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Discrete High Molecular Weight Triarylamine Dendrimers Prepared by Palladium-Catalyzed Amination

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Experimental

General. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. THF and toluene were distilled from sodium benzophenone ketyl under nitrogen. (DPPF)$PdCl_2$ was prepared by standard addition of phosphine to $(CH_3CN)_2PdCl_2$ formed by refluxing $PdCl_2$ in CH_3CN. $Pd(DBA)_2$[1] and N,N-bis(4-bromophenyl)benzenemethanamine[2] were prepared by literature procedures.

Reactions were set-up in an inert atmosphere glove box or by using standard Schlenk or vacuum line techniques. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a GE QE 300 MHz or Brucker AM500 MHz Fourier Transform spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded relative to residual protiated solvent. A positive value of the chemical shift denotes a resonance downfield from TMS. Samples for elemental analysis were submitted to Robertson Microlit Laboratories, Inc.

Representative Example of Procedure I

A Schlenk flask containing 10 mL toluene was charged with 2.1 mg (0.0029 mmol) $Pd[P(o\text{-tolyl})_3]_2$, 2.5 mg (0.0082 mmol) $P(o\text{-tolyl})_3$, 43.0μL (0.349 mmol) 4-bromotoluene, and 88.7 (0.436 mmol) lithium ditolylamide. The reaction was stirred at 90 °C for 1 hour. The solvent was concentrated, and the crude product was purified by column chromatography (100:1 hexane:Et_2O) to give 99 mg (99%) of tritolylamine.

Representative Example of Procedure II

A Schlenk flask containing 30 mL toluene was charged with 13.0 mg (0.0182 mmol) $Pd[P(o\text{-tolyl})_3]_2$, 8.5 mg (0.028 mmol) $P(o\text{-tolyl})_3$, 201 mg (2.09 mmol) NaO-*t*-Bu, 299 mg (1.75 mmol) 4-bromotoluene, and 408 mg (2.07 mmol). The reaction was stirred at 90°C for 8 hours. The solvent was concentrated, and the crude product was purified by column chromatography (100:1 hexane:Et_2O) to give 461 mg (92% yield) of tritolylamine.

Representative Example of Procedure III

A Schlenk flask containing 100 mL toluene was charged with 162 mg (0.289 mmol) $Pd(DBA)_2$, 312 mg (0.563 mmol) DPPF, 3.00g (0.0312 mol) NaO-*t*-Bu, 5.39g (0.0315 mol) 4-bromotoluene, and 1.17g (0.0109 mol) *p*-toluidine. The reaction was stirred at 90°C for 1 day. The reaction was cooled to room temperature, and the volatile materials were removed by rotary evaporation. Sublimation (100°C/0.01 mm Hg) of the residue afforded 2.80 g (89%) of product as a white solid.

4,4',4''-tris(N,N-diphenylamino)triphenylamine (TDATA, 2)[3]

A Schlenk flask containing 30 mL toluene was charged with 13.5 mg (0.0189 mmol) $Pd[P(o\text{-tolyl})_3]_2$, 8.3 mg (0.027 mmol) $P(o\text{-tolyl})_3$, 403 mg (2.30 mmol) lithium diphenylamide, and 327 mg (0.678 mmol) tris(4-bromophenyl)amine. The reaction was stirred at 90 °C for 12 h. After separation of the lithium bromide by filtration, the solvent was removed by rotary evaporation to provide a brown solid. Recrystallization of this solid from THF:EtOH gave a yellow solid (428 mg, 84% yield).

N,N-Bis[N',N'-bis(4-methylphenyl)4-aminophenyl]benzenemethanamine (4)

A Schlenk flask containing 250 mL toluene was charged with 186 mg (0.260 mmol) $Pd[P(o\text{-tolyl})_3]_2$, 217 mg (0.712 mmol) $P(o\text{-tolyl})_3$, 3.39g (0.0167 mol) lithium ditolylamide, and 3.18 g (0.00762 mol) N,N-bis(4-bromophenyl)benzenemethanamine (**3**). The reaction was stirred at 90 °C for 3 h. The mixture was washed with brine (2 x 100 mL) and water (1 x 100 mL). After drying the mixture with Na_2SO_4, evaporation of the solvent gave a brown, oily solid which was crystallized and recrystallized in EtOAc/EtOH to give 4.69 g (95% yield) of yellow needles. ^1H NMR: (300 MHz, C_6D_6) δ 7.24 (d, 7.4 Hz, 2H), 7.10 (d, 8.3 Hz, 10H), 7.04 (d, 8.9 Hz, 5H),

6.95 (d, 8.9 Hz, 4H), 6.89 (d, 8.3 Hz, 8H), 4.66 (s, 2H), 2.08 (s, 12H); $^{13}C\{^{1}H\}$ NMR: (75.6 MHz, C_6D_6) δ 146.77, 144.16, 142.86, 140.19, 132.05, 130.52, 129.16, 127.33, 127.23, 125.93, 124.56, 122.15, 57.23, 21.11. IR (KBr): 3027(m), 2919(m), 2857(m), 1896(w), 1607(s), 1579(m), 1502(vs), 1448(s), 1371(w), 1317(s), 1291(s), 1273(s), 1250(s), 1219(s), 1110(m), 817(s), 724(s), 693(m), 573(s), 567(s), 518(s), 507(s), 458(m), 409(m). MS (EI): 649, 558, 529, 446, 362, 324, 300, 279, 181, 160, 91. HRMS calcd for $C_{47}H_{43}N_3$ (M^+) 649.3457. Found: 649.3452. Anal. Calc'd. for $C_{47}H_{43}N_3$: C, 86.86; H, 6.67; N, 6.47. Found: C, 86.60; H, 6.50; N, 6.24.

