Supporting Information

Catalytic addition of amines to carbodiimides by bis(β-diketiminate)lanthanide(II) complexes and mechanistic studies

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Supporting material

All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. The IR spectra were recorded on a Magna-IR 550 spectrometer. Melting points were determined in sealed Ar-filled capillary tube, and uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Unity Inova-400 spectrometer. Chemical shifts (δ) were reported in ppm. Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and a hexamine buffer. Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument.

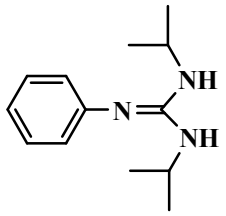
General Procedure for the Reaction of Amines with Carbodiimides Catalyzed by Complex 5 (**Table 3**, Entry 2 as an example).

A 10 mL Schlenk tube under dried argon was charged with **5** (0.0082 g, 0.01 mmol). To the flask were added the aniline ($PhNH_2$) (0.182 mL, 10.96 M, 2.00 mmol), *N,N'*-diisopropylcarbodiimide (*i*PrNCN*i*Pr) (0.312 mL, 6.418 M, 2.00 mmol). The resulting mixture was stirred at 60 °C for 8 min. After the reaction was completed, the reaction mixture was hydrolyzed by water (2 mL), extracted with dichloromethane (3×10 mL), dried over anhydrous Na_2SO_4, and filtered. Then the solvent was removed under reduced pressure, and the final products were further purified by crystallization from *n*-hexane to give the colorless solid **12** (0.4343 g, 99% yield).

Spectroscopic data for the addition products of amines to carbodiimides

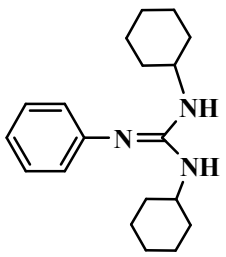
Analytical data:

12



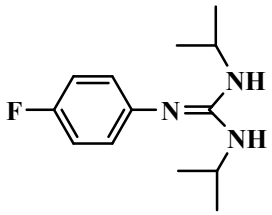
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (m, 2H; C_6H_5), 6.93 (m, 1H; C_6H_5), 6.85 (d, *J* = 7.6 Hz, 2H; C_6H_5), 3.77 (br, 2H; NH), 3.61 (m, 2H; $CH(CH_3)_2$), 1.17 (d, *J* = 6.4 Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 150.4, 129.4, 123.7, 121.5, 43.6, 23.6.

13

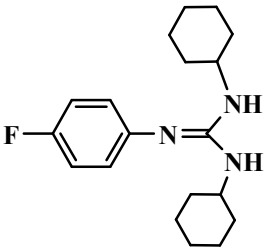


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (m, 2H; C_6H_5), 6.93 (m, 1H; C_6H_5), 6.86 (d, *J* = 8.0 Hz, 2H; C_6H_5), 3.64 (br, 2H; NH), 3.42 (m, 2H; NHCy), 2.03 – 1.05 (m, 20H; Cy); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7, 150.7, 129.5, 123.9, 121.6, 50.5, 34.1, 26.0, 25.2.

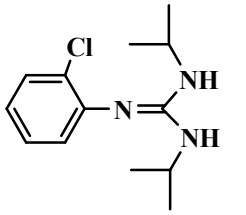
14



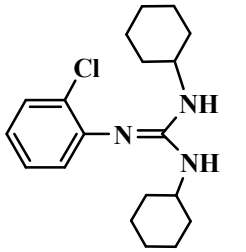
M.p.：130–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93(m, 2H; C_6H_4), 6.76 (m, 2H; C_6H_4), 3.76 (br, 2H; NH), 3.52 (m, 2H; $CH(CH_3)_2$), 1.15 (d, *J* = 6.0 Hz, 12H; $CH(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.0, 144.6, 141.8, 123.4, 122.5, 28.3, 24.2.

15 

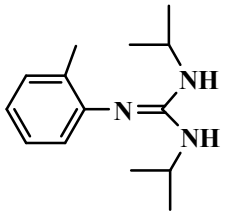
M.p.: 168-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.92 (m, 2 H; C_6H_4), 6.76 (m, 2 H; C_6H_4), 3.59 (br, 2 H; NH), 3.38 (m, 2 H; NHCy), 1.99 – 1.03 (m, 20 H; Cy); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 124.9, 124.8, 116.1, 115.9, 50.4, 34.1, 25.9, 25.2.

16 

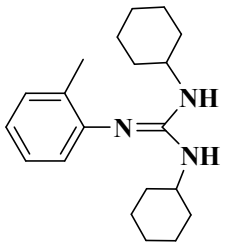
Mp:137–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.0 Hz, 1 H; C_6H_4), 7.13 (m, 1 H; C_6H_4), 6.87 (m, 2 H; C_6H_4), 3.78 (br, 2 H; NH), 3.48 (m, 2 H; CH), 1.18 (m, 12 H) (C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 147.2, 130.1, 128.5, 127.8, 125.5, 122.7, 43.6, 23.6.

