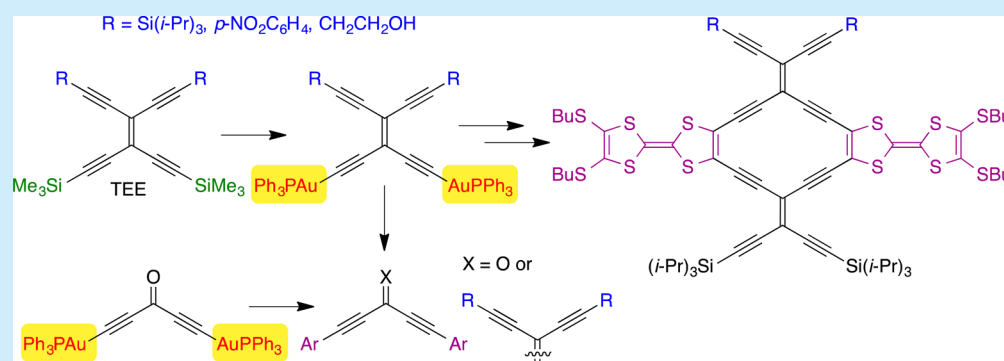


The Gilded Edge in Acetylenic Scaffolding: Pd-Catalyzed Cross-Coupling Reactions of Phosphine–Gold(I) Oligoynyl Complexes

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S Supporting Information



ABSTRACT: Stable bis(gold(I) alkynyl) complexes of tetraethynylethene (TEE) derivatives were readily prepared and employed in Sonogashira-like palladium-catalyzed phosphine–gold(I) halide elimination reactions with aryl iodides and redox-active tetrathiafulvalene (TTF) mono- and bisiodides. This presents a particularly convenient method for the preparation of symmetrical and asymmetrical tetrathiafulvalene (TTF)-fused radiaannulenes in good yields.

Metal-catalyzed coupling reactions of terminal alkynes have allowed the preparation of a large variety of carbon-rich materials, such as π -conjugated oligomers and macrocyclic structures with interesting optical and redox properties.¹ For example, derivatives of tetraethynylethene (TEE) have been used by Diederich et al.^{1c,h} as precursors for perethynylated expanded radialenes, dehydroannulenes, radiaannulenes, and long poly(triacetylene) oligomers. One challenge in the field of acetylenic scaffolding is, however, that terminal alkynes are often not stable² and they are even sometimes explosive. Thus, the unsubstituted TEE rapidly decomposes in the solid state and can spontaneously detonate.³ Instead, trialkylsilyl-protected TEEs usually exhibit excellent stabilities. The bulky triphenylphosphine-gold(I) (AuPPh₃) fragment presents another convenient stabilizing end group for terminal alkynes.⁴ Thus, Bruce et al.^{4d–g} have shown that phosphine–gold(I) complexes of 1,3-butadiyne and oligoynes can be readily prepared and isolated (Figure 1). Incorporation of AuPCy₃ and AuPPh₃ at all four terminal alkyne positions of TEE has also been accomplished.⁵

The stabilization introduced by the gold(I) termini has rendered gold polyyne particularly interesting coupling partners in metal-catalyzed cross-coupling reactions. Thus, gold(I) alkynyl complexes were shown by Bruce, Low, and co-workers^{4e,f,6} to undergo Pd-catalyzed gold(I)–phosphine halide elimination reactions with 1-iodoalkynes and aryl iodides (modified Cadiot–Chodkiewicz and Sonogashira-like cross-coupling reactions), which can be performed under base-free

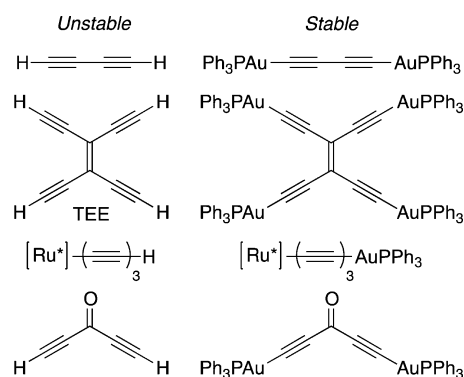


Figure 1. Comparison of stabilities between terminal alkynes and related gold(I) acetylides. [Ru*] = Ru(dppe)Cp*, where dppe = 1,2-bis(diphenylphosphino)ethane and Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl.