4,4'-bis(N,N-ditolylamino)diphenylamine (5)

Compound **4** (4.69 g, 0.00722 mol) was dissolved in 300 mL of THF, and 3.93 g of 10% Pd/C was added. The suspension was shaken in a Parr reactor under 35 Psi of H_2 for 12 hours. The solid was isolated by filtration to give a clear yellow solution, which was concentrated and layered with EtOH. Recrystallization in THF:EtOH gave 4.04 g (100%) of a yellow solid. ^{1}H NMR: (500 MHz, C_6D_6) δ 7.17 (d, 5.2 Hz, 8H), 7.10 (d, 8.5 Hz, 4H), 6.94 (d, 8.2 Hz, 8H), 6.77 (d, 8.4 Hz, 4H), 4.89 (s, 1H), 2.13 (s, 12H); $^{13}C\{^{1}H\}$ NMR: (126 MHz, C_6D_6) δ 146.93, 142.38, 131.86, 130.50, 128.67, 126.59, 124.25, 119.43, 21.09. IR (KBr): 3394(m), 3028(m), 2916(w), 2858(w), 1884(w), 1609(s), 1504(vs), 1315(s), 1271(vs), 1109(m), 1037(w), 1015(w), 913(w), 868(w), 816(s), 712(m), 634(m), 578(s), 564(s), 516(s), 499(s), 460(w), 411(w). MS (EI): 559, 462, 444, 386, 348, 266, 256, 197, 184, 154, 91, 77. HRMS calcd for $C_{40}H_{37}N_3$ (M^+) 559.2987. Found: 559.2989.

Lithium 4,4'-bis(N,N-ditolylamino)diphenylamide (6)

Compound **5** (1.84 g, 0.00329 mol) was dissolved in 50 mL of pentane, and 2.5 mL of a 2.5 M solution of BuLi (0.0063 mol) was added slowly. The reaction was stirred at room temperature for 3 hours. The bright yellow product was isolated by filtration and washed with excess pentane to give 1.7 g (92%). The lithium salt was used without further purification.

Compound 7

A Schlenk flask containing 5 mL toluene was charged with 6.9 mg (0.0097 mmol) Pd[P(*o*-tolyl)$_3$]$_2$, 8.8 mg (0.029 mmol) P(*o*-tolyl)$_3$, 132 mg (0.273 mmol) tris(4-bromophenyl)amine, and 471 mg (0.832 mmol) **6**. The reaction was stirred at 90 °C for 3 hours. Evaporation of the solvent and flash column chromatography on silica gel (2:1 hexane:toluene) gave a yellow solid (338 mg, 64%). ^{1}H NMR: (500 MHz, C_6D_6) δ 7.11 (d, 8.4 Hz, 24H), 7.08 - 7.03 (m, 36H), 6.89 (d, 8.2 Hz, 24H), 2.08 (s, 36H); ^{13}C{^{1}H} NMR: (126 MHz, C_6D_6) δ 146.61, 143.97, 143.59, 143.40, 143.36, 132.35, 130.59, 128.69, 125.52, 125.48, 125.39, 124.85, 21.00. IR (KBr): 3029(m), 2919(w), 2859(w), 1890(w), 1607(s), 1499(vs), 1263(vs), 1106(m), 1016(w), 914(w), 817(s), 715(m), 570(m), 526(m), 456(w). MS (MALDI): M^+ = 1918.8. Anal. Calc'd. for $C_{138}H_{120}N_{10}$: C, 86.39; H, 6.30; N, 7.30. Found: C, 86.03; H, 6.49; N, 7.18.

