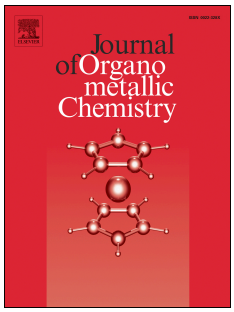
Accepted Manuscript



A mechanistic rationale for the outcome of Sonogashira cross-coupling of 9-bromoanthracene and ethynyltrimethylsilane: An unexpected product 4-(9-anthracenyl)-1,3-bis(trimethylsilyl)-3-en-1-yne

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PII: S0022-328X(18)30838-6

DOI: https://doi.org/10.1016/j.jorganchem.2018.10.015

Reference: JOM 20600

To appear in: *Journal of Organometallic Chemistry*

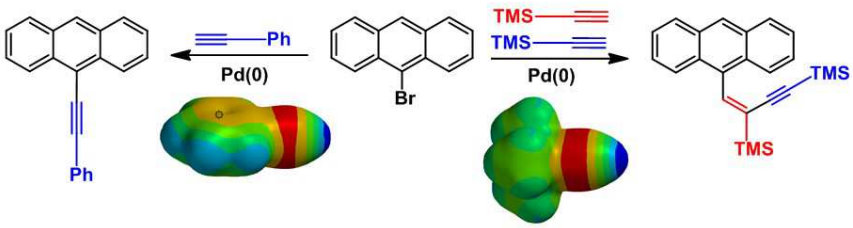
Received Date: 25 September 2018

Revised Date: 17 October 2018

Accepted Date: 19 October 2018

Please cite this article as: K. Nikitin, H. Müller-Bunz, P.J. Guiry, M.J. McGlinchey, A mechanistic rationale for the outcome of Sonogashira cross-coupling of 9-bromoanthracene and ethynyltrimethylsilane: An unexpected product 4-(9-anthracenyl)-1,3-bis(trimethylsilyl)-3-en-1-yne, *Journal of Organometallic Chemistry* (2018), doi: https://doi.org/10.1016/j.jorganchem.2018.10.015.

Graphical abstract



Coupling of bromoanthracene and substituted acetylenes using copper-free palladium catalysis conditions leads to unexpected diverse products: phenylacetylene yields a Sonogashira-type product (left), but the more electron-rich trimethylsilylacetylene gives, in two steps, an insertion product (right).

A mechanistic rationale for the outcome of Sonogashira cross-coupling of 9-bromoanthracene and ethynyltrimethylsilane: an unexpected product 4-(9-anthracenyl)-1,3-bis(trimethylsilyl)-3-en-1-yne

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Abstract: The Sonogashira reaction of 9-bromoanthracene and ethynyltrimethylsilane furnishes not only the anticipated 9-(trimethylsilylethynyl)anthracene and 2-(trimethylsilyl)-aceanthrylene but also (*E*)-4-(9-anthracenyl)-1,3-bis(trimethylsilyl)-but-3-en-1-yne, all in moderate yields. A mechanistic rationale is proposed that invokes the intermediacy of bromo(anthracenyl)bis(triphenylphosphine)palladium(II) that can undergo coupling either directly, or after coordination and migratory insertion of the free alkyne.

Keywords: palladium catalysis, arene-alkyne couplings, enynes, X-ray crystallography, reaction mechanisms

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Dedicated to Professor Richard Puddephatt on the occasion of his 75th birthday, and in recognition of his many pioneering investigations into the chemistry of the platinum metals.

