

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

Janis Louie and John F. Hartwig*

Department of Chemistry, Yale University
P.O. Box 208107, New Haven, Connecticut 06520-8107

Albert J. Fry

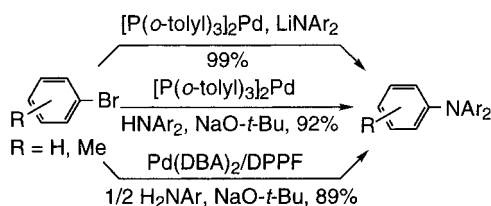
Department of Chemistry, Hall Atwater Laboratory
Wesleyan University, Middletown, Connecticut

Received August 11, 1997

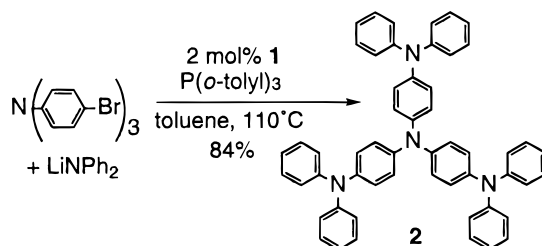
Triarylamines are an important class of compounds because they form stable aminium radical cations. Thus, triarylamines can be building blocks for high-spin polyradicals that have shown ferromagnetic coupling,^{1,2} as well as for conductive polymers.³ Perhaps most commonly, triarylamines have been used as the hole-transport layer in electroluminescent devices.^{4–7} Stable radical cations can also initiate pericyclic reactions,⁸ act as electrocatalysts,^{9,10} or act as mild and selective oxidizing agents.¹¹ The synthesis of arylamine macromolecules¹² has been limited by the modest yields of the copper-mediated Ullmann chemistry, but new palladium-catalyzed methods to form arylamines have emerged recently from our group^{13–17} and Buchwald's group.^{18–21} We report the first use of this palladium-catalyzed chemistry to form pure discrete arylamine oligomers and the largest discrete arylamine dendrimer.

Three new palladium-catalyzed reactions that form triarylamines are shown in Scheme 1. Lithium ditolylamide and 4-bromotoluene reacted in the presence of 1 mol % Pd[P(*o*-tolyl)₃]₂ (**1**) in toluene to produce tritolylamine quantitatively after 1 h at 90 °C. Alternatively, ditolylamine and 4-bromotoluene reacted in the presence of stoichiometric amounts of sodium *tert*-butoxide and 1 mol % Pd[P(*o*-tolyl)₃]₂ to give tritolylamine in 92% yield. A qualitative half-life of 1 h at 90 °C was obtained for the latter reaction. We have previously

Scheme 1



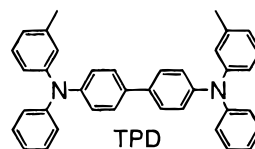
Scheme 2



shown that anilines react with aryl bromides in the presence of catalytic amounts of precursor Pd(DPPF)Cl₂ (DPPF = diphenylphosphinoferrocene) to give diarylamines in high yields.^{15,19} We show here that DPPF-ligated palladium can produce diarylamines or triarylamines. A combination of Pd(DBA)₂ (DBA = dibenzylideneacetone) and DPPF (2.5 mol %) catalyzed the formation of tritolylamine in 89% yield from 4-toluidine and 2.1 equiv of 4-bromotoluene in the presence of 2.1 equiv of sodium *tert*-butoxide.