17 

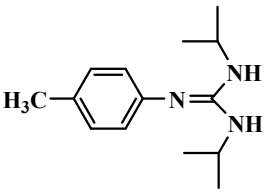
Mp:137–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.33 (d, *J* = 7.6 Hz, 1 H; C_6H_4), 7.15-7.11 (m, 1 H; C_6H_4), 6.92-6.85 (m, 2 H; C_6H_4), 3.55 (br, 2 H; NH), 3.42 (m, 2 H; NHCy), 2.05-1.06 (m, 20 H; Cy); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 147.6, 130.1, 128.7, 127.8, 125.6, 122.6, 50.5, 34.1, 26.0, 25.2.

18 

M.p.：124–125 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (m, 1 H; C_6H_4), 7.08 (d, *J* = 7.6 Hz, 1 H; C_6H_4), 6.90-6.86 (m, 1 H; C_6H_4), 6.78 (d, *J* = 7.2 Hz, 1 H; C_6H_4), 3.76 (br, 2 H; NH), 3.46 (br 2 H; C*H*), 2.14 (m, 3 H; ArCH_3), 1.17-1.15 (m, 12 H; C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 148.6, 131.8, 130.6, 126.9, 123.4, 121.9, 43.4, 23.7, 18.4.

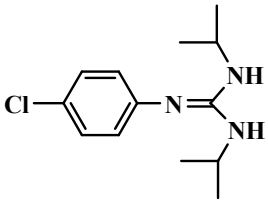
19 

^{1}H NMR (400 MHz, $CDCl_3$): 6.95-6.91 (m, 2H; C_6H_4), 6.80-6.76 (m, 2H; C_6H_4), 3.62 (br, 2H; NH), 3.40 (br, 2H; NHCy), 2.00 (m, 3H; CH_3), 1.97-1.03 (m, 20 H; Cy); ^{13}C NMR (100 MHz, $CDCl_3$): 148.9, 148.7, 131.9, 130.6, 126.8, 123.5, 121.9, 50.4, 34.2, 25.9, 25.2, 18.4.

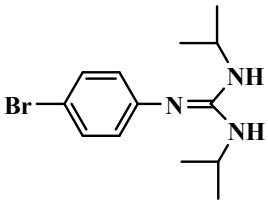
20 

M.p.: 155-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03 (d, *J* = 8.0 Hz, 2 H; C_6H_4), 6.72 (d, *J* = 7.6 Hz, 2 H; C_6H_4), 3.73 (br, 2 H; NH), 3.53 (m, 2 H; CH), 2.26 (s, 3 H; ArCH_3), 1.14-1.12 (m,

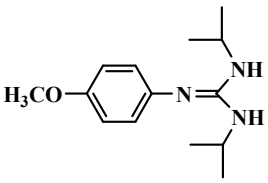
12 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 147.6, 130.7, 130.1, 123.5, 43.4, 23.6, 21.0.

21 

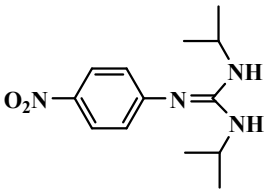
^{1}H NMR (400 MHz, $CDCl_3$): δ = δ = 7.21 (d, *J* = 8.4 Hz, 2 H; C_6H_4), 6.80 (d, *J* = 8.8 Hz, 2 H; C_6H_4), 3.75 (br, 2 H; NH), 3.61 (br, 2 H; CH), 1.17-1.16 (m, 12 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 149.2, 129.4, 126.4, 125.1, 43.5, 23.6.

22 

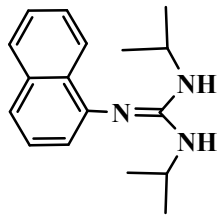
^{1}H NMR ($CDCl_3$): δ = 7.40 (m, 2H; C_6H_4), 6.89 (d, *J* = 8.4 Hz, 2H; C_6H_4), 3.74 (m, 2H; CH), 1.20-1.18 (m, 12H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 149.7, 132.4, 125.6, 114.0, 43.5, 23.6.

23 

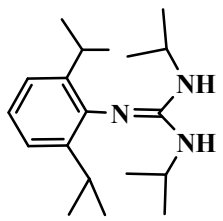
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (s, 4 H; C_6H_4), 3.77 (m, 7 H; OCH_3 and C*H*), 1.18-1.17 (m, 12 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 150.8, 142.7, 124.2, 114.6, 55.4, 43.3, 23.3.

