SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF RIGID MACROMOLECULES
WITH EXTENDED CONJUGATION, USING PALLADIUM-CATALYZED,
ALKYNYLATED POLYHALOARENES

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A synthetic approach to macromolecules of acetylenic arrays and luminescent properties is proposed and the execution of initial steps is described. Palladium-catalyzed coupling of 1,3,5-triiodobenzene with trimethylsilylbuta-1,3-diyn, trimethylsilylocta-1,3,5,7-tetrayne, and trimethylsilylhexadeca-1,3,5,7,9,11,13,15-octayne to yield the new 1,3,5-tris(trimethylsilylbuta-1,3-diynyl)benzene and the proposed 1,3,5-tris(8-(trimethylsilyl)octa-1,3,5,7-tetraynyl)benzene and 1,3,5-tris(trimethylsilyl)hexadeca-1,3,5,7,9,11,13,15-octaynyl)benzene respectively. The proposed three-coordinate Au (I) complexed macromolecules will be derived from the metallation of the aforementioned alkynylated arenes.
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INTRODUCTION

Metallation

Transition metals are known by their ability to form colored ions and complexes. Coordination by ligands can play a part in determining the color in a transition metal complex. The color of a complex depends on the nature of the metal ion; the arrangement of the ligands around the metal ion; and the nature of the ligands surrounding the metal ion. Monovalent gold complexes represent one of the most prominent classes of luminescent transition complexes. The most common form of Au (I) complexes is the two coordinate (AuL₂), but the three coordinate (AuL₃) and the four coordinate (AuL₄) species also exist.

These species differ in the presence of Au-based luminescence, which is usually absent in AuL₄ complexes; exists in AuL₂ complexes only in the presence of Au-Au interactions; and in AuL₃ complexes, exists both with and without Au-Au interactions present. The luminescence exhibited by Au(I) compounds is useful in a variety of applications such as detection of volatile organic compounds, ion sensors, oxygen sensors, and molecular light-emitting devices.

In a recent publication, the Omary group has shown that in a previous approach to metallation, the steric effect in three-coordinate Au (I) complexes of the type (PR₃)₂AuX (X= halide), reduces its luminescent behaviors, and in fact, makes it impossible to synthesize. Furthermore, the Omary group has shown the possibility of a systematic tuning of luminescence by controlling the steric bulk in these Au (I) complexes. Au (I) compounds are typically linear and most drugs based on gold are Au (I) derivatives.

Chromophores, the part of a molecule responsible for its color, usually exist in one of two forms: conjugated pi systems or metal complexes. The metal complex chromophores arise from the binding of a transition metal to ligands. Examples of such chromophores can be seen in
chlorophyll, the green pigment used by plants for photosynthesis, and in colorful minerals such as malachite and amethyst. A luminophore, an atomic grouping in a chemical compound that manifests luminescence, consists of conjugated pi systems or transition metal complexes. In this case, the proposed luminophore is known as a phosphor. Luminophores can be observed in action in fluorescent lights, TV screens, computer monitor screens, organic light-emitting diodes and bioluminescence.

The synthesis of dendrimers with three-coordinate Au (I) complexes is proposed here. Previously, macromolecules with two-coordinate Au (I) complexes were synthesized but luminescence occurred only when there were Au-Au interactions. As mentioned earlier, luminescence readily occurs in three-coordinate Au (I) complexes with or without Au-Au interactions. Presently, we (Selby and Omary groups) are exploring the synthesis of dendritic macromolecules by binding the phosphine at the periphery of the proposed 1,3,5-tris(diphenylphosphino)buta-1,3-diynyl benzene (n=2) to a three-coordinate Au (I) complex, as shown in Scheme 1. By controlling the bulkiness of the three-coordinate Au (I) complexes bound
to the phosphine groups, steric hindrance is reduced, the desired product is obtained, and luminescence is enhanced for the dendrimer. The goal, within the context of this thesis, is to prepare dendrimers with extended conjugation by linking several alkyne groups together (Figure 1, n = 2, 3, or 4). The molecules can be prepared by palladium-catalyzed alkynylation of haloarenes with polyalkyne derivatives. With extended conjugation and its structural rigidity, the proposed dendrimers can act as good chromophores with enhanced light emission.

Synthesis of Polyynes by Hay Coupling

Oxidative coupling of terminal acetylenes in the presence of copper (I) catalysts is the best method of preparing symmetrically substituted polyalkyne derivatives, and has been applied to the coupling of trimethylsilylacetylene and trimethylsilylbutadiyne to yield 1,4-bis(trimethylsilyl)buta-1,3-diyne (BTMSBD) and 1,8-bis(trimethylsilyl)octa-1,3,5,7-tetrayne, (BTMSOT) respectively. The Hay procedure, in which the catalyst is the TMEDA complex of copper (I) chloride, gives good yields in the synthesis of BTMSBD but consistently gave poor yield in the synthesis of BTMSOT. Polyynes (acetylenic arrays) are distinguished from other organic chains by their rigidity, which makes them promising for molecular nanotechnology. Because of the potential medicinal properties of most polyynes, their synthetic pathways are being studied with the hope that these can be replicated industrially by organic synthesis.

