 (Si*Me*$_2$) ppm. *Anal.* Calc. for $C_{42}H_{44}N_4SiZr \cdot (CH_2Cl_2)$ (809.05): C, 63.83; H, 5.73; N, 6.92. Found: C, 63.62; H, 5.73; N, 6.99%.

### 2.7. X-ray data collection and crystal structure determination

The single crystals of compounds **1**–**5** suitable for X-ray diffraction studies were obtained by crystallization in $CH_2Cl_2$. X-ray diffraction data were collected with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) on 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 expanded 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 1.

**Table 1**
Crystal data and refinement results for compounds **1**–**5**

| Compound | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| Empirical formula | $C_{39}H_{38}Cl_2N_4SiTi$ | $C_{85}H_{90}Cl_2N_8Si_2Ti_2$ | $C_{37}H_{39}ClN_4OSiZr$ | $C_{38.5}H_{37}ClN_4SiZr$ | $C_{43}H_{46}Cl_2N_4SiZr$ |
| Molecular mass | 709.62 | 1446.53 | 710.48 | 710.48 | 809.05 |
| Crystal system | monoclinic | triclinic | orthorhombic | triclinic | monoclinic |
| Space group | $C2/c$ | $P\bar{1}$ | $P2(1)2(1)2(1)$ | $P\bar{1}$ | $P2(1)/n$ |
| $a$ (Å) | 37.785(5) | 9.0174(18) | 10.3427(15) | 14.528(4) | 9.0962(10) |
| $b$ (Å) | 8.8115(12) | 14.481(3) | 17.471(3) | 15.231(4) | 14.6873(16) |
| $c$ (Å) | 25.045(4) | 29.662(6) | 18.639(3) | 17.725(4) | 29.677(3) |
| $\alpha$ (°) | 90 | 96.465(3) | 90 | 65.933(4) | 90 |
| $\beta$ (°) | 120.542(2) | 96.072(3) | 90 | 74.965(3) | 92.9210(10) |
| $\gamma$ (°) | 90 | 96.099(3) | 90 | 79.397(4) | 90 |
| $V$ (Å$^3$) | 7181.3(17) | 3799.6(13) | 3368.0(8) | 3444.9(15) | 3959.7(7) |
| $Z$ | 8 | 2 | 4 | 4 | 4 |
| $F(000)$ | 2960 | 1524 | 1472 | 1468 | 1680 |
| $D_{calc}$ (g cm$^{-3}$) | 1.313 | 1.264 | 1.401 | 1.370 | 1.357 |
| $\mu$ (Mo K$\alpha$) (mm$^{-1}$) | 0.454 | 0.362 | 0.477 | 0.465 | 0.479 |
| Reflections collected | 12217 | 15731 | 13951 | 12128 | 16043 |
| Unique reflections | 6187 | 13100 | 5925 | 11024 | 6986 |
| Observed reflections | 5129 | 9343 | 5719 | 6182 | 6268 |
| Goodness-of-fit on $F^2$ | 1.232 | 1.138 | 1.154 | 0.929 | 1.190 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0864, 0.1804 | 0.0999, 0.2298 | 0.0467, 0.0970 | 0.0702, 0.1166 | 0.0670, 0.1446 |
| $R_1$, $wR_2$ (all data) | 0.1046, 0.1884 | 0.1278, 0.2465 | 0.0486, 0.0979 | 0.1237, 0.1343 | 0.0751, 0.1488 |
| Largest difference in peak/hole (e Å$^{-3}$) | 0.473/−0.397 | 0.850/−0.652 | 0.438/−0.475 | 0.597/−0.535 | 1.006/−0.618 |