conditions. This has allowed the synthesis of metal-capped oligoynes with as many as 19 or 24 carbons between the metal centers.^{4f} It should also be noted that phosphine–gold(I) alkynyl complexes, being more stable than copper(I) and silver(I) alkynyl complexes, have themselves found wide interest in supramolecular and materials science, in particular owing to their luminescent properties.⁷

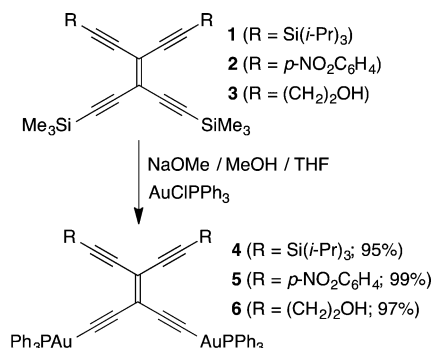
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Here we present the synthesis of new phosphine–gold(I) complexes of functionalized TEEs and their convenient use in Pd-catalyzed reactions, including particularly challenging cyclization reactions for making expanded radiannulenes containing redox-active tetrathiafulvalene (TTF) units. The use of TEE-based phosphine–gold(I) complexes as substrates in such macrocyclizations presents an important improvement relative to a recently reported procedure.⁸

The known TEE derivatives **1**,^{3a} **2**,⁹ and **3**¹⁰ were converted into bis(gold(I) ethynyl) complexes **4**, **5**, and **6** (Scheme 1) in

Scheme 1. Synthesis of Gold(I) Functionalized TEEs



almost quantitative yields by treatment with NaOMe and AuClPPh₃ (commercially available, but also easily prepared from Au;¹¹ see Supporting Information, SI, which also includes a guide for handling the gold complexes). The structures of products **4** and **5** were confirmed by X-ray crystallographic analysis (Figure 2),¹² which did not show any intermolecular

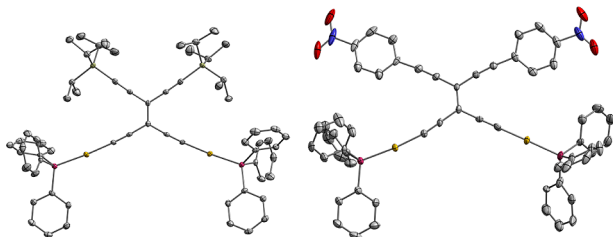
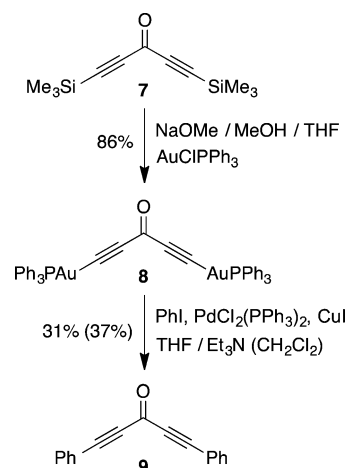


Figure 2. Molecular structures of **4** (left; crystals grown from C₆D₆/hexanes) and **5** (right; crystals grown from CH₂Cl₂/heptanes). Hydrogen atoms and solvent molecules were removed for clarity.

Au–Au interactions. The yield (and full characterization) of **6** is particularly noteworthy, as the corresponding bis-terminal alkyne of this compound was very unstable and it was not possible to isolate it, at least not in our hands. The presence of alcohol groups also complicated the isolation of the complex **6** as it tended to degrade to a black compound.