Palladium-Catalyzed Alkynylation of Polyhaloarenes

Several polyiodoaromatic compounds with hydrogen, methyl, hydroxyl, carboxyl, or nitro substituents have been found to undergo palladium-catalyzed alkynylation. Alkynylation proceeds with all polyiodides tried in reasonable yields to give the corresponding polyalkynyl products. Alkynylation occurred more readily and selectively with trihalo derivatives than with others.
RESULTS AND DISCUSSION

As discussed earlier, in order to avoid steric hindrance between the triphenylphosphine groups attached to the Au on the branches, conjugation is extended by addition of alkyne group(s). When conjugation is extended, the branches are elongated, thereby reducing steric hindrance and enhancing luminescence. The proposed syntheses of the phosphine ligands needed for complexation to Au(I) compounds is shown in Scheme 2. The goal in this thesis is the preparation of the silyl protected polyalkynes 1, 2 and 3.

**Scheme 2. Synthesis of Polyphosphine Ligands.**

Preparation of 1,3,5-Tris(trimethylsilylbuta-1,3-diynyl)benzene 1

To prepare 1,3,5-tris(trimethylsilylbuta-1,3-diynyl)benzene 1, the diyne, 1,4-bis(trimethylsilyl)buta-1,3-diyn 10, is needed. The diyne 10 was prepared according to Scheme 3. Oxidative coupling of terminal acetylenes in the presence of copper(I) catalysts is the best method of preparing symmetrically substituted butadiyne derivatives and has been applied to the
coupling of trimethylsilylacetylene. Better yields are obtained using the Hay procedure in which the catalyst is the tetramethylethlenediamine (TMEDA) complex of copper(I) chloride.\textsuperscript{12}

![Chemical structure](attachment:image.png)

**Scheme 3.** Synthesis of 1,4-bis(trimethylsilyl)buta-1,3-diyne 10.

TMEDA is widely employed as a ligand for metal ions. It forms stable complexes with many metal halides, such as copper (I) chloride, giving complexes that are soluble in organic solvents. In such complexes, the TMEDA serves as a bi-dentate ligand or as a phase transfer catalyst, where it facilitates the migration of copper (I) chloride from one phase into another in the heterogeneous system. Copper (I) chloride is soluble in one phase but insoluble in the other unless the phase transfer catalyst is present. The reaction involves deprotonation by a base (TMEDA), of the acetylenic proton followed by formation of copper (I) Acetylide. A cycle of oxidative addition and reductive elimination on the copper center then creates a new carbon-carbon bond.

Magnetic stirring is sufficient for a 5g scale but mechanical stirring is required for a 50-200g scale to obtain satisfactory oxygenation of the reaction mixture. The reactant, trimethylsilylacetylene, is very volatile in the fast oxygen stream, requiring the use of a dry ice cold finger condenser with a large contact area to prevent a substantial loss of material as an aerosol. On several occasions, the temperature was observed to reach 35°C before 50% of the catalyst had been added. Ice cooling is necessary, for it is important to lower the temperature only to 25°C, otherwise the reaction will become too sluggish. A deep blue-green coloration was observed throughout the addition of the catalyst; evident of a steady rate of oxygen flow. Over-
oxidation occurs when the flow rate is too high, producing a black precipitate; while a green
color fading to be replaced by an orange-red precipitate, is evidence of over-reduction (too low a
flow rate). Both conditions reduce the yield of 10. The material was purified by recrystallization
with methanol followed by sublimation to give 86% yield of pure 10. The nuclear magnetic
resonance (NMR) spectrum for the diyne 10 is shown in Figure 1. The spectrum shows a singlet
for the eighteen methylysilyl protons in 1, 4-bis(trimethylysilyl)buta-1, 3 diyne at δ 0.19.

Solvent protons often interfere with simple NMR spectra recorded in solution. A large
range of deuterated solvents, such as chloroform (CDCl₃), contains small quantities of
undeuterated solvent, CHCl₃, which gives rise to a singlet at δ 7.24. Water may be present in the
chloroform as a contaminant with a broad single peak at δ 1.5 and acetone at δ 2.17. Spectra are
usually recorded against tetramethylsilane (TMS) as the internal standard set at δ 0. Signals from
atoms in trimethylsilyl groups will commonly have chemical shifts close to the reference TMS
peak at δ 0. Also, compounds such as high temperature silicone “stopcock grease,” which have
polysiloxanes (silicones) in them will show peaks from the methyl groups attached to the silicon
atoms, close to the TMS reference peak at δ 0.07 in CDCl₃.¹¹

The next step in the preparation of 1 is the selective deprotection of 10, using
methyllithium-lithiumbromide complex, to remove only one silyl group giving
trimethylsilylbuta-1,3-diyn 11 as shown in Scheme 4. Methyllithium-lithiumbromide complex
is both strongly basic and highly nucleophilic due to the partial negative charge on the carbon
atom, and is therefore particularly reactive towards electron and proton donors. The amount of
base used is just enough to selectively deprotect one end of compound 10. Reactions involving
methyllithium require anhydrous conditions (in this case, dry diethyl ether), because the
compound is highly reactive toward water, oxygen and carbon dioxide. Most reactions involving
Figure 1. $^1$H NMR spectrum of 10 in CDCl$_3$. 
methyllithium are conducted inside glove boxes or using Schlenk techniques. Reaction of 10 with one equivalent of methyllithium-lithiumbromide complex in diethylether followed by treatment with ammonium chloride gave 11 in 65% yield after purification by distillation.