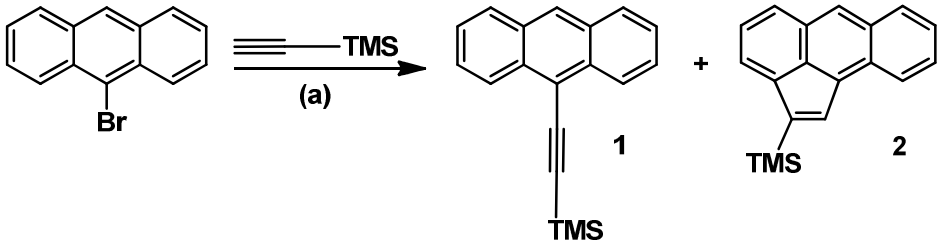
1. Introduction

9-(Trimethylsilylethynyl)anthracene, **1**, has been widely used as a precursor for a wide range of applications, including photo- and electro-luminescent molecules [1-3], anthracene-stacked oligomers [4], triptycene-based molecular rotors [5,6], species immobilized on nanoparticles [7], cross-linked polymers [8], syntheses of fullerene fragments [9,10], electrochemical behaviour of tetracenes and pentacenes [11], and in sensitive probes for mechanical stress in polymers [12]. The obvious synthetic route via a palladium-catalyzed cross-coupling of 9-bromoanthracene and ethynyltrimethylsilane turns out to be exquisitely sensitive to the experimental conditions (catalyst and base used, solvents, temperatures) and gives rise to a number of products.

2. Results and discussion

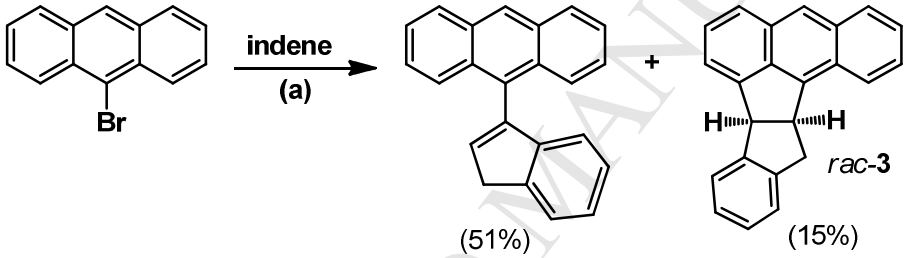
2.1. Syntheses and structures

In 1997, Tour reported the successful synthesis (84% yield) of 9-(trimethylsilyl-ethynyl)anthracene, **1**, as a red solid via Negishi cross-coupling of trimethylsilylethynyl lithium and 9-bromoanthracene with $ZnCl_2$, $Pd(dba)_2$ and PPh_3 in THF at 75 °C [13]. However, since this procedure requires such scrupulously dry conditions, other routes have also been investigated. In 2001, Dang and Garcia-Garibay found, surprisingly, that the analogous Sonogashira reaction using $PdCl_2(PPh_3)_2$, PPh_3, $CuSO_4/Al_2O_3$ and Et_3N in refluxing benzene gave **1** only as a minor product, and instead yielded 2-(trimethylsilyl)-aceanthrylene, **2**, in the ratio 16:84, respectively [14] (Scheme 1). Under the same conditions, but in a sealed tube, this ratio was amplified to 7:93. Since then, this peri-cyclopentenelation process has been exploited to produce polycyclic systems that represent fragments of fullerenes [9,10].



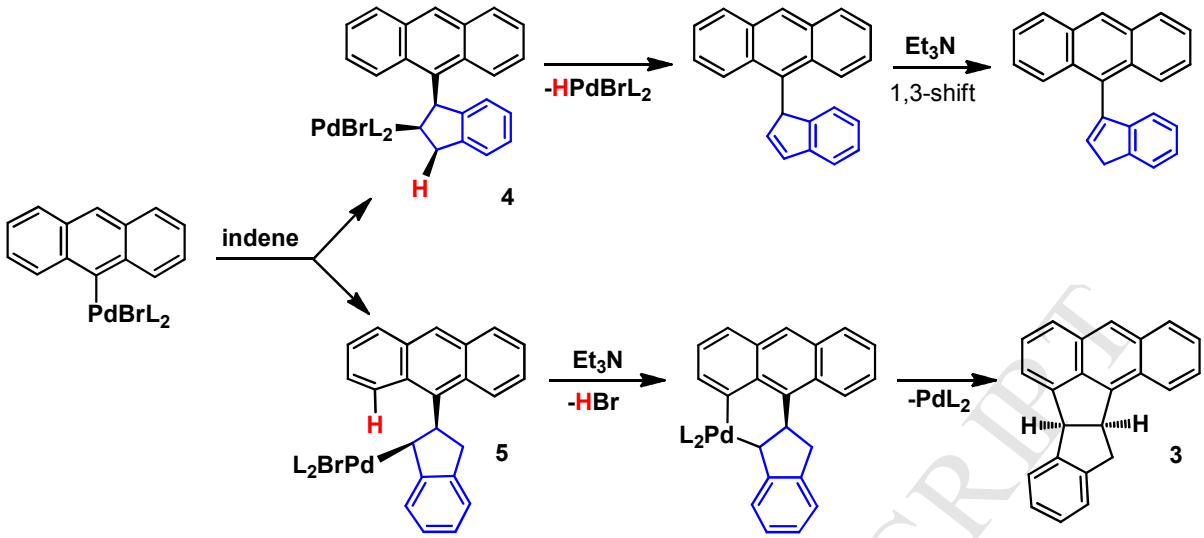
Scheme 1. Synthesis of **1** and **2**; (a) $PdCl_2(PPh_3)_2$, PPh_3, $CuSO_4/Al_2O_3$, Et_3N, benzene, reflux.

