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Mendeleev Commun., 2014, **24**, 114–116
Mendeleev Communications

Dimeric zirconium complex bearing a dianionic *ansa*-bis(aminopyridinato) ligand

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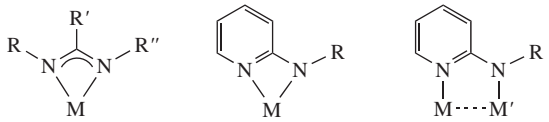
DOI: 10.1016/j.mencom.2014.03.017

The reaction of a lithium *ansa*-bis(aminopyridinato) ligand {L = $[N(2\text{-}C_5H_4N)SiMe_2CH_2]_2^{2-}$} with $ZrCl_4$ afforded the dimeric complex $[LZrCl(\mu\text{-}Cl)]_2$ which was characterized by X-ray structure analysis and found active in catalyzing ethylene polymerization.

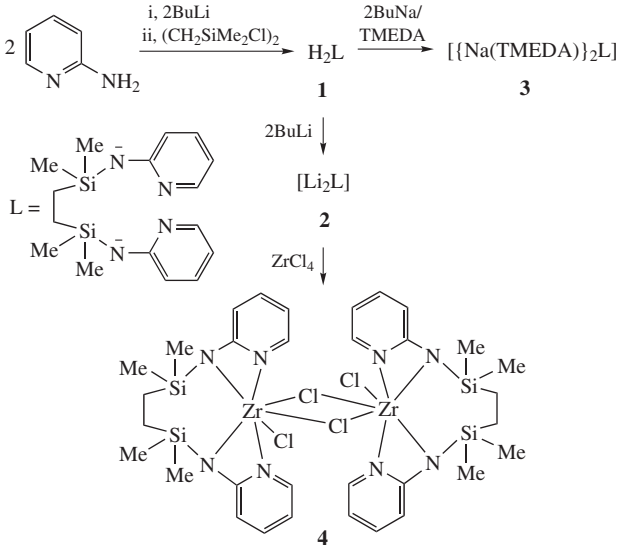
The exploration of ancillary ligand systems supporting catalytically active metal centres is a long-standing demand in coordination chemistry. Monoanionic amidinate ligands (**A**) are generally considered sterically equivalent to η^5-cyclopentadienyl (Cp) and isoelectronic with π-allyl ligands, and they represent an important class in the array comparable to the Cp system.[1,2] They are four-electron, monoanionic and N-donor bidentate chelates, providing a great diversity by variation of substituents on the conjugated N–C–N backbone. Their steric and electronic properties are easily tunable to fit different metal centres.[3] As the closest 'relatives' of amidinates, pyridyl amido ligands like $[N(R)(Py)]^-$ with flexible bonding modes such as the strained N,N′-chelating fashion (**B**) and the bimetallic bridging binding fashion (**C**), have attracted much attention.[4,5] A wide variety of aminopyridinate metal complexes have been studied due to their novel structural features and catalytic applications.[6–8] Recent research in our group has focused on bridged bis(amidinate) Group IV metal complexes because of their great potential in producing polyolefins with unique properties.[9–14] In contrast to the bridged biscyclopentadienyl $\eta^5:\eta^5$ species, the bridged bis(amidinate) could be regarded as a $\eta^3:\eta^3$ system. Since the latter is more electron-deficient than the former, it is supposedly helpful to enhance the electrophilic behaviour of a metal centre and then improve its activity for olefin polymerization. This inspired us to develop a special N-functionalized aminopyridinato ligand by introducing a linker between two aminopyridinato moieties. The new ligand is similar to a bridged bis(amidinate) species possessing the $\eta^3:\eta^3$ environment. Herein, we report the synthesis, fluorescence and catalytic properties of a dimeric zirconium complex based on the linked pyridyl amido ligand.



