The Largest Discrete Oligo(*m*-aniline). An Exponential Growth Strategy Using Palladium-Catalyzed Amination of Aryl Sulfonates

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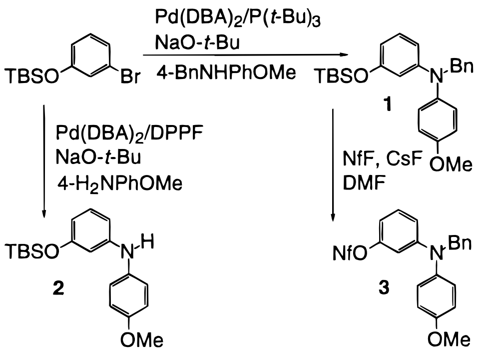
Diarylamines[1,2] and triarylamines[3−6] have become a focal point for studies on high spin polyradicals and for investigations of potential organic ferromagnets. Polyradicals resulting from oxidation of polyarylamines containing cross-conjugated nitrogens have shown local ferromagnetic interaction among the unpaired spins.[7] However, the synthesis of complex triarylamines is not straightforward. Conventional routes to triarylamines rely on high-temperature, modest yielding copper Ullmann chemistry.[4,8] In contrast, mild palladium-catalyzed routes to triarylamines have been developed recently.[9−11] Important for the work in this paper, palladium-catalyzed amination chemistry can now be conducted with aryl triflates.[12−14] We report the use of an exponential growth strategy[15−17] employing palladium-catalyzed aryl perfluorosulfonate amination to generate the largest *meta*-linked, linear arylamine oligomer.[18,19]

Our exponential growth strategy includes (1) a methoxy-substituted *N*-aryl substituent to provide an NMR handle, good solubility, and facile purification; (2) triarylamines as targets to provide stable radical cations and to eliminate the potential for cross-linking during synthesis; and, most important, (3) chain termini that have orthogonally protected functionality: an *N*-benzylamine that generates the necessary diarylamine by hydrogenolysis and a *tert*-butyldimethylsilyl (TMS) ether that generates an aryl nonaflate by reaction with $F_9C_4SO_2F$ and CsF in DMF.[20]

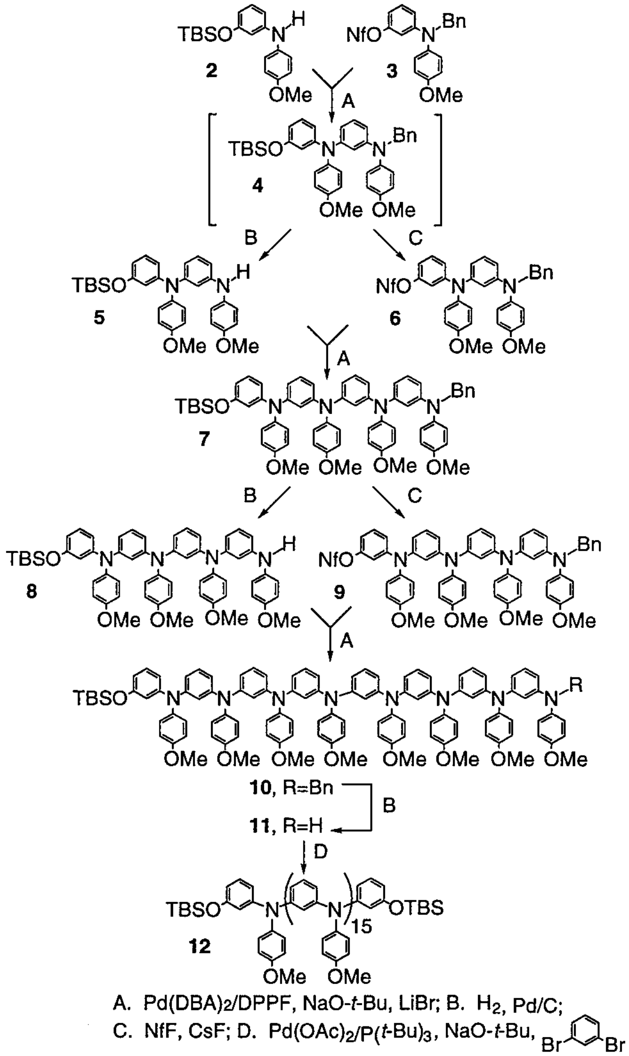
As shown in Scheme 1, the TBS protected-monomer **1** was prepared from the reaction between 3-BrC_6H_4-OTBS and *N*-Bn−*p*-anisidine in the presence of Pd(DBA)$_2$ (DBA = dibenzylideneacetone), P(*t*-Bu)$_3$,[21] and 1.2 equiv of NaO-*t*-Bu in toluene at 110 °C. The complementary amine monomer **2** was prepared in quantitative yield by the palladium-catalyzed reaction of 3-BrC_6H_4OTBS and *N*-Bn−*p*-anisidine using DPPF (DPPF = diphenylphosphinoferrocene) as ligand and 1.2 equiv of NaO-*t*-Bu in toluene at 110 °C. Monomer **1** was converted to the nonaflate **3** in the presence of 1.2 equiv of perfluorobutylsulfonyl fluoride (NfF) and 1 equiv of CsF in dry DMF.