Dang's and Garcia-Garibay's latter observation parallels an initial attempt to prepare 9-(2-indenyl)anthracene [15], *en route* to 9-(2-indenyl)triptycene that was subsequently utilized in an organometallic molecular brake [16]. Once again, unexpected cyclization to form the indenyl-fused anthracene, *rac*-**3**, resulted (Scheme 2).



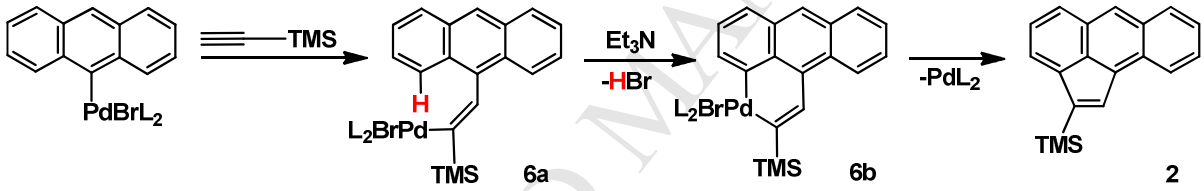
Scheme 2. Synthesis of **3**; (a) $PdCl_2[P(o\text{-tol})_3]_2$, (2 mol %), DMF, 100 ºC.

In retrospect, it is evident that the two possible modes of insertion of indene into the aryl-palladium linkage of 9-(anthracenyl)$Pd(Ph_3P)_2Br$, generated from 9-bromoanthracene and the catalytic species $Pd(Ph_3P)_2$, can lead to intermediates **4** and **5** (Scheme 3). In the former case, *syn*-elimination of $HPdL_2Br$ occurs readily to yield 9-(1-indenyl)anthracene (that subsequently isomerizes to its 3-indenyl counterpart). In contrast, intermediate **5** lacks a suitably positioned hydrogen *syn* to palladium, and instead undergoes intramolecular palladation of the adjacent anthracene ring to form the polycycle **3**.



Scheme 3. Proposed mechanistic routes for the indenylation of 9-bromoanthracene.

Analogously, the lack of a hydrogen *syn* to palladium in intermediate **6a** (Scheme 4) also leads, via cyclization to **6b**, to the aceanthrylene **2**.

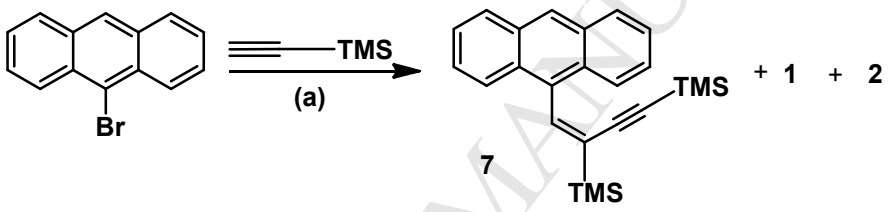


Scheme 4. Palladium-catalyzed formation of aceanthranylene, **2**.