A **B** **C**

Bridged aminopyridine **1** is designed to be the precursor of a dianionic tetradentate ligand. It was prepared by successive treating 2-aminopyridine with 1 equiv. of butyl lithium and half a molar of 1,2-bis(chlorodimethylsilyl)ethane. Compound **1** was obtained as an oil-like residue after all volatiles were removed from corresponding solution. Nevertheless, it could turn into white solid as recrystallized in hexane. Two forms of the product showed the same NMR spectra. Therefore, the oil species ligand precursor could be used for the following reactions without further purification. Lithiation of compound **1** with 2 equiv. of BuLi in diethyl ether gave diamido lithium **2** which appeared as white precipitate when concentrating the resulting solution. Once the precipitate formed, it was hard to be dissolved again. As a result, product **2** was presumed to be a polymeric species according to its poor solubility. Then, sodium derivative **3** was prepared in the presence of neutral donor TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in the same way as the lithium species. It gave **3** as light yellow thin layer crystals in a yield of 95%. The single crystal X-ray diffraction analysis of **3** failed due to its poor quality. Without isolation, compound **2** could be used as the ligand transfer reagent to react with zirconium tetrachloride. Zirconium complex **4** was formed in a yield of 81% as yellow crystals (Scheme 1).[†]

The single crystals of compound **4** were grown in CH_2Cl_2 and examined by X-ray diffraction analysis. The molecule of



Scheme 1

[†] All manipulations and reactions were performed under an inert atmosphere of nitrogen using standard Schlenk techniques. Solvents were predried with sodium, distilled from sodium–benzophenone (diethyl ether and hexane) and stored over molecular sieves (4 Å). Dichloromethane was purified by distillation from CaH_2. BuLi and metal chlorides were purchased from Alfa Aesar. Glassware was oven-dried at 150 °C overnight. The NMR spectra were recorded on a Bruker DRX-300 instrument, and solvent resonances were used as internal references for ^1H and ^{13}C NMR spectra. Elemental analyses were performed with a Vario EL-III analyzer.

complex **4** (Figure 1)‡ possesses a dimeric configuration. Each Zr centre is heptacoordinated and linked *via* double μ-Cl bridges, resulting in a planar $[ZrCl]_2$ bimetallic core. The tetradentate bridged bis(aminopyridinato) ligand bites Zr, with Zr–N_{amido} [2.185(5) Å], Zr–$N_{pyridyl}$ [2.271(5) Å] bonds and N(1)–Zr(1)–N(2) angle [60.09(18)°] of each aminopyridinato moiety. Its two amino pyridyl planes have an angle of 28.25° to each other and they are close to be perpendicular to the $[ZrCl]_2$ core. The horizontal rhombus core in the molecule of **4** possesses lateral lengths of 2.6204(17) and 2.6692(15) Å and the related bite angle Cl–Zr–Cl of 75.73(5)°. The Zr(1)–Cl(1) bond is 2.4166(18) Å long, occupying the axial position. It is much shorter than the previous two and it is almost perpendicular to the horizontal Zr(1)–N(2), Zr(1)–N(3), Zr(1)–N(4) and Zr(1)–Cl(2A). The similar core unit could also be observed in $[\{PhN(2\text{-}Py)\}_2ZrCl(\mu\text{-}Cl)]_2$ which was prepared by Polamo and co-workers through a 'direct reaction' way,[15] and the corresponding geometric data are 2.5935(13) and 2.6497(13) Å and 78.89(4)°, respectively. For those Group IV metal complexes with the monoanionic aminopyridinato ligands, they generally adopted a propeller-like configuration as forming tris(aminopyridinato) species.[16,17] That also gave a sterically well-protected environment for the metal centre, six nitrogen–metal bonds, which would make the metal centre inert or lower its activity. In comparison, the utilization of the new dianionic ligand in complex **4** has brought great change in structure and weakened the disadvantage to metal centre as each Zr connecting with four nitrogen atoms.

