

Supporting Information for

**C–N Bond Formation via Ligand-Induced Nucleophilicity at a Coordinated
Triamidoamine Ligand**

Annalese F. Maddox,^a Karla A. Erickson,^a Joseph M. Tanski,^b and Rory Waterman^{a,*}

^aDepartment of Chemistry, University of Vermont, Burlington, VT 05405-0125 and

^bDepartment of Chemistry, Vassar College, Poughkeepsie, NY, 12604

General Considerations

All reactions were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox. Celite-454 was heated to a temperature above 180 °C under dynamic vacuum for at least 8 h. Benzene-*d*₆ was purchased from Cambridge Isotope Laboratory, degassed, and dried over NaK alloy. Elemental analyses were performed on an Elementar microCube. NMR spectra were recorded with either a Bruker ARX or Varian Inova 500 MHz spectrometer in benzene-*d*₆ and are reported with reference to residual solvent resonances ($\delta = 7.16$ and 128.0) unless otherwise noted. A Varian Inova 500 spectrometer was used to record HMQC spectra with a standard pulse sequence. Infrared spectra were collected on a Bruker Alpha FT-IR with an ATR plate at a resolution of 1 cm⁻¹. Complexes **1a**,¹ **1b**,¹ **3**,² and **5**² were prepared according to reported procedures. All other chemicals were obtained from commercial suppliers and dried or purified by conventional means.

[N,N,N,N,N,N-N(CH₂CH₂NSiMe₃)₂(CH₂CH₂NC(N^{*i*}PrSiMe₃)(N^{*i*}Pr))]ZrNH^{*i*}Bu (2a). A cold, 2 mL ethereal solution of *N,N'*-diisopropylcarbodiimide (40 mg, 0.32 mmol) was added drop-wise to a cold, 3 mL ethereal solution of **1a** (184 mg, 0.35 mmol), and the resulting solution was stirred at ambient temperature 14 h. The solution was then filtered through Celite, concentrated until incipient crystallization under reduced pressure

then warmed sufficiently to redissolve solids, and cooled to $-30\text{ }^{\circ}\text{C}$ yielding 73 mg (0.113 mmol, 65% relative to carbodiimide) of colorless crystals. ^1H (500.1 MHz): 4.15 (s, NH, 1 H), 3.95 (septet, CH, 1 H), 3.39 (m, CH₂, 2 H), 3.22 (m, CH, 1 H), 3.17 (m, CH₂, 2 H), 3.00 (m, CH₂, 2 H), 2.45 (m, CH₂, 2 H), 2.34 (m, CH₂, 4 H), 1.60 (s, C(CH₃)₃, 9 H), 1.45 (d, CH(CH₃)₂, $J = 10\text{ Hz}$, 3 H), 1.40 (d, CH(CH₃)₂, $J = 5\text{ Hz}$, 3 H), 1.07 (d, CH(CH₃)₂, $J = 5\text{ Hz}$, 3 H), 1.03 (d, CH(CH₃)₂, $J = 5\text{ Hz}$, 3 H), 0.42 (s, CH₃, 9 H), 0.38 (s, CH₃, 9H), 0.15 (s, CH₃, 9 H) $^{13}\text{C}\{^1\text{H}\}$ (125.8 MHz): 170.8 (s, C=N), 59.1 (s, CH₂), 57.2 (s, CH₂), 54.9 (s, CH₂), 49.6 (s, CH), 48.3 (s, CH₂), 48.0(s, CH₂), 48.0(s, CH), 44.9 (s, CH₂), 34.9 (s, CH₃), 27.3 (s, CH₃), 26.2 (s, CH₃), 25.3 (s, CH₃), 23.52 (s, CH₃), 23.1 (s, CH₃), 2.7 (s, CH₃), 2.6 (s, CH₃), 2.0 (s, CH₃). IR: 3209 s (ν_{NH}), 2951 m, 2506 s, 1658 s (ν_{CN}), 1587 s, 1488 m, 1436 m, 1382 w, 1357 w, 1239 m, 1200 m, 1153 w, 1116 w, 1065 w, 1033 w, 1000 w, 972 m, 940 m, 906 m, 827 s, 783 s, 743 s, 680 m, 582 m, 556 w, 524 w, 442 w, 423 w. Anal. Calcd. for C₂₆H₆₃N₇Si₃Zr: C, 48.09; H, 9.78; N, 15.10. Found: C, 47.72; H, 9.65; N, 14.97.