The NMR spectrum of 11 is shown in Figure 2. The spectrum reveals two singlets; one for the nine methylsilyl protons at \( \delta \) 0.19 and the other for the terminal acetylene proton at \( \delta \) 2.08.

![Diagram](image)

**Scheme 4.** Synthesis of trimethylsilylbuta-1,3-diyne 11.

The final step in the preparation of 1,3,5-tris(trimethylsilylbuta-1,3-diynyl)benzene 1 involves coupling of 11 with a 1,3,5-trihalobenzene using a palladium catalyst. In our first attempt to synthesize 11, we chose 1,3,5-tribromobenzene as our halo derivative because it is commercially available and relatively inexpensive. However, the reaction of 11 with 1,3,5-tribromobenzene using tetrakis(triphenylphosphine)palladium conditions, afforded the mono-substituted product, (4-(3,5-dibromophenyl)buta-1,3-diynyl)trimethylsilane) and the di-substituted product(1-bromo-3,5-bis(4-(trimethylsilyl)buta-1,3-diynyl)benzene) instead (Scheme 5). No tri-substituted 1 was observed.

![Diagram](image)

**Scheme 5.** Synthesis of 4-(3,5-dibromophenyl)buta-1,3-diynyl)trimethylsilane & 1-bromo-3,5-bis(4-(trimethylsilyl)buta-1,3-diynyl)benzene.
Figure 2. $^1$H NMR spectrum of 11 in CDCl$_3$. 

Me$_3$Si—$\equiv$—H  
2.09 (s, 1H, CH)  
0.19 (s, 9H, Si(CH$_3$)$_3$)
Nuclei tend to be deshielded by groups which withdraw electron density. Deshielded nuclei resonate at higher $\delta$ values, whereas shielded nuclei resonate at lower $\delta$ values. An electron withdrawing substituent like bromine causes a downfield shift. Figure 3 shows three accountable peaks for the mono-substituted product, A in Scheme 5; a singlet for the nine methylsilyl protons at $\delta$ 0.20, a doublet for the two equivalent aromatic protons by the alkyne chain at $\delta$ 7.51, and a triplet for the aromatic proton between the two bromine atoms, farthest downfield at $\delta$ 7.62. The doublet and the triplet are in a 2:1 ratio as indicated by integration.

The reaction was tried again using a different palladium catalyst (Scheme 6). The reaction of 11 with tribromobenzene using tris(dibenzylideneacetone) dipalladium conditions did not give the desired tri-substituted 1. This time only the di-substituted product, B, was obtained as verified with NMR analysis. Figure 4 below shows three signals for the di-substituted product, B. A singlet for the eighteen methylsilyl protons at $\delta$ 0.22, a triplet for the aromatic proton between the two chains at $\delta$ 7.45, and a doublet for the two equivalent aromatic protons beside the bromine atom farthest downfield at $\delta$ 7.56. The doublet and the triplet are in a 2:1 ratio as indicated by integration.

Scheme 6. Synthesis of 1-bromo-3, 5-bis(4-(trimethylsilyl)buta-1,3-diynyl)benzene.
Figure 3. $^1$H NMR spectrum of the mono-substituted A in CDCl$_3$. 

0.20 (s, 9H, Si(CH$_3$)$_3$) 
7.51 (d, 2H, aromatic) 
7.62 (t, 1H, aromatic)
**Figure 4.** $^1$H NMR spectrum of the di-substituted B in CDCl$_3$. 

- 7.56 (d, 2H, aromatic)
- 7.45 (t, 1H, aromatic)
- 0.22 (s, 18H, Si(CH$_3$)$_3$)
In the literature, iodine-substituted haloarenes have been shown to react more readily and selectively than bromine-substituted ones. Mixed bromoiodobenzens were found to alkynylate more rapidly at the iodo positions, and some selective reactions were easily achieved. Therefore to obtain the expected product, i.e. the tri-substituted benzene 1 with no side products, triiodobenzene was synthesized under the conditions listed in Scheme 7 by a known procedure.

\[
\text{Br} \quad \text{Br} \quad \text{Br} \\
\text{Br} \quad \text{Br} \\
\text{Br} \quad \text{Br} \\
\text{I} \quad \text{I} \quad \text{I}
\]

**Scheme 7. Synthesis of Triiodobenzene 12.**

The NMR spectrum of 1,3,5-triiodobenzene is shown in Figure 5. In the NMR spectrum of benzene, the ring protons experience deshielding because the induced magnetic field has the same direction as the external applied field, and their chemical shift is at \( \delta 7.3 \) compared to \( \delta 5.6 \) of the vinylic protons in cyclohexene. The three equivalent aromatic protons of 1,3,5-triiodobenzene appear as a singlet, pushed further downfield by the deshielding effect of the three iodine atoms on the benzene ring (\( \delta 7.99 \)).