24 

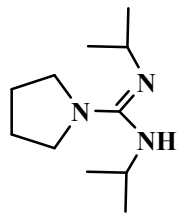
^{1}H NMR ($CDCl_3$): δ = 7.40 (d, *J* = 12.0 Hz, 2H; C_6H_4), 6.87 (d, *J* = 8.0 Hz, 2H; C_6H_4), 3.79 (s, 2H; CH), 1.19 (s, 12H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 150.5, 141.0, 125.7, 122.9, 43.5, 23.3.

25 

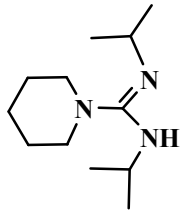
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.0 Hz, 1H; $C_{10}H_7$), 7.78 (d, *J* = 7.6 Hz, 1H; $C_{10}H_7$), 7.45 (m, 4H; $C_{10}H_7$), 6.91 (d, *J* = 7.2 Hz, 1H; $C_{10}H_7$), 3.88 (br, 2H; NH), 3.63 (m, 2 H; C*H*), 1.18 (m, 12H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 150.2, 147.1, 135.1, 129.9, 128.1, 126.8, 126.1, 125.0, 124.7, 121.7, 118.1, 43.6, 23.7.

26 

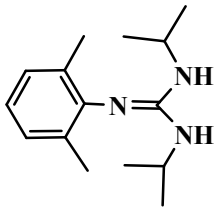
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 7.2 Hz, 2H; C_6H_3), 6.98-6.94 (m, 1H; C_6H_3), 4.19(br, 2H; NH), 3.43-3.19 (m, 2H; ArCH), 3.11-3.04 (m, 2 H; CH), 1.25-1.04 (m, 24 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 147.7, 144.3, 141.6, 123.2, 122.3, 43.5, 42.7, 28.0, 23.9.

27 

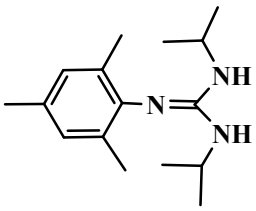
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.38 (s, 2H; C*H*), 3.26(m, 4 H; α-CH_2), 1.80 (s, 4 H; β-CH_2), 1.11 (m, 12 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 47.9, 43.6, 26.3, 24.8.

28 

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.36 (m, 2 H; CH), 3.04 (br, 4 H; CH_2), 1.52 (br, 6 H; CH_2), 1.09 (m, 12 H; CH_3); ^{13}C NMR (100 MHz, CDCl3): δ = 156.7, 49.1, 46.6, 26.0, 24.9, 24.0.

29 

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09-7.04 (m, 3H; C_6H_3), 3.21-3.09 (m, 2H; NH), 3.56(m, 2H; CH), 2.64 (s, 6H; $ArCH_3$), 1.12-1.08 (m, 24 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 148.7, 144.3, 141.5, 123.3, 122.4, 42.6, 28.0, 23.9.

30 

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (s, 2H; C_6H_3), 2.22 (s, 2H; NH), 2.06 (s, 7H; $ArCH_3$), 1.15-1.10 (br, 14 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 148.0, 143.7, 130.7, 130.5, 128.6, 77.3, 23.7, 20.8, 18.2.

References

[1] T. G. Ong, G. P. A. Yap and D. S. Richeson, *J. Am. Chem. Soc.* **2003**, *125*, 8100.

[2] A. R. Katritzky, N. M. Khashab and S. Bobrov, Helv. *Chim. Acta.* **2005**, *88*, 1664.

[3] X. M. Zhang, C. Y. Wang, C. W. Qian, F. B. Han, F. Xu and Q. Shen, *Tetrahedron* **2011**, *67*, 8790.

[4] Q. H. Li, S. W. Wang, S. L. Zhou, G. S. Yang, X. C. Zhu and Y. Y. Liu, J. Org. Chem. **2007**, *72*, 6763.

[5] E. W. Thomas, E. E. Nishizawa, D. C. Zimmermann and D. J. Williams, J. Med. Chem. **1989**, *32*, 228.

Table S1. Crystallographic data (unit cell) for complexes **1-3** and **5**

	1	**2**	**3**	**5**
a (Å)	11.2725(13)	11.5227(15)	12.4327(8)	10.9466(15)
b (Å)	20.602(2)	19.681(3)	19.2691(12)	11.5259(16)
c (Å)	19.583(2)	20.917(3)	24.7480(16)	19.195(2)
α (deg)	90	90	90	101.515(2)
β (deg)	91.485(3)	90	90	96.956(2)
γ (deg)	90	90	90	115.923(2)
V (Å^3)	4546.4(9)	4743.5(12)	5928.8(7)	2073.8(5)