Penta-1,3-diyne-3-one, first prepared by Liang¹³ in 1933, is not very stable at ambient temperature,¹⁴ but its silylated derivative **7** (Scheme 2) is easy to handle and was used as a key precursor for TEE in a synthesis developed by Diederich et al.^{3a} Conversion of **7** to the corresponding gold(I) complex **8** was previously reported,^{4g} but we managed to increase the yield significantly (from 50% to 86%) by increasing the reaction time (Scheme 2); the product conveniently precipitated from the methanolic solution. Next, we subjected this gold species to a Pd-catalyzed cross-coupling reaction with iodobenzene, which gave the product **9**. The yield was rather modest (31% or 37% using either THF/Et₃N or CH₂Cl₂ as the solvent), but for

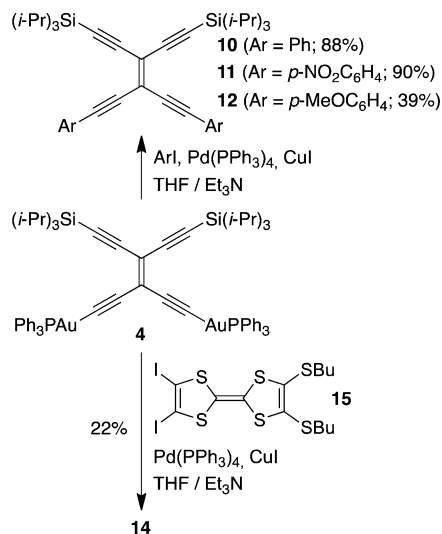
Scheme 2. Synthesis of Bis(gold(I) ethynyl)ketone and Pd-Catalyzed Coupling Thereof



comparison, protodesilylation of **7** followed by reaction of the unstable intermediate with iodobenzene under Sonogashira conditions did not give the desired product, at least not in our hands.

Significantly higher yields of cross-coupling products could be obtained from the TEE gold(I) substrate **4**. Thus, treatment of this complex with iodobenzene or 4-iodonitrobenzene under Sonogashira conditions in THF/Et₃N gave products **10** and **11**, respectively, in excellent yields (Scheme 3). Coupling with 4-

Scheme 3. Pd-Catalyzed Reactions with Gold(I) Functionalized TEE



iodoanisole under similar conditions gave the product **12**, but in a lower yield of 39% ascribed to the influence of the electron-donating methoxy group on the aryl iodide.

With the demonstration of relatively simple coupling reactions with TEE and penta-1,4-diyne-2-one gold(I) alkynyl complexes, our next objective was to expand the scope of such reactions in more challenging acetylenic scaffolding chemistry. Charge-transfer chromophores combining TEE electron acceptor(s) and TTF donor(s) have attracted our interest as compounds, which can exist in several redox states with unique UV–vis–NIR optical properties.¹⁵ For example, we have recently devised a synthetic protocol for the TTF-fused

radiaannulene **13** (Figure 3),⁸ which exhibited particularly interesting redox and optical properties. This compound,

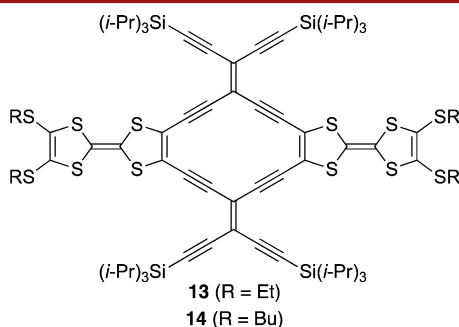


Figure 3. TTF-functionalized radiaannulenes.

containing both endo- and exocyclic double bonds in the central ring, was made by an intermolecular cyclization of the corresponding TTF-bisiodide and the TEE **1** after removal of the two trimethylsilyl protecting groups. The yield of this conversion, involving four cross-couplings, was rather low (10%). We therefore became interested in investigating whether the use of AuPPh₃ complexes could improve the yield of cyclization.