[N,N,N,N,N,N-N(CH₂CH₂NSiMe₃)₂(CH₂CH₂NC(N^{*i*}PrSiMe₃)(N^{*i*}Pr))]ZrNHPPh (2b). A 2 mL benzene solution of *N,N'*-diisopropylcarbodiimide (46 mg, 0.36 mmol) was added drop-wise to a 5 mL benzene solution of **1b** (200 mg, 0.37 mmol) and stirred 1 h. The resulting solution was filtered through Celite and lyophilized. The powder was dissolved in minimal pentane, and the solution was filtered then concentrated before cooling to $-30\text{ }^{\circ}\text{C}$ to afford 237 mg (0.35 mmol, 97%) of **2b** as a colorless microcrystalline powder. ^1H (500.1 MHz): 7.33 (t, C₆H₅, $J = 5\text{ Hz}$, 2 H), 6.95 (d, C₆H₅, $J = 5\text{ Hz}$, 2 H), 6.78 (t, C₆H₅, $J = 5\text{ Hz}$, 1 H), 6.35 (s, NH, 1 H) 3.94 (m, CH₂, 2 H), 3.48 (m, CH, 2 H) 3.27 (m, CH, 2H), 3.15 (m, CH₂, 2 H), 3.05 (m, CH₂, 2 H), 2.62 (m, CH₂, 2

H), 2.38 (m, CH₂, 2 H), 2.31 (m, CH, 2 H), 1.63 (d, CH(CH₃)₂, *J* = 5 Hz, 3 H), 1.55 (d, CH(CH₃)₂, *J* = 5 Hz, 3 H), 1.02 (d, CH(CH₃)₂, *J* = 5 Hz, 3 H), 0.98 (d, CH(CH₃)₂, *J* = 5 Hz, 3 H), 0.49 (s, CH₃, 9 H), 0.46 (s, CH₃, 9 H), 0.12 (s, CH₃, 9 H) ¹³C{¹H} (125.8 MHz): 171.7 (s, C=N), 128.51 (s, CH), 118.3 (s, CH), 115.7 (s, CH), 56.3 (s, CH₂), 56.0 (s, CH₂), 54.1 (s, CH), 49.0 (s, CH₂), 48.9 (s, CH₂), 48.2 (s, CH), 44.1 (s, CH₂), 44.0 (s, CH₂), 26.0 (s, CH₃), 25.0 (s, CH₃), 24.6 (s, CH₃), 23.1 (s, CH₃), 2.2 (s, CH₃), 2.0 (s, CH₃), 1.3 (s, CH₃). IR: 3230 s (ν_{NH}), 2948 m, 2510 s, 1646 s (ν_{CN}), 1590 s, 1487 m, 1457 m, 1439 m, 1381 w, 1365 w, 1333 w, 1279 m, 1240 m, 1210 m, 1152 w, 1128 w, 1067 m, 1029 m, 1002 m, 938 s, 901 s, 828 s, 785 s, 748 s, 691s, 678 m, 659 m, 585 m, 573 m, 520 m, 481 m, 440 m. Anal. Calcd. for C₂₈H₅₉N₇Si₃Zr: C, 50.25; H, 8.89; N, 14.65. Found: C, 50.16; H, 9.01; N, 14.52.

[*N,N,N,N,N,N*-N(CH₂CH₂NSiMe₃)₂(CH₂CH₂NC(^{*i*}PrSiMe₃)(^{*i*}Pr))]ZrCl (4**).**

A 2 mL benzene solution of *N,N'*-diisopropylcarbodiimide (52 mg, 0.41 mmol) was added drop-wise to a 5 mL benzene solution of **3** (200 mg, 0.41 mmol) and stirred for 30 min at ambient temperature. The resulting solution was filtered through Celite and lyophilized. The powder was dissolved in minimal pentane, and the solution was filtered then concentrated before cooling to -30 °C to afford 250 mg (0.40 mmol, 98%) of **4** as a colorless microcrystalline powder. ¹H (500.1 MHz): 3.94 (m, CH, 1 H), 3.45 (m, CH₂, 2 H), 3.24 (m, CH₂, 2 H), 3.13 (m, CH₂, 2 H), 3.06 (m, CH₂, 2 H), 2.59 (m, CH₂, 2 H), 2.36 (m, CH₂, 2 H), 2.30 (m, CH, 1 H), 1.63 (d, CH(CH₃)₂, *J* = 5 Hz, 3 H), 1.56 (d, CH(CH₃)₂, *J* = 5 Hz, 3 H), 1.01 (d, CH(CH₃)₂, *J* = 5 Hz, 3 H), 0.98 (d, CH(CH₃)₂, *J* = 5 Hz, 3 H), 0.47 (s, CH₃, 9 H), 0.46 (s, CH₃, 9 H), 0.12 (s, CH₃, 9 H). ¹³C{¹H} (125.8 MHz): 171.7 (s, C=N), 55.9 (s, CH₂), 55.9 (s, CH₂), 54.0 (s, CH), 48.9 (s, CH₂), 48.9 (s, CH₂), 48.0 (s,

CH), 44.0(s, CH₂), 43.9 (s, CH₂), 25.8 (s, CH₃), 24.9 (s, CH₃), 24.5 (s, CH₃), 23.07 (s, CH₃), 2.2 (s, CH₃), 1.9 (s, CH₃), 1.3 (s, CH₃). IR: 2952 w, 2896 w, 2859 w, 1621 w (ν_{CN}), 1490 m, 1472 m, 1448 m, 1421 m, 1327 w, 1243 m, 1219 m, 1150 w, 1116 w, 1046 w, 972 m, 916 s, 828 s, 746 s, 678 m, 616 m, 546 w, 404 w. Anal. Calcd. for C₂₂H₅₃ClN₆Si₃Zr: C, 43.13; H, 8.72; N, 13.72. Found: C, 42.80; H, 8.65; N, 13.47.