More recently, the route to **1** employing the Sonogashira reaction has been very markedly improved. Typically, reaction of 9-bromoanthracene and ethynyltrimethylsilane in the presence of $PdCl_2(PPh_3)_2$, CuI, Et_3N and piperidine at 110 °C furnished the desired product in 75% yield [17]; it has since been improved to 98% [18]. A synthesis using THF as solvent has also been reported [19]. The principal differences between the reactions leading to the alkynylanthracene, **1**, or the aceanthrylene, **2**, are the changes in solvent, identity of the copper salt, and relative ratios of the anthracene and alkyne. The former case (Et_3N, piperidine, CuI, 4-fold excess of alkyne) yields **1** almost quantitatively whereas the latter (benzene, $CuSO_4/Al_2O_3$, and 2.7-fold excess of alkyne) yields primarily **2**, and is even better in the absence of copper [9,14]. The palladium catalyst, temperature and length of reaction

are unchanged. We note, however, that in many cases where a Cu salt is not listed as a reagent it is still present in the solvent in trace quantities as a stabilizer.

As shown in Scheme 5, we here report the isolation and structural characterization of another product of the palladium-catalyzed cross-coupling of 9-bromoanthracene and ethynyltrimethylsilane using $PdCl_2(PPh_3)_2$ (2 mol%), Et_3N and THF at 70 °C for 24 h to give, in approximately equal yields, 9-(trimethylsilylethynyl)anthracene, **1**, 2-(trimethylsilyl)-aceanthrylene, **2**, and, remarkably, also (*E*)-4-(9-anthracenyl)-1,3-bis(trimethylsilyl)-but-3-en-1-yne, **7**, that was characterized spectroscopically and whose structure was confirmed by X-ray crystallography (Figure 1).



Scheme 5. Palladium-catalyzed reaction of ethynyltrimethylsilane with 9-bromoanthracene; (a) $PdCl_2(PPh_3)_2$ (2 mol %), Et_3N, THF, 70 °C, 24 h.

The enyne **7** crystallizes with four independent molecules in the unit cell. The average ene-yne bond distances were 1.331 and 1.210 Å, respectively, and this unit made an average torsion angle of 57.7° with the anthracene plane. The molecule contains three different carbon-silicon bond environments in which the mean sp^3-C—Si, sp^2-C—Si and *sp*-C—Si distances are noticeably dissimilar, 1.855, 1.892 and 1.832 Å, respectively.

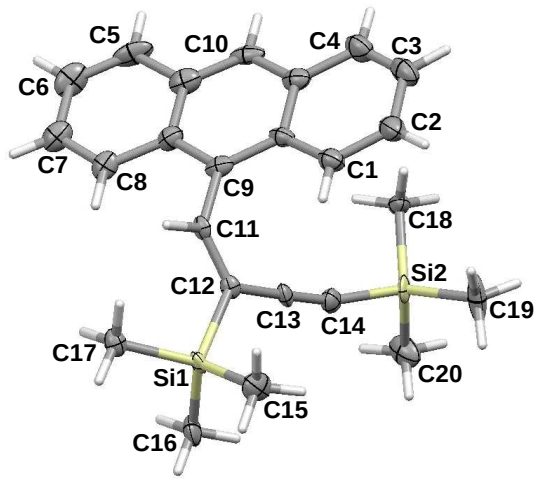
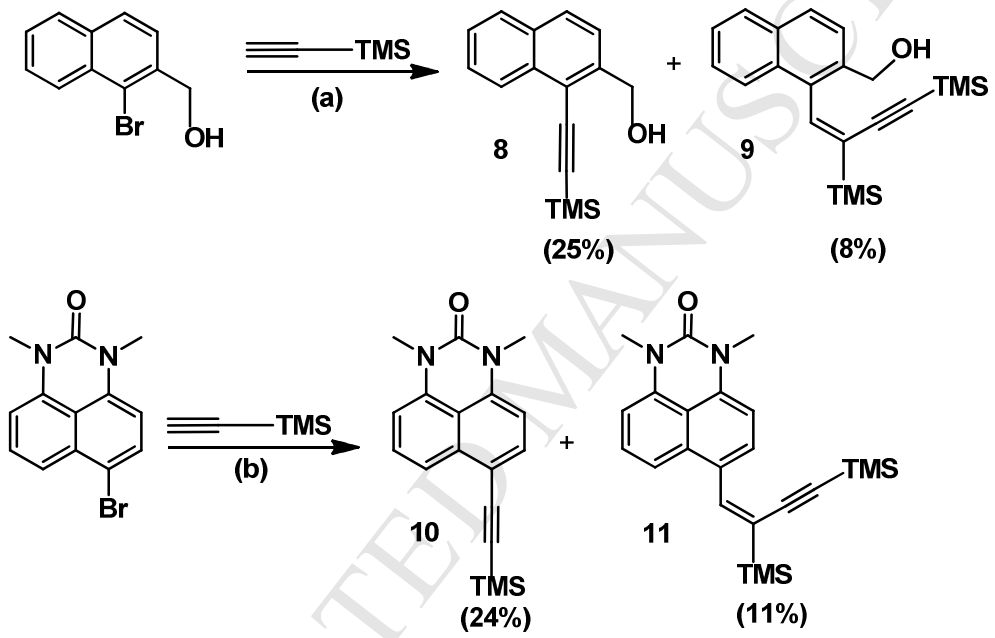