Triiodobenzene was tributynylated with (trimethylsilyl)butadiyne, employing a bis(triphenylphosphine)dichloropalladium-cuprous iodide catalyst as shown in Scheme 8. Triiodobenzene was found to undergo tri-alkynylation with trimethylsilylbutadiyne in 36hr at 50°C to yield 1 in a 47% isolated yield. The NMR spectrum of 1 in CDCl₃ (Figure 8) shows a singlet at \( \delta 0.17 \) for the protons of the methyl groups and a singlet at \( \delta 7.44 \) for the three equivalent aromatic protons.
Figure 5. $^1$H NMR spectrum of 12 in CDCl$_3$. 

7.99 (s, 3H, aromatic)
Figure 6. $^1$H NMR spectrum of 1 in CDCl$_3$. 

7.49 (s, 3H, aromatic) 
0.22 (s, 27H, Si(CH$_3$)$_3$)
**Scheme 8.** Synthesis of 1,3,5-tris(trimethylsilylbuta-1,3-diynyl)benzene 1.

*Attempted Preparation of 1,3,5-Tri(6-(trimethylsilyl)hexa-1,3,5-triynyl)benzene 2*

The synthesis of polynes with an odd number of alkyne linkages is more difficult than those with an even number, such as 1 described above. Nevertheless, we sat out to synthesize 1,3,5-tri(6-(trimethylsilyl)hexa-1,3,5-triynyl)benzene 2, which contains three alkyne groups in each arm of the dendrimer. The preparation of 2 is outlined in Scheme 9. The reaction of trimethylsilylpropynal (14) and 1,3,5-triethynylbenzene (13) give the triol (15). Treatment of 15 with PCC oxidizes the alcohol groups to carbonyls. A Wittig reaction of the carbonyl with CBr₄/PPh₃ followed by treatment with n-BuLi give the desired 1,3,5-tri(6-(trimethylsilyl)hexa-1,3,5-triynyl)benzene 2.

The trimethylsilylpropynal 14, needed for the preparation of 2, was prepared according to Scheme 10. n-Butyllithium is an organolithium reagent and a very strong base, which is used here with a di-substituted amide, DMF in a carbonyl addition reaction to synthesize the aldehyde, trimethylsilylpropynal. Due to the large difference between the electronegativities of carbon (2.55) and lithium (0.98), the C-Li bond is highly polarized. Though n-BuLi is not ionic, it can
Scheme 9. Proposed synthesis of 1,3,5-tri(6-(trimethylsilyl)hexa-1,3,5-triynyl)benzene 2.

often be considered to react as the butyl anion, \( n{-}\text{Bu}^- \), and a lithium cation, Li\(^+\), for practical purposes. Reflecting its "electron-deficient character," n-BuLi is highly reactive toward Lewis bases, deprotonating the trimethylsilylacetylene. The aldehyde 14 was purified by distillation and stored over dry ice due to its instability. \(^1\)H NMR confirmed the product (Figure 7).

**Figure 7.** $^1$H NMR spectrum of 14 in CDCl$_3$. 

- 9.2 (s, 1H, CHO)
- 0.25 (s, 9H, Si(CH$_3$)$_3$)
From the figure above, the aldehyde 14 shows a singlet for the nine trimethylsilyl protons at $\delta$ 0.15 and a singlet for the aldehyde proton at $\delta$ 9.2. A shielded proton has a relatively greater electron density and absorbs upfield (to the right) in a $^1$H NMR spectrum. Aliphatic aldehyde protons show a characteristic signal at $\delta$ 9-10. The methylsilyl protons are shielded by the alkyl groups, which are electron-releasing substituents.

1,3,5-Triethynylbenzene 13 was prepared in two steps according to Scheme 11. Trimethylsilylacetylene readily reacts with bromoarenes under PdCl$_2$(PPh$_3$)$_2$ conditions to produce 1,3,5-tris(2-(trimethylsilyl)ethynyl)benzene 17 in 70% yield. The $^1$H NMR of 17 (Figure 8) shows a singlet for the twenty-seven methylsilyl protons at $\delta$ 0.20 and a singlet for the three aromatic protons at $\delta$ 7.46. The second step involves removal of the methylsilyl groups by hydrolysis of 17 with alcoholic KOH to afford 1,3,5-triethynylbenzene 13 in 92% isolated yield. The $^1$H NMR for 13 in CDCl$_3$ (Figure 9) shows a singlet for the three terminal alkyne protons at $\delta$ 3.08 and another singlet for the three aromatic protons at $\delta$ 7.54.


The next step in the preparation of 2 would involve reaction of 13 with $n$-BuLi followed by nucleophilic addition to the aldehyde 14. Unfortunately, trimethylsilylpropynal 14 is very unstable and decomposed before reaction with the trianion of 13. This approach to elongating the conjugation was temporally abandoned in favor of the easier prepared “symmetrical” alkyne derivatives, such as 1 and 3.
Figure 8. $^1$H NMR spectrum of 17 in CDCl$_3$. 

7.46 (s, 3H, aromatic) 
0.20 (s, 27H, Si(CH$_3$)$_3$)
Figure 9. $^1$H NMR spectrum of 13 in CDCl$_3$. 

7.54 (s, 3H aromatic) 
3.08 (s, 3H, CH)
Preparation of 1,3,5-Tris(8(trimethylsilyl)octa-1,3,5,7-tetraynyl)benzene 3

1,3,5-Tris(8(trimethylsilyl)octa-1,3,5,7-tetraynyl)benzene 3 can be prepared, analogously to compound 1, according to Scheme 12. 1,8-bis(trimethylsilyl)octa-1,3,5,7-tetrayne 18 must first be prepared by oxidative coupling of 11 as shown in Scheme 13. As previously mentioned, oxidative coupling of terminal acetylenes in the presence of copper(I) catalysts is the best method of preparing symmetrically substituted polyyne derivatives.