The exponential growth strategy is summarized in Scheme 2 and requires the palladium-catalyzed reaction of amine monomer **2** with nonaflate monomer **3** to form the triarylamine linkage.[22,23] Reactions between **2** and **3** in the presence of 1.2 equiv of either NaO-*t*-Bu or Cs$_2$CO$_3$ and catalytic amounts of Pd(DBA)$_2$/DPPF or BINAP gave coupled product **4** in only 40−60% yield by ^{1}H NMR spectroscopy with an internal standard. However, reaction of **2** with **3** in the presence of 1.2 equiv of LiBr gave yields of dimer **4** ranging from 95 to 100%.

Scheme 1



Scheme 2



A. Pd(DBA)$_2$/DPPF, NaO-*t*-Bu, LiBr; B. H$_2$, Pd/C; C. NfF, CsF; D. Pd(OAc)$_2$/P(*t*-Bu)$_3$, NaO-*t*-Bu,

Monomers **2** and **3** were, therefore, coupled in the presence of 1.5 mol % Pd(DBA)$_2$, 3 mol % DPPF, and 1.2 equiv of NaO-*t*-Bu/LiBr in toluene at 110 °C. Due to difficulties in separating residual amine **2** and dimer **4**, a mixture of these two materials was separated from the remaining reaction components by column chromatography and was carried forward. The mixture was redissolved in THF, and the benzyl group of **4** was removed with 300 psi of H$_2$ over Pd/C to produce pure, deprotected dimer **5** in 56% yield based on **3** for the two-step process. In a separate procedure, the mixture of **2** and **4** was redissolved in dry DMF and reacted with NfF

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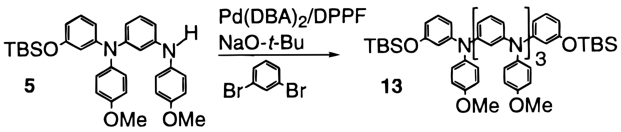
Scheme 3



and CsF to give dimer **6** in 42% yield for the two-step process after recrystallization from EtOH.

Palladium-catalyzed reaction of dimers **5** and **6** on a 0.01 mmol scale produced **7** in 98% yield by ^{1}H NMR spectroscopy. Tetramer **7** was isolated in 59% yield on a 1 mmol scale after column chromatography. Debenzylation of **7** with 300 psi of H_2 over Pd/C in THF gave amine-terminated **8**, and addition of NfF and CsF to **7** in DMF gave nonaflate-terminated **9**. Palladium-catalyzed reaction of **8** and **9** furnished octamer **10** in 62% yield after column chromatography. Debenzylation of **10** with 1 atm of H_2 over Pd/C in THF gave amine-terminated **11**.

