Synthesis and Study of the First N-Aryl Acyclic

Diaminocarbene and its Transition Metal Complexes

Evelyn L. Rosen, Matthew D. Sanderson, Shanmuganathan Saravanakumar and Christopher W. Bielawski*

University of Texas at Austin Department of Chemistry and Biochemistry Austin, TX 78712 email: bielawski@cm.utexas.edu

SUPPORTING INFORMATION

General Considerations. THF was distilled from CaH₂ under an atmosphere of nitrogen prior to use. Benzene was distilled from sodium and benzophenone under nitrogen and then degassed by performing three consecutive freeze-pump-thaw cycles. Chloro(1,5-cyclooctadiene)rhodium(I) dimer was purchased from Strem Chemicals and used without further purification. p-Nitrobenzylbromide was purchased from Alfa Aesar and stored at -20 °C prior to use. All other chemicals were purchased from Aldrich or Alfa Aesar and used without further purification. N,N'-Bis(2,6-di-iso-propylphenyl)formamidine (7) and N_N dimesitylformamidine (14) were synthesized according to literature procedures.¹ ¹H NMR spectra were recorded using a Varian Unity Plus 300 or 400 spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protio solvent as an internal standard (CDCl₃, 7.24 ppm; C₆D₆, 7.15 ppm; DMSO- d_6 , 2.50 ppm). Coupling constants are expressed in Hertz (Hz). ¹³C NMR spectra were recorded using a Varian Gemini 300 spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the solvent as an internal standard (CDCl₃, 77.0 ppm; C₆D₆, 128.0 ppm; DMSO-*d*₆, 39.5 ppm). ¹³C NMR spectra were routinely run with broadband decoupling. IR spectra were recorded using a Perkin-Elmer Spectrum BX FT-IR system. High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E or a Karatos MS9 instrument and are reported as m/z (relative intensity). Elemental analyses were performed at Midwest Microlabs, LLC, Indianapolis, IN. X-ray crystal structure data was collected for compounds 8 (CCDC 653951), 10 (CCDC 653949), and 15 (CCDC 653950), and deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

N,*N*'-Bis(2,6-di-*iso*-propylphenyl)-*N*,*N*'-dimethylformamidinium iodide (8). *N*,*N*'-Bis(2,6-di-*iso*propylphenyl)formamidine (1.06 g, 2.93 mmol) was dissolved in acetonitrile (15 mL) in a 20 mL vial. After sodium bicarbonate (253 mg, 3.01 mmol), methyl iodide (978 mg, 6.89 mmol), and a stir bar were added, the vial was sealed with a Teflon lined cap. The reaction mixture was then stirred at 110 °C for 8 h. After cooling to ambient temperature, the solution was concentrated under reduced pressure. The resulting solids were dissolved in CH₂Cl₂ and washed with water (3 x 30 mL) to remove inorganic byproducts. The organic phase was subsequently dried with sodium sulfate and then concentrated under reduced pressure. Residual solids were then dissolved in hot THF and precipitated by adding diethyl ether. Filtration afforded the desired compound as a white powder (1.04 g, 69% yield). Crystals suitable for X-ray analysis were obtained by vapor diffusion of diethyl ether into a saturated methylene chloride solution of the compound. ¹H NMR (300 MHz, DMSO- d_6): δ 8.92 (s, 1H), 7.62 (m, 1H), 7.52 (m, 3H), 7.42 (m, 2H), 3.59 (s, 3H), 3.00 (m, 2H), 2.80 (m, 2H), 2.69 (s, 3H), 1.39 (d, 6H, J=6.7), 1.32 (m, 12H), 1.23 (d, 6H, J=6.7). ¹³C NMR (75 MHz, DMSO- d_6): δ 156.04, 144.33, 143.92, 139.88, 133.17, 131.49, 130.57, 125.38, 125.03, 47.74, 28.32, 28.14, 25.34, 23.96, 23.49, 22.61. HRMS: [M⁺] calcd for C₂₇H₄₁N₂: 393.3270; found: 393.3273. Anal. Calcd (%) for C₂₇H₄₁N₂I: C, 62.3, H, 7.94, N, 5.38. Found: C, 62.08, H, 7.82, N, 5.35.