Scheme 12. Synthesis of 1,3,5-tris(8(trimethylsilyl)octa-1,3,5,7-tetraynyl)benzene 3.

Caution should be applied to the reaction in Scheme 13. An explosion was encountered during solvent evaporation (no heat should be applied during evaporation), due care should be taken with acetylenic compounds of extended conjugation as in 18, in an atmosphere of oxygen. The experiment should be conducted in a well-ventilated hood behind a safety shield and away from any source of ignition. Dilution of exit gases with nitrogen is strongly advised.
The tetrayne 18 was purified by sublimation to give off white crystals. After sublimation, 18 should be kept out of light. It is believed that the color change from off-white to yellowish brown on exposure to light can be explained by the fact that conjugated systems have unique properties that give rise to strong colors. The $^1$H NMR spectrum of 18 (Figure 10) shows a singlet for the eighteen methylsilyl protons at $\delta$ 0.188.

![Scheme 13. Synthesis of 1,8-bis(trimethylsilyl)octa-1,3,5,7-tetrayne 18.](image)

The final two steps in the preparation of 3 involves the selective removal of one silyl group using MeLi-LiBr to give the terminal alkyne 19, followed by the Pd catalyzed coupling of 19 with 1,3,5-triiodobenzene to give the desired product 3.
Figure 10. $^1$H NMR spectrum of 18 in CDCl$_3$. 

0.19 (s, 18H, Si(CH$_3$)$_3$)
FUTURE WORK

The future work on this project involves deprotection of the silyl derivatives 1-3 by hydrolysis with alcoholic KOH to give the tris-terminal polyynes 4-6 as shown in Scheme 2. Reaction of the polyynes 4-6 with a strong base, n-BuLi, followed by treatment with chlorodiphenylphosphine will give the phosphines 7-9. These phosphine ligands will be used to form Au(I) complexes for luminescence studies.
CONCLUSIONS

We have successfully prepared polyynes 1 and 3 in moderate yields. These polyynes were prepared for use in the preparation of luminescent three-coordinate Au(I) complexes. The elongation of the conjugated alkynes should provide less steric hindrance in the Au(I) complexes proposed. A decrease in steric will enhance the luminescence properties.
EXPERIMENTAL

**General Methods.** Unless otherwise stated, all starting materials were purchased from Aldrich Chemical Co. and were used without further purification. All atmosphere sensitive reactions were done under nitrogen, over an anhydrous calcium sulfate gas drying unit. Solvents used, were of reagent grade and purified in the following manner: diethyl ether was distilled over sodium/benzophenone, triethylamine was distilled over calcium hydride, tetrahydrofuran was distilled over potassium/benzophenone, and dimethyl formamide was distilled over anhydrous magnesium sulfate. All NMR solvents (CDCl₃, with and without TMS) were stored over 4 Å molecular sieves prior to use. Analytical TLC was performed on Aluminium backed, pre-coated silica gel plates and visualization was accomplished with UV light. Flash column chromatography was carried out with silica gel (60Å mesh) from 40-63µm.

All NMR spectra were obtained at room temperature with a Varian VXR-500 spectrometer and a Varian Gemini-200 spectrometer, employing a deuterium sample of internal lock unless noted otherwise. The operating frequencies of the \(^1\text{H}\) and \(^{13}\text{C}\ \{^1\text{H}\}\) NMR spectra were 499.82 and 125.67 MHz, respectively. The \(^1\text{H}\) chemical shifts are reported relative to CHCl₃ (7.24ppm) and \(^{13}\text{C}\ \{^1\text{H}\}\) chemical shifts are reported relative to CDCl₃ (77.0ppm). Reported melting points were obtained with a Mel-Temp capillary apparatus and are uncorrected.
1,3,5-tris(trimethylsilylbuta-1,3-diynyl)benzene (I)\(^{10}\) (with triiodobenzene/ Pd \((PPh_3)_2Cl_2\)). To a 100 mL two-necked, round-bottomed flask, triiodobenzene (1.0 g, 2.2 mmol) was dissolved in freshly distilled triethylamine (12 mL). To the solution was added 50 mg copper (I) iodide, trimethylsilylbuta-1,3-diyne (1.36 g, 11.13 mmol) and Pd \((PPh_3)_2Cl_2\) (0.10 g, 0.132 mmol), stirred under N\(_2\) gas at 50\(^\circ\)C for 36 hr. The reaction mixture was filtered and evaporated under reduced vacuum. Separation by column chromatography afforded 9 as an off white solid (0.45 g, 47% yield) eluting as the third fraction with hexanes. mp 95-98\(^\circ\)C, \(^1\)H, NMR (500MHz, CDCl\(_3\)) \(\delta\) 7.49 (s, 3H, aromatic), 0.22 (s, 27H, Si(CH\(_3\))\(_3\)).
1,3,5-tri(6-(trimethylsilyl)hexa-1,3,5-triynyl)benzene (2). The synthesis of this compound was not attempted due to the severe instability of one of its starting material, trimethylsilylpropynal, 14.