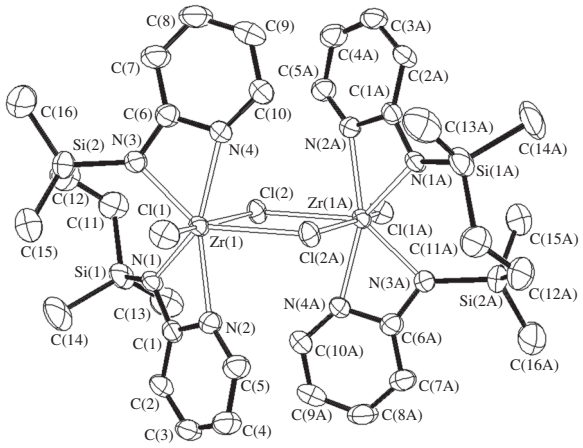


Figure 1 Molecular structure of complex **4**. Selected bond lengths (Å) and bond angles (°): Zr(1)–N(1) 2.185(5), Zr(1)–N(2) 2.271(5), Zr(1)–Cl(1) 2.4166(18), Zr(1)–Cl(2) 2.6204(17), Zr(1)–Cl(2A) 2.6692(15), N(1)–C(1) 1.373(8), N(2)–C(1) 1.352(8), Si(1)–N(1) 1.750(5); N(1)–Zr(1)–N(2) 60.09(18), N(2)–Zr(1)–N(4) 156.02(18), N(3)–Zr(1)–Cl(1) 90.38(16), N(4)–Zr(1)–Cl(1) 89.41(14), Cl(1)–Zr(1)–Cl(2A) 89.18(6), Cl(2)–Zr(1)–Cl(2A) 75.73(5), Zr(1)–Cl(2)–Zr(1A) 104.27(5), N(2)–C(1)–N(1) 109.9(5). Symmetry codes: (i) $-x+1, -y, -z$.

Zr(1)–N(4) and Zr(1)–Cl(2A). The similar core unit could also be observed in $[\{PhN(2\text{-}Py)\}_2ZrCl(\mu\text{-}Cl)]_2$ which was prepared by Polamo and co-workers through a 'direct reaction' way,[15] and the corresponding geometric data are 2.5935(13) and 2.6497(13) Å and 78.89(4)°, respectively. For those Group IV metal complexes with the monoanionic aminopyridinato ligands, they generally adopted a propeller-like configuration as forming tris(aminopyridinato) species.[16,17] That also gave a sterically well-protected environment for the metal centre, six nitrogen–metal bonds, which would make the metal centre inert or lower its activity. In comparison, the utilization of the new dianionic ligand in complex **4** has brought great change in structure and weakened the disadvantage to metal centre as each Zr connecting with four nitrogen atoms.

It was interesting to find that crystalline complex **4** could emit strong yellow fluorescent light as imposed under ultraviolet light, which was a kind of potentially useful electroluminescent nature for electronic devices. As a result, the luminescent property of **4** in dilute solutions was investigated. Two absorption bands were observed with maxima at 234 and 299 nm in the UV-VIS spectrum of complex **4** in CH_2Cl_2 solution. Then, the fluorescence spectra were recorded with excitation wavelengths of 234 and 299 nm (Figure 2). It shows two broad emission bands at 361 and 702 nm. The former 361 nm band is invisible, while the latter 702 nm band belongs to the visible light zone. However, the intensity of invisible light is much stronger than that of visible light. Moreover, it is

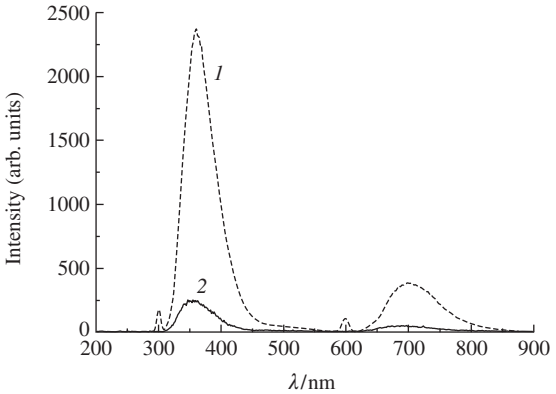


Figure 2 Fluorescence spectra of zirconium complex **4** in CH_2Cl_2 solution at 298 K with excitation wavelengths of (*1*) 234 and (*2*) 299 nm.