N,N'-Bis(2,6-di-*iso*-propylphenyl)-*N,N'*-dimethyldiaminocarbene (9). In a nitrogen-filled glovebox, a high pressure vial was charged with **8** (445 mg, 0.85 mmol), sodium hydride (95%, 41 mg, 1.71 mmol), potassium *tert*-butoxide (9.5 mg, 0.09 mmol), and a stir bar. After dry THF (15 mL) was added, the vial was sealed, removed from the glovebox, and stirred at 70 °C for 16 h. After cooling to ambient temperature, the crude reaction mixture was brought back into a nitrogen-filled glovebox then concentrated under reduced pressure. The resulting pale yellow solid was re-dissolved in toluene and passed through a 0.2 µm PTFE filter under an atmosphere of nitrogen. The resulting yellow solution was concentrated to afford the desired compound as a yellow solid (255.4 mg, 77% yield). ¹H NMR (400 MHz, benzene-*d*₆): δ 7.21 (m, 1H), 7.10 (m, 3H), 6.99 (d, 4H, *J*=7.4), 3.54 (s, 3H), 3.42 (m, 4H), 2.34 (s, 3H), 1.40 (d, 6H, *J*=6.9), 1.29 (d, 6H, *J*=6.9), 1.22 (m, 12H). ¹³C NMR (75 MHz, benzene-*d*₆): δ 248.87, 148.310, 145.00, 144.42, 144.28, 126.70, 123.73, 51.29, 37.62, 28.79, 28.05, 25.55, 23.98, 23.56, 23.02. HRMS: [M + H⁺] calcd for C₂₇H₄₁N₂: 393.3270; found: 393.3273.

N,N'-Bis(2,6-di-*iso*-propylphenyl)-*N,N'*-dimethyldiaminocarbene rhodium (1,5-cyclooctadiene) chloride (10). In a nitrogen-filled glovebox, free carbene 9 (255.4 mg, 0.6505 mmol) was dissolved in dry toluene (15 mL). The carbene solution was then added to a flask containing $[Rh(cod)Cl]_2$ (150 mg, 0.30 mmol) and a stir bar. The combined reaction mixture was then stirred at ambient temperature for 16 h. Removal of solvent under reduced pressure afforded a yellow solid which was then purified by

column chromatography (media: silica gel; eluent: hexanes followed by 10:1 hexanes:ethyl acetate) to yield the desired compound as a bright yellow solid (318 mg, 76% yield). Crystals suitable for X-ray analysis were obtained by vapor diffusion of pentane into a saturated methylene chloride solution of the complex. ¹H NMR (300 MHz, benzene- d_6): δ 7.35 (d, 1H, *J*=6.4), 7.22 (t, 1H, *J*=7.8), 7.07 (t, 1H, *J*=7.7), 6.97 (d, 2H, *J*=6.1), 6.86 (d, 1H, *J*=6.1), 5.06 (m, 2H), 4.59 (s, 3H), 4.54 (m, 2H), 3.79 (b, 1H), 3.14 (m, 1H), 2.82 (m, 1H), 2.73 (b, 1H), 2.49 (s, 3H), 2.42 (m, 1H), 1.96 (m, 3H), 1.84 (d, 3H, *J*=6.4), 1.78 (m, 2H), 1.39 (d, 3H, *J*=6.7), 1.35 (d, 3H, *J*=6.9), 1.29 (m, 2H), 1.25 (d, 3H, *J*=6.7), 1.18 (d, 3H, *J*=6.9), 1.12 (d, 3H, *J*=4.6), 1.10 (d, 3H, *J*=4.9), 0.86 (d, 3H, *J*=6.7). ¹³C NMR (100 MHz, CDCl₃): δ 211.65 (d, *J*=45.6), 147.30, 147.00, 145.77, 144.16, 143.98, 143.64, 128.70, 128.32, 124.72, 123.32, 123.18, 95.23 (d, *J*=6.7), 93.41 (d, *J*=7.5), 68.74 (d, *J*=15.7), 65.87 (d, *J*=14.2), 52.19, 45.28, 45.27, 35.80, 30.24, 28.76, 28.53, 28.25, 27.12, 26.88, 26.72, 26.04, 26.00, 25.82, 23.74, 22.78, 22.72, 22.56. HRMS: [M⁺] calcd for C₃₅H₅₂N₂RhCl: 638.2874; found: 638.2872. Anal. Calcd (%) for C₃₅H₅₂N₂RhCl: C, 65.77, H, 8.20, N, 4.38. Found: C, 65.82, H, 8.07, N, 4.38.