![1,3,5-tri(6-(trimethylsilyl)hexa-1,3,5-triynyl)benzene (2)](image)

1,4-bis(trimethylsilyl)buta-1,3-diyne (10). A. Copper (I) chloride – tetramethylethylenediamine complex. A 1L, three-necked, round-bottomed flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and bubbler is charged with acetone (360 mL) and copper (I) chloride (20.0g, 202mmol). After the flask is purged with nitrogen, the mixture is stirred and N, N, N, N–tetramethylethylenediamine (TMEDA) (10 mL, 66mmol) is added. Stirring is maintained for over 30min, and the solid material is allowed to settle, leaving a clear deep blue-green solution of the CuCl-TMEDA catalyst, which is used in the oxidative coupling reaction.

B. 1,4-Bis(trimethylsilyl)buta-1,3-diyne (BTMSBD). A 3-L, 3-necked flask, equipped with a mechanical stirrer, dry ice cold-finger condenser, sintered gas inlet, and a swan-neck
adapter which supports a thermometer and rubber septum is charged with acetone (1200 mL) and trimethylsilylacetylene (200g, 2.04mol). The reaction mixture is agitated and a rapid stream of oxygen is passed through the solution, while vigorously stirring it. The supernatant solution containing the CuCl-TMEDA catalyst is transferred by syringe in 10 mL portions into the reaction flask. The solution was blue-green for every step that includes the catalyst. The temperature rises as the catalyst is added and had reached 35°C after about 50% of the catalyst has been added. External ice cooling was applied to moderate the exothermic reaction. (Refer to results and discussion). The remaining catalyst was added and the temperature was maintained in the range of 25-35°C for 4.0 hr. When the reaction is complete, there should be no evidence of trimethylsilylacetylene condensing on the cold trap. Agitation and oxidation were then stopped and the solution stirred overnight.

The solution was concentrated under vacuum and the residue dissolved in pentane (600 mL) and shaken in a separatory funnel with 3M aqueous hydrochloric acid (600 mL). The phases were separated and the aqueous phase washed with pentane (3 x 400 mL). The combined organic layers were washed with saturated aqueous sodium chloride (200 mL), dried over Na₂SO₄ and evaporated to dryness. The solid residue was dissolved in hot methanol (1600 mL) to which has been added 3M aqueous hydrochloric acid (20 mL). Water was added dropwise until recrystallized material was permanently present. The solution was allowed to cool, finally in ice, and crude bis(trimethylsilyl)butadiyne (BTMSBD, 155. 86g) was collected. A further 23.63g of the crude product was obtained from the mother liquors via recrystallization. The crude material was sublimed to give 10 as white crystals (171g, 86% yield), mp 111-113°C (lit.18 107-108°C), ¹H NMR (500MHz, CDCl₃) δ 0.19 (s, 18H, Si(CH₃)₃).
Trimethylsilylbuta-1,3-diyne (11). Inside the glove box, MeLi-LiBr complex (1.5M) in ether (412 mL, 618 mmol) was added to a freshly distilled ether solution of 1,4-bis(trimethylsilyl)-1,3-diyne, 10 (80.0 g, 411 mmol) and stirred at room temperature. After reaction completion (4.0 hr), the mixture was quenched with a saturated aqueous solution of NH₄Cl (400 mL) and extracted with ethyl ether (3 X 400 mL). The organic extracts were washed with water (3 X 400 mL), dried over Na₂SO₄, and concentrated under vacuum. The monosilylated diyne, 11, was purified by distillation and collected over dry ice as a colorless oil (32.54 g, 64.7% yield), ¹H NMR (500 MHz, CDCl₃) δ 2.08 (s, 1H, CH), 0.19 (s, 9H, Si(CH₃)₃).

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\begin{align*}
\text{A} & : \quad \text{Si} \quad \equiv \equiv \equiv \quad \text{Br} \\
\text{B} & : \quad \text{Si} \quad \equiv \equiv \equiv \quad \text{Br}
\end{align*}
\]

(4-(3,5-dibromophenyl)buta-1,3-diyln)trimethylsilane (A), 1-bromo-3,5-bis(4-(trimethylsilyl)buta-1,3-diyln)benzene (B) (with tribromobenzene/ Pd(PPh₃)₄). In a dried 100 mL round-bottomed Schlenk flask, 1,3,5-tribromobenzene (2.24 g, 7.11 mmol) and trimethylsilylbuta-1,3-diyne (5.22 g, 42.7 mmol) were dissolved in 50 mL of freshly distilled triethylamine. The reaction flask was flushed with nitrogen for 15 min, then a mixture of tetrakis(triphenylphosphine)palladium (1.47 g, 1.27 mmol) and copper (I) iodide (193 mg, 1.01 mmol) was added, and the suspension stirred under nitrogen for 66 hr at room temperature in the absence of light. After removal of solvents by evaporation, the residue was suspended in 150 mL.
diethyl ether and washed twice with 150mL water. The organic phase was dried over magnesium sulfate, and then evaporated to give a dark viscous liquid. Separation by column chromatography on silica gel, afforded six different fractions, with the mono-substituted product, A (0.31 g) eluting as the first fraction and the di-substituted product, B (0.34 g), eluting as the third fraction with hexanes. For A, $^1$H NMR (200MHz, CDCl$_3$) $\delta$ 7.62 (t, $J = 4.7$Hz; 1H, aromatic), 7.51 (d, $J = 4.5$Hz; 2H, aromatic), 0.20 (s, 9H, Si(CH$_3$)$_3$) and for B, $^1$H NMR (200MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 3.4$Hz; 2H, aromatic), 7.45 (t, $J = 3.4$Hz; 1H, aromatic), 0.20 (s, 9H, Si(CH$_3$)$_3$).