Amine-terminated octamer **11** was used to prepare hexadecamer **12** in 45% yield by reaction with 0.48 equiv of 1,3-dibromobenzene as shown at the bottom of Scheme 2. Hexadecamer **12** is the largest symmetric *m*-oligoaniline prepared to date and remains freely soluble in organic solvents such as toluene, benzene, THF, and EtOAc. A related, short, symmetric *meta*-linked triarylamine oligomer was prepared for comparison to **12** by analogous chemistry. The palladium-catalyzed reaction between 1,3-dibromobenzene and 2.1 equiv of amine-terminated dimer **5** gave tetramer **13** in 78% yield (Scheme 3).

The composition of each oligomer was readily determined by integrating the ^{1}H NMR resonances of the TBS and Bn end groups vs the N−H and methoxy resonances of the monomer units. Integration of the methoxy protons showed that two, four, and eight N-aryl groups were present per TBS, Bn, or amino group in unsymmetrical dimers, tetramers, and octamers, respectively. The symmetrical tetramer **13** and hexadecamer **12** displayed two and eight methoxy substituents per TBS group, respectively. In addition, the mass spectra of oligomers **5**−**13** gave the expected molecular weight.

We used cyclic voltammetry to evaluate whether chain length effects the chemical potential of the different oligomers. In contrast to conjugated, triarylamine dendrimers that show an increased reduction potential with size,[9] the cross-conjugated triarylamine oligomers in this work showed little correlation of size with chemical potential. Cyclic voltammetry of 1 mM tetramer **7** with 0.1 M BuN_4PF_6 in tetrahydrofuran using a carbon electrode showed at least three oxidation waves, the first of which was observed at 0.391 V vs Ag/AgCl. The first of at least four oxidation potentials of hexadecamer **12** occurred at 0.332 V vs Ag/AgCl.

ESR studies to determine whether high spin structures can be observed by chemical oxidation of these samples are encouraging. Initial studies showed that oxidation of oligomers **7**, **12**, and **13** in CH_2Cl_2 at room temperature with 1 equiv of [bis(trifuoroacetoxy)iodo]benzene (PIFA)[24] or thianthrenium perchlorate (Th-ClO_4)[25] produced radical monocations, and we have observed these radicals by ESR at room temperature.[26] In addition, preliminary studies showed that addition of 2 equiv of these oxidants to oligomers **7** and **12** in butyronitrile generated at 70 K signals for an $\Delta m = \pm 2$ transition at 1600 G,[27] suggesting that these oxidations produced dications with triplet character.[28]

Studies on the temperature dependence of these signals, clear determinination that the $\Delta m = \pm 2$ and $\Delta m = \pm 1$ signals correspond to the same material, and quantitation of the observed signals will be the subject of ongoing studies in our laboratory, along with continued synthetic studies toward dendrimeric *meta*-linked triarylamines, linear *para*-linked oligomeric triarylamines, and side-chain and terminally functionalized versions of the materials in this work. From the synthetic studies reported here, it is clear that palladium-catalyzed chemistry presents a significant new route to triarylamine macromolecules that will prove to have interesting electronic and magnetic properties.

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Supporting Information Available: Text giving detailed preparative procedures and spectroscopic characterization and figures giving cyclic voltammograms for **1**−**3** and **5**−**12** (15 pages). Ordering and Internet access information is given on any current masthead page.

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(26) X-Band measurements of monocations were made on 1 mM solutions containing 1 equiv of $ThClO_4$ or $(CF_3CO_2)_2IPh$ in dry CH_2Cl_2 at 295 K on a Varian E9 spectrometer interfaced with a Macintosh computer. The microwave power was 10 mW for **7** and **13**, and was 2 mW for **12**. The modulation amplitude was 0.5 G for **7** and **13**, and was 1.0 G for **12**.

(27) X-Band measurements of dications were made on 1 mM samples in butyronitrile at 70 K. A modulation amplitude of 4 G and a microwave power of 0.2 mW was used to observe the $\Delta m = \pm 1$ transitions. A modulation amplitude of 20 G and a microwave power of 5 mW was used to observe the $\Delta m = \pm 2$ transitions.

(28) Similar to studies by Janssen and Abe cited above, the ability to observe the cation radicals was solvent dependent. In contrast to these studies, however, the monocation radicals of **7** and **12** were not observed in THF solvent and the $m \pm 2$ transitions were not observed in dichloromethane.

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