N,N'-Bis(2,6-di-iso-propylphenyl)-N,N'-dimethyldiaminocarbene bis(carbon monoxide) rhodium chloride (12). Rhodium complex 10 (39.5 mg, 0.0616 mmol) was dissolved in CDCl₃ (2 mL) in a 10 mL round bottom flask. The flask was equipped with a stir bar and then fitted with a rubber septum vented by a needle. The reaction was placed into a Parr pressure vessel and charged with carbon monoxide (100 PSI). The mixture was then stirred at room temperature for 1 h. The resulting vellow solution was concentrated under reduced pressure to give a dark yellow oil. The oil was then redissolved and concentrated from hexanes three times to aid in the removal of the liberated 1,5cyclooctadiene, which afforded the desired compound as a yellow solid (34.7 mg, 96% yield). 1 H NMR (300 MHz, benzene- d_6): δ 7.18 (m, 2H), 7.05 (m, 2H), 6.87 (m, 2H), 4.20 (m, 1H), 3.90 (s, 3H), 3.79 (m, 1H), 3.17 (m, 2H), 2.46 (s, 3H), 1.73 (d, 3H, J=6.4), 1.48 (d, 3H, J=6.7), 1.30 (d, 3H, J=6.9), 1.24 (d, 3H), 1.20 (d, 3H, J=6.9), 1.05 (d, 3H, J=6.9), 0.99 (d, 3H, J=6.7), 0.92 (d, 3H, J=6.7). ¹³C NMR (100 MHz, benzene- d_6): δ 204.85 (d, J=39.6), 187.28 (d, J=53.8), 184.60 (d, J=76.3), 146.85, 146.83, 145.58, 144.49, 144.08, 142.71, 129.54, 129.50, 125.14, 124.77, 124.06, 123.74, 52.89, 44.64, 29.30, 29.00, 28.57, 27.58, 27.30, 26.93, 26.14, 25.55, 24.16, 22.94, 22.75, 22.57. HRMS: [M⁺] calcd for C₂₉H₄₀N₂O₂RhCl: 586.1833; found: 586.1838. IR (KBr): 2068, 1984 cm⁻¹. Anal. Calcd (%) for C₂₉H₄₀N₂O₂RhCl: C, 59.34, H, 6.87, N, 4.77. Found: C, 59.55, H, 6.85, N, 4.73.

N,N'-Dimesityl-*N,N'*-di(*p*-nitrobenzyl)formamidinium bromide (15). A 20 mL vial was charged with *N,N'*-dimesitylformamidine (166 mg, 0.590 mmol), acetonitrile (8 mL), and a stir bar. Afterward, *p*-nitrobenzyl bromide (255 mg, 1.18 mmol) and sodium bicarbonate (49.7 mg, 0.592 mmol) were then added. The vial was sealed with a Teflon lined cap and the resulting reaction mixture was heated at 110

°C for 48 h with stirring. After cooling to ambient temperature, the solution was washed with water (3 x 30 mL) and extracted with CH₂Cl₂. The organic phase was then dried with Na₂SO₄ and then concentrated under reduced pressure. The resulting pale yellow powder was dissolved in hot THF and precipitated by adding diethyl ether. Subsequent filtration afforded the desired compound as a white microcrystalline powder (271 mg, 73% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated THF solution of the compound. ¹H NMR (400 MHz, CDCl₃): δ 11.63 (s, 1H), 8.10 (d, 4H, *J*=8.7), 7.66 (d, 4H, *J*=8.7), 6.43 (s, 4H), 5.45 (s, 4H), 2.07 (s, 6H), 1.63 (s, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 158.92, 148.44, 139.59, 139.51, 134.02, 132.08, 131.44, 129.36, 123.87, 60.78, 20.65, 19.21. HRMS: [M – H⁺] calcd for C₃₃H₃₅N₄O₄Br: 629.1763; found: 629.1763. Anal. Calcd (%) for C₃₃H₃₅N₄ O₄Br•0.5H₂O: C, 61.88, H, 5.59, N, 8.87. Found: C, 62.08, H, 5.51, N, 8.73.

N,N'-Dimesityl-*N,N'*-dimethylformamidinium iodide (16). A glass vial equipped with a stir bar was charged with *N,N'*-dimesitylformamidine (350 mg, 1.25 mmol) and acetonitrile (10 mL). Sodium bicarbonate (133 mg, 1.58 mmol) and methyl iodide (690 mg, 4.86 mmol) were then added. The vial was then sealed with a Teflon lined cap and the solution was stirred at 80 °C for 12 h. After cooling to ambient temperature, the crude reaction mixture was filtered through Celite and then concentrated under reduced pressure. The resulting white solid was triturated with diethyl ether and then filtered to afford the desired product as a white powder (391.3 mg, 72% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.45 (s, 1H), 7.14 (s, 2H), 7.07 (s, 2H), 3.50 (s, 3H), 2.63 (s, 3H), 2.37 (s, 6H), 2.31 (s, 3H), 2.27 (s, 9H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 156.18, 140.75, 139.74, 138.88, 134.39, 134.04, 133.79, 129.48, 129.37, 45.68, 37.30, 20.55, 20.45, 17.30, 17.00. HRMS: [M⁺] calcd for C₂₁H₂₉N₂: 309.2331; found 309.2332.

Reference:

1 Taylor, E. C.; Ehrhart, W. A. J. Org. Chem. 1963, 28, 1108.













.





















S18















.

.

DiPP,MeFormamidinium 50 C

S33