1-Bromo-3,5-bis(4-(trimethylsilyl)buta-1,3-diynyl)benzene (B)$^{20}$ (with tribromobenzene/ Pd$_2$(dba)$_3$). A 250 mL round-bottomed Schlenk flask was charged with 1,3,5-tribromobenzene (3.22 g, 10.2 mmol), copper (I) iodide (38.9 mg, 0.204 mmol), triphenylphosphine (287 mg, 1.09 mmol), tris (dibenzylideneacetone) dipalladium (0) (122 mg, 0.133 mmol) and freshly distilled triethylamine (112 mL). The reaction flask was flushed with nitrogen for 15min, then trimethylsilylbuta-1,3-diyn (5.00 g, 40.9 mmol) was added via a syringe. Reaction was stirred under nitrogen for 48 hr at 70-75°C in the absence of light. When the reaction was complete as indicated by TLC, the solvent was removed under reduced pressure and the remaining residue dissolved in hexanes. Separation by column chromatography on silica gel afforded a di-substituted product benzene (above, 0.2 g) eluting as the second fraction with hexanes. $^1$H NMR (200MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 3.4$Hz; 2H, aromatic), 7.45 (t, $J = 3.4$Hz; 1H, aromatic), 0.20 (s, 9H, Si(CH$_3$)$_3$).
Triiodobenzene (12). 1,3,5-Tribromobenzene (4.40 g, 14.0 mmol), KI (14.00 g, 84.14 mmol), Ni powder (8.00 g), I₂ (20.40 g) and freshly distilled DMF (50 mL) were charged into a 250 mL round-bottomed Schlenk flask. The flask was evacuated on the vacuum line at 0°C for 15 min. The mixture was refluxed under N₂ at 185-190°C for 3.0 hr. A bluish-green color change was observed while the reaction mixture solidified. After cooling, the solution was poured into a 1000 mL separation funnel and washed with 3% aqueous HCl (200 mL) and CH₂Cl₂ (200 mL) until all material, except for Ni powder, was transferred into the funnel. The CH₂Cl₂ layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (2 x 40 mL). The combined CH₂Cl₂ phase was washed with distilled water (3 x 100 mL) and dried over MgSO₄. The solvent was evaporated, leaving a light-brown crude product (3.80 g). This was further purified by sublimation at 60°C overnight to remove most C₆H₃I₂Br and other impurities. The residue was sublimed at 120 to 140°C to give 12 as fluffy white crystals (1.26 g, 19.8% yield) mp 184°C, ¹H NMR (500MHz, CDCl₃) δ 7.99 (s, 3H, aromatic), purity 100% by NMR.

Trimethylsilylpropynal (14). A freshly distilled THF (70 mL) solution of trimethylsilylacetylene (14.4 mL, 100 mmol) and stirred under nitrogen, at room temperature for 20 min. Then n-BuLi (2.5 M) in hexanes (45.0 mL, 110 mmol) was added dropwise to the solution, while the temperature was kept at 10 -15°C by an ice-water bath. After stirring at room temperature for 1 hr, the mixture was transferred to an efficiently stirred mixture of distilled DMF (27 mL, 348 mmol) and THF (80 mL) at -25°C over a period of 45 min. The white suspension was
allowed to reach room temperature, stirred for 1hr, heated to 30°C for 15min and poured into 200mL 5% H₂SO₄ at 0°C. After three extractions with diethyl ether (DEE), the water layer was stirred overnight under nitrogen with a fresh portion of DEE to which was added a trace of hydroquinone. The water layer was extracted four times with DEE and the combined organic layers were washed with a saturated ammonium chloride solution, dried over magnesium sulfate and concentrated under reduced vacuum. Distillation (trace of hydroquinone added, bp. 44-45°C/20mm) yielded 14 as a colorless oil (3.22g, 25.2% yield), which was collected in an ice-cold receiver and stored in the cold. ¹H, NMR (200MHz, CDCl₃) δ 9.2 (s, 1H, CHO), 0.25 (s, 9H, Si(CH₃)₃).