H_2L {L = $[N(2\text{-}C_5H_4N)SiMe_2CH_2]_2^{2-}$} **1**. BuLi (1.6 mol dm^{-3}, 4.25 ml) was injected to a solution of 2-aminopyridine (0.64 g, 6.8 mmol) in Et_2O (~20 ml) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. Solution of 1,2-bis(chlorodimethylsilyl)ethane (0.733 g, 3.4 mmol) in hexane was added, and the mixture was additionally stirred for 5 h. Then, it was filtered and dried *in vacuo* to give a pale yellow oil-like residue. The oil was dissolved in hexane and white crystals of **1** were isolated after concentration (yield 1.08 g, 96%), mp 85–87 °C. ^{1}H NMR (300 MHz, C_6D_6) δ: 8.139 (t, 2H, 6-$H_{Pyridyl}$), 7.009 (m, 2H, 4-$H_{Pyridyl}$), 6.319 (t, 2H, 5-$H_{Pyridyl}$), 6.023 (d, 2H, 3-$H_{Pyridyl}$), 3.720 (s, 2H, NH), 0.882 (s, 4H, CH_2CH_2), 0.313 (s, 12H, 2$SiMe_2$). ^{13}C NMR (75 MHz, C_6D_6) δ: 160.863 (*ipso*-$C_{Pyridyl}$), 148.879 (6-$C_{Pyridyl}$), 137.408 (4-$C_{Pyridyl}$), 113.493 (5-$C_{Pyridyl}$), 110.379 (3-$C_{Pyridyl}$), 8.491 (CH_2CH_2), –1.659 ($SiMe_2$). Found (%): C, 57.77; H, 7.91; N, 16.55. Calc. for $C_{16}H_{26}N_4Si_2$ (%): C, 58.13; H, 7.93; N, 16.94.

[{Na(TMEDA)}$_2$L] **3**. The solution of BuNa (0.615 g, 7.69 mmol) and TMEDA (1.16 ml, 7.69 mmol) in hexane (~20 ml) was added to the suspension of **1** (1.27 g, 3.84 mmol) in hexane (30 ml) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. It was filtered to remove the precipitate and the filtrate was concentrated to give light yellow thin layer crystals of **3** (2.22 g, 95 %). ^{1}H NMR (300 MHz, C_6D_6) δ: 7.841 (d, 2H, 6-$H_{Pyridyl}$), 7.094 (t, 2H, 4-$H_{Pyridyl}$), 6.466 (d, 2H, 3-$H_{Pyridyl}$), 6.148 (t, 2H, 5-$H_{Pyridyl}$), 1.893 (s, 24H, NMe_2 of TMEDA), 1.833 (s, 8H, CH_2 of TMEDA), 0.854 (s, 4H, CH_2CH_2), 0.459 (s, 12H, 2$SiMe_2$). ^{13}C NMR (75 MHz, C_6D_6) δ: 171.865 (*ipso*-$C_{Pyridyl}$), 149.263, 136.738, 115.627, 105.950 (6,4,3,5-$C_{Pyridyl}$), 57.566 (CH_2 of TMEDA), 45.551 (NMe_2 of TMEDA), 11.161 (CH_2CH_2), –0.295 ($SiMe_2$).

[LZrCl(μ-Cl)]$_2$ **4**. BuLi (1.6 mol dm^{-3}, 3.66 ml) was injected to the solution of **1** (0.969 g, 2.93 mmol) in Et_2O (~30 ml) at 0 °C. The mixture was warmed to room temperature and stirred for 5 h. $ZrCl_4$ (0.683 g, 2.93 mmol) was added at –78 °C, the mixture was warmed to the ambient temperature and stirred overnight. After being dried *in vacuo*, it was extracted with CH_2Cl_2. The extract was concentrated to yield yellow crystalline **4** (1.18 g, 81%), mp 187–188 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.773 (s, 2H, 6-$H_{Pyridyl}$), 7.475 (t, 2H, 4-$H_{Pyridyl}$), 6.478–6.300 (m, 4H, 3,5-$H_{Pyridyl}$), 0.995 (s, 4H, CH_2CH_2), 0.291 (s, 12H, 2$SiMe_2$). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.774 (*ipso*-$C_{Pyridyl}$), 143.733, 142.748, 112.966, 112.400 (6,4,5,3-$C_{Pyridyl}$), 10.615 (CH_2CH_2), 0.270 ($SiMe_2$). Found (%): C, 37.98; H, 4.88; N, 11.53. Calc. for $C_{32}H_{48}Cl_4N_8Si4Zr_2 \cdot (CH_2Cl_2)_{1/6}$ (%): C, 38.79; H, 4.89; N, 11.25.