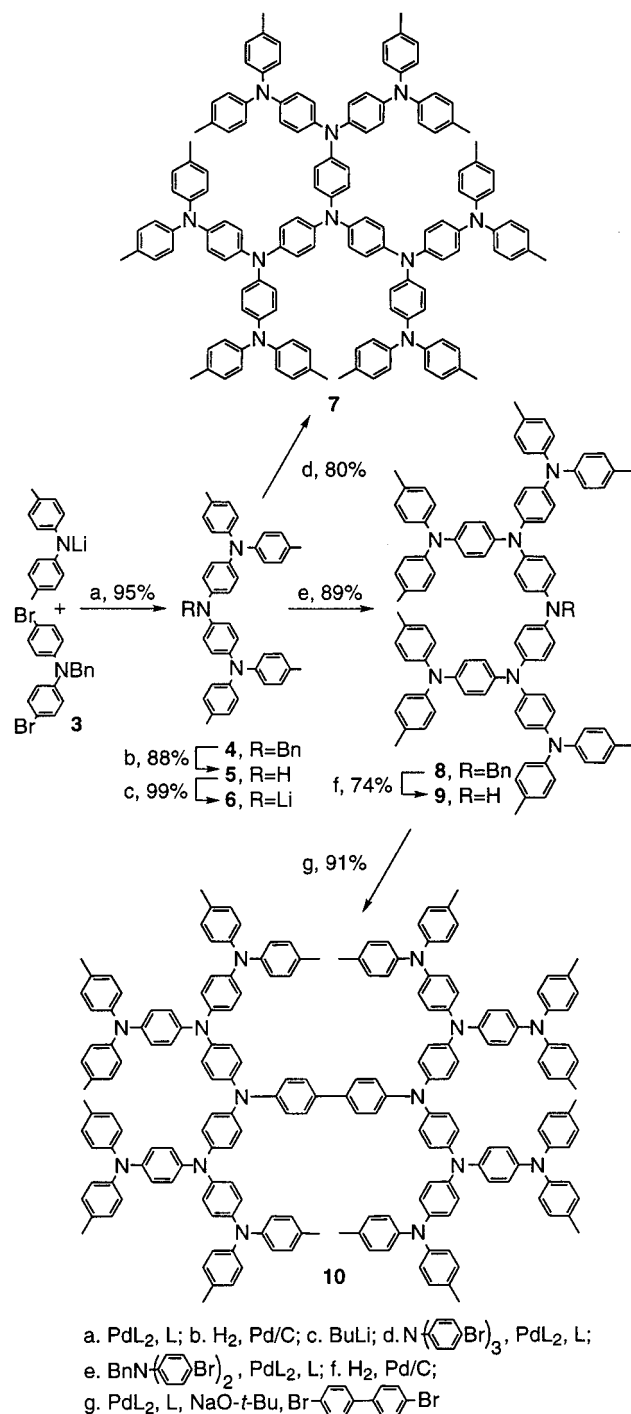
Most important for this work, these reactions suggested that we could use this chemistry to produce electronically interesting triarylamine dendrimers in high yields that were previously prepared in modest yields. The first generation dendrimer 4,4',4''-tris(*N,N*-diphenylamino)triphenylamine (TDATA, **2**) was prepared from tris(4-bromophenyl)amine and 3.3 equiv of lithium ditolylamide in the presence of 2 mol % catalyst **1** (Scheme 2) in 84% isolated yield. This molecule was prepared in only 22% yield by copper chemistry.²²

Low yields from Ullmann chemistry have prevented the preparation of higher generation triarylamine dendrimers. We demonstrate here that the palladium chemistry can produce larger hyperbranched arylamines. Employing a convergent strategy²³ we prepared the largest triarylamine starburst dendrimer, as shown at the top of Scheme 3. Reaction of *N,N*-bis(4-bromophenyl)benzenemethanamine²⁴ (**3**) and 2.2 equiv of lithium ditolylamide in the presence of 2 mol % **1** in toluene gave benzyl-protected **4** in 95% isolated yield by precipitation and recrystallization from THF:EtOH (1:1). Debencylation of **4** with 50 psi of H₂ over Pd/C gave amine **5** in 88% yield after purification by precipitation and recrystallization from THF:EtOH (1:1). Reaction of lithium amide **6**, generated from lithiation of **5**, and 0.3 equiv of tris(4-bromophenyl)amine in the presence of 3.5 mol % **1** gave second generation dendrimer **7**. Starburst **7** is soluble in benzene, toluene, and tetrahydrofuran and was isolated in 80% yield by recrystallization from THF:EtOH. This material was judged pure by both ¹H and ¹³C NMR spectroscopy. Silica gel chromatography gave analytically pure material in 64% yield. The overall yield of starburst **7** from **3** was a remarkably high 70% after recrystallization and 56% after chromatography.