Compound 8

A Schlenk flask containing 250 mL toluene was charged with 63.4 mg (8.87×10^{-5} mol) Pd[P(*o*-tolyl)$_3$]$_2$, 107 mg (3.52×10^{-4} mol) P(*o*-tolyl)$_3$, 2.27g (0.00544 mol) N,N-bis(4-bromophenyl)benzenemethanamine (**3**), and 6.52 g (0.0115 mol) of **6**. The reaction was stirred at 110°C for 12 hours. Evaporation of the solvent and flash column chromatography on silica gel (2:1 toluene:hexane) gave a yellow solid (6.65 g, 89%). ^{1}H NMR: (500 MHz, C_6D_6) δ 7.24 (d, 7.4 Hz, 2H), 7.12 - 6.99 (m, 39H), 6.92 (d, 9.0 Hz, 4H), 6.89 (d, 8.2 Hz, 16H), 4.66 (s, 2H), 2.09 (s, 24H); ^{13}C{^{1}H} NMR: (126 MHz, C_6D_6) δ 146.64, 144.18, 143.71, 143.60, 142.48, 140.12, 132.26, 130.56, 129.18, 127.37, 127.22, 125.97, 125.48, 125.21, 124.76, 122.15, 57.18, 21.12. IR (KBr): 3030(m), 2919(m), 2859(w), 1892(w), 1580(w), 1313(s), 1266(vs), 1108(m), 1015(m), 915(w), 813(s), 715(s), 568(m), 526(s), 458(w), 412(w). MS (FAB matrix 3NBA): 1374, 1283, 1117, 1011, 828, 739, 687, 613, 558, 460, 307, 290, 242, 186, 154, 147. Anal. Calc'd. for $C_{99}H_{87}N_7$: C, 86.43; H, 6.38; N, 7.13. Found: C, 86.13; H, 6.61; N, 6.91.

Compound 9

Compound **8** (6.45 g, 0.00469 mol) was dissolved in 400 mL of THF, and 3.5 g of 10% Pd/C was added. The suspension was shaken in a Parr reactor under 35 Psi of H_2 for 1 week.

The solid was isolated by filtration to give a clear yellow solution, which was concentrated and layered with EtOH to give a yellow solid (4.40 g, 74%). Analytically pure material was obtained from column chromatography on silica gel with 1:1 hexane:toluene eluent. ^{1}H NMR: (500 MHz, C_6D_6) δ 7.12 - 7.08 (m, 36H), 6.89 (d, 7.5 Hz, 16H), 6.71 (d, 8.1 Hz, 4H), 4.85 (s, 1H), 2.08 (s, 24H); $^{13}C\{^1H\}$ NMR: (126 MHz, C_6D_6) δ 146.05, 143.22, 142.89, 141.33, 139.16, 131.60, 129.92, 126.07, 124.96, 124.22, 124.09, 118.85, 20.46. IR (KBr): 3395(m), 3028(s), 2918(m), 2859(w), 1890(s), 1609(s), 1500(vs), 1314(m), 1265(s), 1172(w), 1108(m), 1016(w), 915(w), 816(vs), 715(s), 570(s), 527(s), 457(w), 414(w). MS (FAB matrix 3NBA): 1284, 1194, 1089, 1011, 726, 649, 559, 460, 307, 289, 181, 154. Anal. Calc'd. for $C_{92}H_{81}N_7$: C, 86.01; H, 6.36; N, 7.63. Found: C, 86.33; H, 6.45; N, 7.42. HRMS calcd for $C_{92}H_{81}N_7$ (M^+) 1283.6553 Found: 1283.6551.

Compound 10

A Schlenk flask containing 5 mL toluene was charged with 3.5 mg (0.0049 mmol) Pd[P(*o*-tolyl)$_3$]$_2$, 5.2 mg (0.017 mmol) P(*o*-tolyl)$_3$, 54.2 mg (0.564 mmol) NaO-*t*-Bu, 22.7 mg (0.0728 mmol) 4,4'-dibromobiphenyl, and 202 mg (0.157 mmol) **5**. The reaction was stirred at 90°C for 12 hours and allowed to cool to room temperature. The yellow solid was triturated with hot toluene and hot THF and was isolated by filtration to give 91% (180 mg) of product that was >90% pure by ^{1}H and ^{13}C NMR spectrometry. A portion of this material was further purified for microanalysis by column chromatography on silica gel with 2:1 xylenes:hexane eluent. ^{1}H NMR: (500 MHz, *p*-$CD_3C_6D_4CD_3$) δ 7.46 (d, 8.4 Hz, 4H), 7.34 (d, 8.0 Hz, 4H), 7.24 - 7.18 (m, 64H), 7.13 (d, 8.4 Hz, 16H), 7.00 (d, 8.1 Hz, 32H), 2.27 (s, 48H); $^{13}C\{^1H\}$ NMR: (126 MHz, *p*-$CD_3C_6D_4CD_3$) δ 147.68, 146.50, 144.11, 144.06, 143.20, 143.01, 132.20 (two overlapping resonances), 128.57, 125.92, 124.11, 123.64, 123.23, 123.14, 122.86, 121.91, 21.05. IR (KBr): 3027(m), 2922(m), 2856(m), 1606(m), 1580(s), 1498(s), 1446(s), 1311(m), 1266(s), 1178(w), 1113(m), 1043(w), 1014(w), 812(s), 714(m), 650(w), 619(w), 569(m), 540(m), 524(m). MS (MALDI): M^+ = 2719.6. Anal. Calc'd. for $C_{196}H_{168}N_{14}$: C, 86.56; H, 6.23; N, 7.21. Found: C, 86.28; H, 6.36; N, 6.95.

Notes and References:

(1) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1992**, *28*, 110.

(2) Paventi, M.; Hay, A. S. *J. Org. Chem.* **1991**, *56*, 5875-5782.

(3) Sasaki, S.; Iyoda, M. *Chem. Lett.* **1995**, 1011-1012.