‡ *Crystal data for* **4**: M = 995.54 crystals are hexagonal, space group $R\bar{3}$, a = 28.338(2) and c = 14.5350(16) Å, V = 10108.6(16) Å^3, Z = 9, d_{calc} = 1.472 g cm^{-3}, μ(MoKα) = 0.861 mm^{-1}, T = 293(2) K, $2\theta_{max}$ = 50.00°, R_1 [3594 unique reflections with $I > 2\sigma(I)$] = 0.0522, R_w = 0.1589, 18366 reflections (R_{int} = 0.1282), GOF = 1.019.

Data were collected on a Bruker Smart Apex CCD diffractometer area detector using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The collected frames were processed with the SAINT proprietary software and an absorption correction was applied (SADABS) to the collected reflections.[21,22] The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the SHELXTL software.[23] Structure refinements were made on F^2 using the full-matrix least-squares technique.

CCDC 939927 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2014.

noted that the shorter wavelength of 234 nm could only give weak fluorescent light while 299 nm could excite much more intense emission.

Group IV metal complexes with aminopyridinato ligands were good non-cyclopentadienyl olefin polymerization catalysts. A series of mononuclear titanium complexes containing *ansa*-aminopyridinato ligands $[O\{Si(R^2_2)N(2\text{-}C_4H_2N\text{-}4\text{-}R^1\text{-}5\text{-}X)\}_2]^{2-}$ (X = CH or N, R^1 = H or Me, R^2 = Me or Pr^i), which were active towards olefin polymerization, was reported.[18] More recently, a group of metal complexes based on aminosilyl-substituted aminopyridinato ligands having good performance in ethylene polymerization was reported.[19] Therefore, a primary catalytic activity investigation was carried out for complex **4** towards the polymerization of ethylene. At room temperature and atmospheric pressure, the activity of **4** was 1.81×10^5 (g PE) mol^{-1} h^{-1} after activation by methylaluminoxane at an Al/Zr ratio of 1000. The performance is still much smaller than that for the Cp_2ZrCl_2 standard [6.27×10^5 (g PE) mol^{-1} h^{-1}].[20] In contrast to those analogous tris(aminopyridinato) zirconium complexes in a propeller-like configuration, its efficiency would be better due to less N atoms surrounding Zr. On the other hand, its dimeric configuration presumably would break up into two mononuclear moieties in the solution state of polymerization reaction, which could give the Zr centre more space to contact ethylene molecules. Moreover, by adjusting various polymerization reaction conditions, its activity is presumed to be improved remarkably.

In conclusion, a new *ansa*-bis(aminopyridinato) zirconium complex $[LZrCl(\mu\text{-}Cl)]_2$ {L = $[N(2\text{-}C_5H_4N)SiMe_2CH_2]_2^{2-}$} has been readily prepared. Structural studies revealed the dimeric feature of complex **4**. Compound **4** can emit fluorescent light in both solid and solution states after excitation by UV irradiation. It represents a novel potential precursor of Group IV free of Cp ligands and showed moderate activity of 1.81×10^5 (g PE) mol^{-1} h^{-1} in the polymerization of ethylene.

This work was supported by the Natural Science Foundation of China (grant nos. 20702029 and 21272142) and the Natural Science Foundation of Shanxi Province (2008011024).

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Received: 23rd August 2013; Com. 13/4189