- Wienk, M. M.; Janssen, R. A. J. *Chem. Commun.* **1996**, 267–268.
- Stickley, K. R.; Selby, T. D.; Blackstock, S. C. *J. Org. Chem.* **1997**, 62, 448–449.
- Ishikawa, M.; Kawai, M.; Ohsawa, Y. *Synth. Met.* **1995**, 40, 231–238.
- Tanaka, H.; Tokito, S.; Taga, Y.; Okada, A. *Chem. Commun.* **1996**, 2175–2176.
- Kuwabara, Y.; Ogawa, H.; Inada, H.; Noma, N.; Shirota, Y. *Adv. Mater.* **1994**, 6, 677–679.
- Shirota, Y.; Kobata, T.; Noma, N. *Chem. Lett.* **1989**, 1145–1148.
- Naito, K.; Miura, A. *J. Phys. Chem.* **1993**, 97, 6240–6248.
- Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Raul, A.; Pabon, J.; Reynolds, D. W.; Wirth, D. D.; Chiou, H.-S.; Marsh, B. K. *Acc. Chem. Res.* **1987**, 20, 371–378.
- Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, 113, 577.
- Steckhan, E. *Top. Curr. Chem.* **1987**, 142, 1.
- Dapperheld, S.; Steckhan, E.; Brinkhaus, K.-H.; Esch, T. *Chem. Ber.* **1991**, 124, 2557–2567.
- New dendrimer structures may serve as supports in combinatorial chemistry synthesis. Kim, R. M.; Manna, M.; Hutchins, S. M.; Griffin, P. R.; Yates, N. A.; Bernick, A. M.; Chapman, K. T. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, 93, 10012–10017.
- Hartwig, J. F. *Synlett* **1997**, 4, 329–340.
- Louie, J.; Driver, M. S.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1997**, 62, 1268–1273.
- Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, 118, 7217–7218.
- Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, 36, 3609.
- Louie, J.; Paul, F.; Hartwig, J. F. *Organometallics* **1996**, 15, 2794–2805.
- Marcoux, J. F.; Wagaw, S.; Buchwald, S. L. *J. Org. Chem.* **1997**, 62, 1568–1569.
- Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, 118, 7215–7216.
- Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996**, 61, 1133.
- Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1348.

Scheme 3



An even larger dumbbell-shaped *N,N'*-diphenyl-*N,N'*-(*m*-tolyl)benzidine (TPD) analog **10** was prepared as shown at the bottom of Scheme 3. Aryl bromide **3** was reacted with 2.2 equiv of lithium amide **6** in the presence of 2 mol % **1** in toluene to give benzyl-protected **8** in 89% isolated yield. Debencylation of **8** with 50 psi of H_2 over Pd/C gave amine **9** in 74% yield by precipitation and recrystallization from THF:EtOH (1:1). Reaction of **9** with 0.5 equiv of 4,4'-dibromobiphenyl in the presence of 6.7 mol % **1** and stoichiometric amounts of NaO-*t*-Bu gave a dumbbell-shaped **10** in 91% yield. Dumbbell **10** was less soluble than starburst **7**, but it dissolved in xylenes and anisole. Chromatography yielded analytically pure samples of a bright yellow solid that fluoresced in solution.

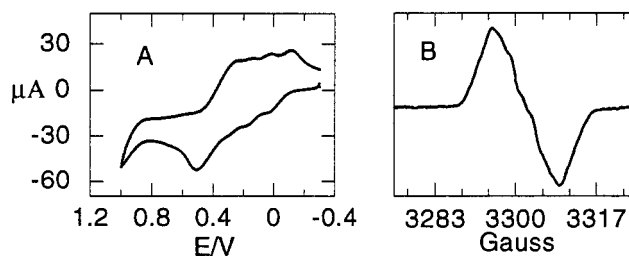
(22) Sasaki, S.; Iyoda, M. *Chem. Lett.* **1995**, 1011–1012.(23) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 138–175.(24) Paventi, M.; Hay, A. S. *J. Org. Chem.* **1991**, 56, 5875–5878.