Figure 1. Molecular structure of 4-(9-anthracenyl)-1,3-bis(trimethylsilyl)-but-3-en-1-yne, **7**, which crystallizes with four independent molecules in the unit cell. In the one shown, selected bond distances (Å) and angles (deg) are: C(9)-C(11) 1.474(7), C(11)-C(12) 1.338(7), C(12)-C(13) 1.423(7), C(13)-C(14) 1.218(7), C14)-Si(2) 1.829(5); C(9)-C(11)-C(12) 127.1(5), C(11)-C(12)-C(13) 119.7(5), C(12)-C(13)-C(14) 179.5(5), C(13)-C(14)-Si(2) 167.2(5).

The packing of the molecules in **7** (see ESI Figure S1) reveals that the enyne units are aligned face-to-face as enantiomeric pairs and the anthracenyls are arranged in an almost parallel fashion to form an outer wall which encloses them. This differs markedly from the very first report of enyne stacking in the Y-shaped molecule $(C_6F_5)CH=C(C\equiv CPh)_2$ in which the structure is dominated by face-to-face interactions of phenyl and pentafluorophenyl rings and the enyne units are sandwiched between phenyl groups [20].

In related earlier work it had been noted that the reaction of 1-bromo-2-(hydroxymethyl)naphthalene with ethynyltrimethylsilane catalyzed by $Pd(PPh_3)_4$ and CuI in piperidine gave the ethynylnaphthalene, **8**, together with a small amount of the double adduct, **9**, (Scheme 6) that was characterized by NMR spectroscopy [21]. Much more

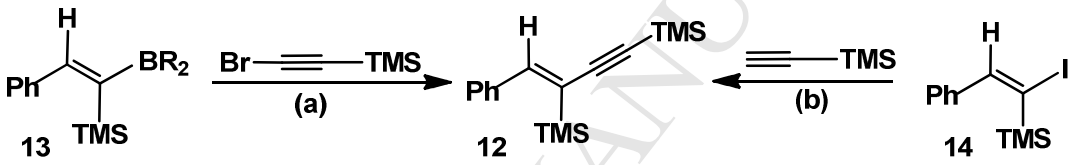
recently, the Sonogashira reaction of a dialkylperimidone with ethynyltrimethylsilane to form **10** gave a low yield of the double adduct, **11**, that was characterized by X-ray crystallography [22]. The structure of the but-3-en-1-yne moiety in **11** may be compared to that that found here in **7**; the double and triple C-C bond distances in **11** are 1.358 and 1.213 Å, respectively, and the enyne unit has rotated only 38.6° out of the naphthalene plane compared to 57.7° in **7**, which of course has an additional proximate benzo ring.



Scheme 6. Syntheses of 1,3-bis(trimethylsilyl)-but-3-en-1-ynes **9** and **11**; (a) $Pd(PPh_3)_4$ (5 mol %), piperidine, 80 °C;(b) $Pd_2(dba)_3$ (5 mol %), CuI (10 mol %), TMS-alkyne (600 mol %), PPh_3, Et_3N, DMF, 50-55 °C.

The above-mentioned double and triple carbon-carbon bond distances in **7** may also be compared to those in a series of bis-(TMS-terminated enynes) connected by a spacer, such as a phenyl ring or a substituted thiophene, in which the analogous double and triple bonds have average values of 1.348 and 1.203 Å, respectively [23].