1,3,5-triethynylbenzene (13). Desilylation of 1,3,5-tris(trimethylsilyl)ethynyl)benzene (2.00g, 5.45mmol) was achieved by stirring the compound in a saturated potassium hydroxide solution of methanol for 4 hr. Extraction of the organic product with diethyl ether and subsequent column chromatography on silica gel with hexanes/diethyl ether (1:1) yielded 13 (750mg, 92%) as a fluffy white solid. ¹H, NMR (200MHz, CDCl₃) δ 7.54 (s, 3H, aromatic), 3.08 (s, 3H, CH).
1,3,5-tris(2-(trimethylsilyl)ethynyl)benzene (17). In a 250mL round-bottomed Schlenk flask, 1,3,5-tribromobenzene (2.50g, 7.94mmol) and trimethylsilylacetylene (11.7mL, 80.0mmol) were dissolved in 60mL freshly distilled THF and 15mL of dry triethylamine. A mixture of tetrakis(triphenylphosphine)palladium (1.47g, 1.26mmol) and copper (I) iodide (193mg, 1.01mmol) was added, and the suspension stirred for 36 hr. at room temperature in the absence of light. When the reaction was complete as indicated by TLC, the solvent was removed under reduced pressure and the remaining residue dissolved in 100mL of diethyl ether and washed twice with 100mL of water, and the organic phase was dried over magnesium sulfate. Removing the solvent and separation by column chromatography on silica gel afforded 17 as an off white solid (2.05g, 70.4 % yield) eluting as the second fraction with hexanes. ¹H, NMR (200MHz, CDCl₃) δ 7.46 (s, 3H, aromatic), 0.20 (s, 27H, Si(CH₃)₃).

1,8-bis(trimethylsilyl)octa-1,3,5,7-tetrayne (18). A. Copper (I) chloride – tetramethylethlenediamine complex. A 500 mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar, rubber septum, nitrogen inlet tube, and bubbler is charged with acetone (180 mL) and copper (I) chloride (10.0g, 101mmol). After the flask is purged with nitrogen, the mixture is stirred and N,N,N,N–tetramethylethlenediamine (TMEDA) (5 mL, 33mmol) is added. Stirring is maintained for over 30mins, and the solid material is allowed to
settle, leaving a clear deep blue-green solution of the CuCl-TMEDA catalyst, which is used in the oxidative coupling reaction.

B. 1,8-bis(trimethylsilyl)octa-1,3,5,7-tetrayne (BTMSOT). A 2-L, 3-necked flask, equipped with a mechanical stirrer, dry ice cold-finger condenser, sintered gas inlet, and a swan-neck adapter, which supports a thermometer, and rubber septum is charged with acetone (300 mL) and trimethylsilylbuta-1,3-diyne (34.45 g, 290.0 mmol). The reaction mixture is agitated and a rapid stream of oxygen is passed through the solution, while vigorously stirring it. The supernatant solution containing the CuCl-TMEDA catalyst is transferred by syringe in 10 mL portions into the reaction flask. The solution was blue-green for every step that includes the catalyst. The temperature rises as the catalyst is added and had reached 35°C after about 50% of the catalyst has been added. External ice cooling was applied to moderate the exothermic reaction. The remaining catalyst was added, and the temperature was maintained in the range of 25-35°C for 4.0 hr. When the reaction is complete, there should be no evidence of trimethylsilylacetylene condensing on the cold trap. Agitation and oxidation were then stopped, and the solution stirred overnight.

The solution was concentrated under vacuum and the residue dissolved in pentane (150 mL) and shaken in a separatory funnel with 3M aqueous hydrochloric acid (150 mL). The phases were separated and the aqueous phase washed with pentane (3 x 150 mL). The combined organic layers were washed with saturated aqueous sodium chloride (50 mL), dried over Na₂SO₄ and evaporated to dryness. The solid residue was dissolved in hot methanol (500 mL) to which has been added 3M aqueous hydrochloric acid (4 mL). Water was added dropwise until recrystallized material was permanently present. The solution was allowed to cool, finally in ice, and a crude product (11.07 g) was collected. The crude material was sublimed to give 18 as off
white crystals (10.25g, 15% yield) mp 94-95°C, $^1$H NMR (500MHz, CDCl$_3$) $\delta$ 0.19 (s, 18H, Si(CH$_3$)$_3$).

Future Syntheses

Hydrolysis of 1 using alcoholic KOH will yield 1,3,5-tri(buta-1,3-diynyl)benzene 4. Reacting this deprotected compound with $n$-BuLi followed by chlorodiphenylphosphine, produces 1,3,5-tris(diphenylphosphino)buta-1,3-diynyl benzene 7, which will then hold the three-coordinate Au (I) complex at the chain ends as 20.
Hydrolyzes of 3 via alcohol KOH will yield 1,3,5-tri(octa-1,3,5,7-tetraynyl) benzene 6.

Reacting the deprotected compound with \textit{n}-BuLi followed by treatment with chlorodiphenylphosphine, will yield 1,3,5-tris(diphenylphosphino)octa-1,3,5,7-tetraynyl)benzene 9, which will then hold the three-coordinate Au (I) complexes at the chain ends as 21.
Deprotecting one of the silyl groups on 1,16-bis(trimethylsilyl)hexadeca-1,3,5,7,9,11,13,15-octayne will yield trimethylsilylhexadeca-1,3,5,7,9,11,13,15-octayne, which will be employed in substitution onto a benzene ring, then hydrolyzed to yield 1,3,5-tri(heptadeca-1,3,5,7,9,11,13,15-octaynyl)benzene. Reacting the deprotected compound with n-
BuLi followed by treatment with chlorodiphenylphosphine, will yield 1,3,5 tris(diphenylphosphino)hexadeca-1,3,5,7,9,11,13,15-octaynyl)benzene, which will then hold the three-coordinate Au (I) complexes at the chain ends as 22.
REFERENCES