Macrocycle **14** (Figure 3) with peripheral butylthio groups was chosen as the first target; the rationale behind choosing these peripheral groups was to enhance the solubility in order to achieve molecules with potential for further acetylenic scaffolding. Subjecting complex **4** and the known TTF-bisiodide **15**¹⁶ to the phosphine–gold(I) halide elimination reaction afforded TTF-radiaannulene **14** in a 22% yield (Scheme 3), that is, a doubling of the yield relative to that obtained previously for **13** and corresponding to a yield of 68% for each of the four individual couplings.

In order to reduce the number of byproducts in the cyclization step and to be able to construct asymmetrical macrocycles, we decided to develop a stepwise protocol (Scheme 4). First, TEE **1** was desilylated and then subjected to a Sonogashira cross-coupling with two molecules of the known TTF-iodide **16**,¹⁷ which furnished the product **17**. Iodination of each TTF unit upon treatment with sodium hexamethyldisilazide (NaHMDS) followed by 1,2-diiodoethane subsequently gave the bisiodide **18**. The yield is 55% after isolation of the pure product by column chromatography, which causes significant decomposition and loss of material. When used as a substrate for subsequent reactions, passing the compound **18** through a short plug of silica was sufficient. Treating **18** with **4** or **5** under Pd catalysis finally gave the radiaannulenes **14** and **19** in yields of 57% and 39%, respectively (Table 1). For comparison, using instead **1**, after removal of the two trimethylsilyl groups, as a substrate (i.e., with free terminal acetylene moieties) for the cyclization reaction, the radiaannulene **14** was only obtained in a yield of 12%.

In conclusion, we have prepared stable gold(I) alkynyl complexes of TEE (and of a TEE precursor), which are convenient building blocks for acetylenic scaffolding (expanding the work of Bruce, Low, and co-workers^{4e,f,6}), using Pd-catalyzed cross-coupling reactions with aryl iodides as coupling partners. This presents an attractive alternative to generating otherwise unstable terminal alkynes as intermediates. In particular, gold(I) alkynyl complexes were useful precursors

Scheme 4. Stepwise Synthesis of Symmetrical and Asymmetrical TTF-Radiaannulenes

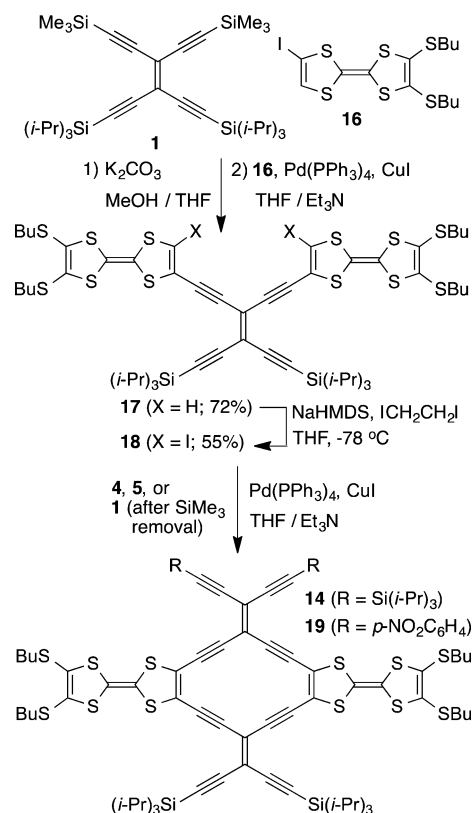


Table 1. Yields of Cyclization Reactions Corresponding to Last Step in Scheme 4

entry	starting material	product (yield)
1	4	14 (57%)
2	5	19 (39%)
3	1 ^a	14 (12%)

^aCompound **1** was first treated with K₂CO₃ in MeOH/THF to remove the trimethylsilyl groups. This intermediate was passed through a short plug of silica, concentrated in vacuo, and then used directly in the cyclization reaction.

for TTF-fused radiaannulenes, and we hope that they will allow us in future work to construct even more elaborate and challenging two-dimensional TTF–acetylene scaffolds.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, X-ray crystallographic data, and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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