Although metal-catalyzed synthetic routes to enynes from terminal alkynes have been comprehensively reviewed [24], the only previously reported specifically designed syntheses of 1,3-bis(trimethylsilyl)-but-3-en-1-ynes, of type **12**, include the Cu-mediated cross-coupling reaction of (*E*)-alk-1-enyldisiamylboranes, **13**, with (trimethylsilyl)ethynyl bromide [25] and the Sonogashira coupling of (*E*)-α-iodovinylsilanes, **14**, with (trimethylsilyl) acetylene [26] (Scheme 7). It is also noteworthy that in 1988 Ishikawa reported that treatment of ethynyldimethylphenylsilane with $Pd(PPh_3)_4$ at 100 °C produced the tail-to-tail dimer (*E*)-1,4-bis(dimethylphenylsilyl)but-3-en-1-yne in low yield [27].



Scheme 7. Alternative routes to 1,3-bis(trimethylsilyl)-but-3-en-1-ynes; (a) CuI, NaOH, THF; (b) $Pd(PPh_3)_4$ (5 mol %), CuI, piperidine, RT.

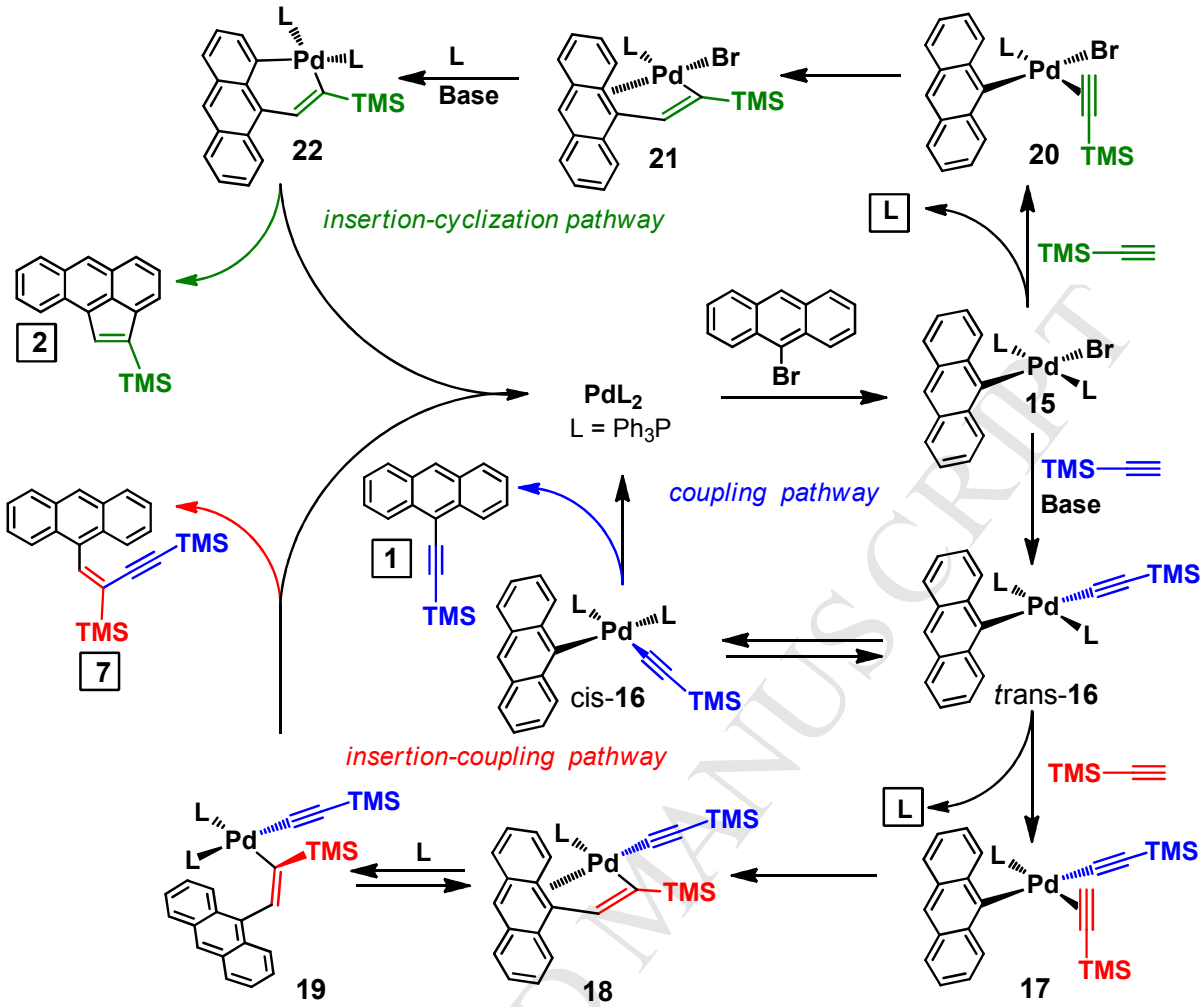
2.2. Mechanistic rationale

The observation of the enyne **9** was initially attributed to subsequent carbopalladation of the alkynyl-hydroxymethylnaphthalene, **8** [21]. Likewise, suspecting that formation of **11** arose by Pd-catalyzed addition of the alkyne to **10**, a commonly invoked scenario [28], the authors carried out a control reaction whereby **10** was treated with excess alkyne under the same reaction conditions, but only starting material was recovered [22]. Apparently, the alkynes **8** and **10** and enynes **9** and **11** are formed competitively rather than sequentially.

It is particularly relevant to note reports by Canty and co-workers whereby multiple head-to-tail alkyne insertions and concomitant cyclizations have been detected [29]. These observations were consistent with the view that such □daisy-chain″ processes occur via a

partial Sonogashira process involving incorporation of several PhC≡CH molecules into an arylpalladium intermediate. It is noteworthy that added CuI did not affect the reaction specificity.