[*N,N,N,N,N,N*-N(CH₂CH₂NSiMe₃)₂(CH₂CH₂NC(N^{*i*}PrSiMe₃)(N^{*i*}Pr))]ZrMe

(6). A 1.5 mL benzene solution of *N,N'*-diisopropylcarbodiimide (30 mg, 0.24 mmol) was added to 2 mL benzene solution of **5** (105 mg, 0.23 mmol) at -30 °C, and the resulting solution was stirred for 30 min while gradually warming to ambient temperature. The solution was lyophilized yielding 85 mg (0.14 mmol, 63%) of product. Colorless crystals were obtained from a cooled ether solution. ¹H (500.1 MHz): 3.85 (m, CH(CH₃)₂, 1H), 3.46 (m, CH₂, 2H), 3.27 (m, CH₂, 2H), 3.21 (m, CH(CH₃)₂, 1H), 3.1 (m, CH₂, 1H), 3.02 (m, CH₂, 1H), 2.38 (m, CH₂, 2H), 2.25 (m, CH₂, 2H), 2.19 (m, CH₂, 2H), 1.41 (d, CH(CH₃)₂, *J* = 6.5 Hz, 3H), 1.37 (d, CH(CH₃)₂, *J* = 6.5 Hz, 3H), 1.08 (d, CH(CH₃)₂, *J* = 6.5 Hz, 3H), 1.03 (d, CH(CH₃)₂, *J* = 6.5 Hz, 3H), 0.64 (s, CH₃, 3H), 0.39 (s, CH₃, 3H), 0.37 (s, CH₃, 3H), 0.15 (s, CH₃, 3H). ¹³C{¹H} (125.8 MHz): 171 (s, C=N), 59.1 (s, CH₂), 56.8 (s, CH₂), 49.5 (s, CH), 47.7 (s, CH₂), 47.5 (s, CH₂), 47.4 (s, CH₂), 45.1 (s, CH), 34.9 (s, CH₃), 25.6 (s, CH₃), 24.8 (s, CH₃), 23.7 (s, CH₃), 1.81 (s, CH₃), 1.72 (s, CH₃), 1.59 (s, CH₃). IR: 2958 w, 2842 w, 2170 m, 1489 m, 1438 m, 1243 m, 1201 m, 1078 m, 903 m, 825 m, 736 m, 579 m, 425 m. Anal. Calcd. for C₂₃H₅₆N₆Si₃Zr: C, 46.65; H, 9.53; N, 14.19. Found: C, 45.98; H, 9.55; N, 13.97

X-Ray structure determinations. X-Ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (MoKα, λ = 0.71073 Å) at 125 K. Suitable

crystals of each complex **2a** and **4** were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least squares procedures on F^2 with SHELXTL (version 6.14).³ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. The hydrogen atom on nitrogen atom N(5) of **2a**, H(5), was located in the Fourier difference map and refined freely.

Table SI-1. Crystal data and structure refinement parameters for **2a** and **4**.

compounds	2a	4
formula	C ₂₆ H ₆₃ N ₇ Si ₃ Zr	C ₂₂ H ₅₃ ClN ₆ Si ₃ Zr
MW	649.32	612.64
crystal system	triclinic	triclinic
<i>a</i> /Å	10.3406(5)	9.517(3)
<i>b</i> /Å	10.3645(5)	10.057(4)
<i>c</i> /Å	17.2962(8)	19.313(6)
α /°	88.5340(10)	76.739(5)
β /°	87.1460(10)	80.800(3)
γ /°	77.7520(10)	62.440(3)
<i>V</i> /Å ³	1809.07(15)	1592.0(10)
space group	P-1	P-1
<i>Z</i>	2	2
θ range/°	2.01 to 31.95	2.17 to 27.88
<i>m</i> /mm ⁻¹	0.428	0.563
<i>N</i>	30146	7558
<i>N</i> _{ind}	11517	7558
<i>R</i> _{int}	0.0245	0.0000
<i>R</i> ₁ ^a (<i>I</i> > 2 <i>s</i> (<i>I</i>))	0.0329	0.0260
<i>wR</i> ₂ ^b (<i>I</i> > 2 <i>s</i> (<i>I</i>))	0.0804	0.0616
$\Delta\rho_{\max}$; $\Delta\rho_{\min}$ /e Å ³	1.013; -0.463	0.815; -0.293
GoF on <i>R</i> ₁	1.034	1.048

$$^a R_1 = \frac{\sum (|F_o| - |F_c|)}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

References

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