Figure 1. (A) Cyclic voltammogram of **7**. (B) EPR spectrum for the radical cation of **7**.

TPD (MW = 516) has a glass transition temperature of only 60 °C, a property which limits the operating temperature of the devices containing this material.^{4,7} Increasing the molecular weight should increase the glass-transition temperature,⁷ and TDATA **2** (MW = 747) has a glass transition temperature of 89 °C.⁶ Differential scanning calorimetry (DSC) showed that starburst **7** (MW = 1918) has a glass-transition temperature of 169 °C; it melts at 278 °C.

Although clearly nonplanar, starburst **7** is an electron rich triarylamine and yields a highly delocalized radical. Cyclic voltammetry of 0.1 mM **7** with 0.1 M Bu_4NPF_6 in tetrahydrofuran with use of a carbon electrode showed at least four oxidation waves, the first of which was seen at negative potentials vs Ag/Ag^+ (−0.050 mV, Figure 1a). This potential is substantially lower than that of triethylamine ($E_1^\circ = 0.400$ mV) or TDATA **2** ($E_1^\circ = 0.060$ mV) under the same conditions.²⁵ Chemical oxidation of 0.1 mM **7** by 1 equiv of [bis(trifluoroacetoxy)iodo]benzene in tetrahydrofuran at room temperature gave a bright yellow solution. The EPR spectrum of this radical cation consisted of a broad signal with a spectral width of 34 G, as shown in Figure 1b.²⁶ Proton hyperfine, $a(120\text{H})$, broadened the spectrum so that clear resolution of the ^{14}N line pattern was not observed, but the multiline pattern indicates multiple couplings to nitrogen. The same spectrum was obtained by oxidation with ferrocenium tetrafluoroborate (Fc^+BF_4^-). The radical cation of starburst **7** is relatively stable at room temperature, displaying a qualitative half-life of 1 h.

In summary, the high-yield formation of triarylamines by palladium-catalyzed chemistry can be used to produce high molecular weight arylamines with high glass-transition temperatures, low redox potentials, and the ability to produce delocalized radical cations. We are continuing to investigate the electron spin properties of this molecule, while preparing larger dendrimers and linear arylamine oligomers.

Acknowledgment. We thank Veronika Szalai for help with the EPR experiments and the Department of Energy (DE-RG02-96ER14678), a DuPont Young Professor Award, a Union Carbide Innovative Recognition Award, a National Science Foundation Young Investigator Award, a Dreyfus Foundation New Faculty Award, and a Camille Dreyfus Teacher-Scholar award for support for this work. J.F.H. is a fellow of the Alfred P. Sloan Foundation. We thank Johnson-Matthey Alpha/Aesar for a loan of palladium chloride.

Supporting Information Available: General amination and workup procedures, detailed experimental procedures, as well as spectroscopic and analytical characterization for compounds **2** and **4–10** (5 pages). See any current masthead page for ordering and Internet access instructions.

JA972806D

(25) Voltammetry was carried out with the aid of a EG & G Princeton Applied Research Versastat Model 270/250 computer-driven electrochemical data acquisition system, using the EG & G version 4.10 software to generate waveforms and acquire data. A carbon and a Ag/AgNO_3 electrode were used as the working and reference electrodes, respectively. All runs were performed on 0.1 mM solutions in dry THF in the presence of 0.1 M Bu_4NPF_6 .

(26) X-band measurements were made on 0.2 mM **7** and 1 equiv of $(\text{CF}_3\text{CO}_2)_2\text{IPh}$ in dry THF at 295 K on a Varian E9 spectrometer interfaced with a Macintosh Computer. The microwave power was 10 mW, and the modulation amplitude was 0.5 G.