We propose a plausible copper-free mechanism (Scheme 8) to account for the formation of all three products, **1**, **2** and **7** in roughly equal quantities. Upon the generation of bis-phosphine active species $(Ph_3P)_2Pd(0)$ oxidative addition of the 9-anthracenyl bromide gives the Pd(II) intermediate *trans*-**15**. At this point, palladium coordination to the alkyne enhances the base-promoted formation of the palladium acetylide, *trans*-**16**, which, after isomerization to *cis*-**16** and subsequent reductive elimination, leads to the ″normal□ coupling product 9-(trimethylsilylethynyl)anthracene, **1** (blue coupling pathway). However, *trans*-**16** can undergo a competitive process whereby coordination of the terminal alkyne, always present in excess, also occurs to give intermediate *trans*-**17**. Now, migratory insertion affords the anthracene coordinated alkenyl palladium intermediate **18** as the *cis*-isomer. However, upon recoordination of phosphine, the square planar Pd geometry is restored in **19**, and reductive elimination proceeds with retention of the olefin geometry to afford the enyne product **7** and regenerate the Pd(0) catalytic species (red insertion-coupling pathway). Of course, in the insertion-cyclization route, (green in Scheme 8) the intermediate, **15**, can also bind to the alkyne in an η^2 fashion giving complex **20** which, after migratory insertion, affords intermediate **21**. This species, having bromide, a good leaving group, attached to Pd, undergoes cyclopalladation to give **22** which is poised to yield aceanthrylene **2** and regenerate the Pd(0) species thus closing this catalytic cycle.



Scheme 8. Proposed mechanism for the generation of alkyne **1**, cyclic **2** and enyne *E*-**7** (L = Ph_3P). The presence of the trimethylsilyl substituent (CIP priority Si > C) leads to the designation of (*E)* stereochemistry in the final product **7**.

Clearly, these mechanisms have a common precursor intermediate, **15**, and the overall outcome of the process strongly depends on the ability of the ethynyl group to coordinate directly to the Pd(II) forming intermediates **17** and **20** in sufficient quantities, a factor that may also be dependent on the concentration of the phosphine; in the absence of such coordination only the □normal″ Sonogashira product, **1**, can be expected. Our attempts to obtain insertion or/and cyclization products in a very closely related reaction using

ethynylbenzene under various conditions were unsuccessful - entirely consistent with observations earlier reported by the Garcia-Garibay group [14].

One could perhaps rationalize this remarkable discrepancy in the behaviour of trimethylsilyl- and phenyl-alkynes in terms of the steric size of the substituents. In that case, *lower yields* of the insertion products **2** and **7** might be expected with the bulky TMS derivative. However, a perceptive reviewer raised the possibility that the difference in the building up of steric constraints between the TMS group and the neighbouring bromine (in **21**) or with the ethynyl ligand (in **18**) versus the lower strain engendered by the two-dimensional phenyl substituent may be a factor. The presence of the TMS group could destabilize the respective precursor intermediates, **20** and **17**, resulting in their higher kinetic energy, thus providing competition with the direct formation of the normal cross-coupling product.

We also suggest that a major cause of this difference lies in the electronic properties of the ethynyl fragment in both compounds. Our preliminary DFT level electron structure calculations indicate that the accessibility of the electron density associated with the carbon-carbon triple bond of the TMS system is significantly better than in the phenyl analogue (Figure 2). This electron density is critical to the ability of the ethynyl moiety to coordinate to the palladium in an η^2 fashion – the crucial process governing the formation of cyclization and insertion products **2** and **7**. In that case, the relatively reduced electron density in the triple bond may be sufficient to explain the dearth of such products in the reactions employing phenylacetylene.

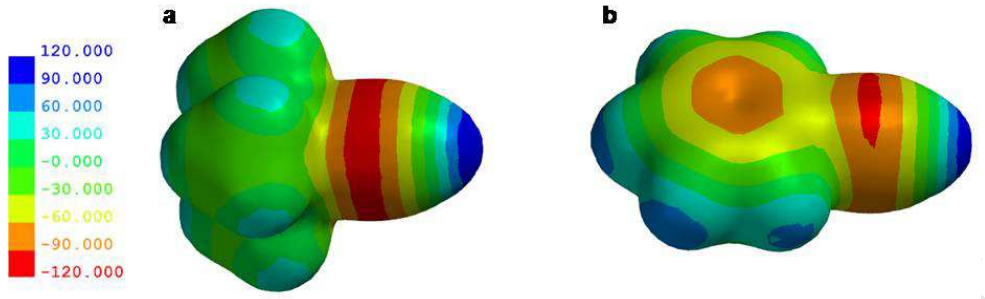


Figure 2. Representation of the charge distribution through an electrostatic potential map in: a) trimethysilylacetylene; b) phenylacetylene (blue - positive, red - negative potential, mV).

3. Conclusion

Under a range of experimental conditions, including a copper-free protocol, the reaction of 9-bromoanthracene and ethynyltrimethylsilane furnishes not only the anticipated Sonogashira product 9-(trimethylsilylethynyl)anthracene, **1**, or the earlier reported 2-(trimethylsilyl)aceanthrylene, **2**, but also the unexpected (*E*)-4-(9-anthracenyl)-1,3-bis(trimethylsilyl)-but-3-en-1-yne, **7,** whose structure was confirmed by X-ray crystallography.

A mechanistic rationale is proposed that invokes the formation of a common arylpalladium(II)bromide intermediate, **15**, that can follow each of three pathways. Specifically, (a) Sonogashira coupling, (b) an insertion-coupling leading to en-1-yne **7**, and (c) the insertion-cyclization route giving the aceanthrylene **2**. The distribution of electron density in the alkyne component is suggested to be the key factor affecting the balance between these three reaction pathways.

4. Experimental Section

4.1 General comments

All reactions were carried out under an atmosphere of dry nitrogen. Column chromatography was carried out on a Buchi Sepacor machine with UV absorbance detector

using silica gel particle size 40-63 mm. NMR spectra were acquired on a Varian VNMRS 500 MHz spectrometer, and assignments were based on standard ^{1}H-^{1}H and ^{1}H-^{13}C two-dimensional techniques. DFT calculations were carried out as described in previous reports from this laboratory [30].

4.2 Syntheses

Compounds **1, 2, 7**: To a stirred mixture of 9-bromoanthracene (193 mg, 0.75 mmol), triethylamine (0.8 mL) and bis(triphenylphosphine)palladium dichloride (10 mg, 0.015 mmol) in THF (2 ml) ethynyltrimethylsilane (0.22 mL, 1.5 mmol) was added, and the mixture was stirred at 70 ºC during 24 h, after which time the solvent and amine were removed under reduced pressure. The residue was separated by flash chromatography (silica, hexane-ethyl acetate) to give three main fractions containing: (a) 10 mg of unreacted 9-bromoanthracene (0.04 mmol); (b) a red oily material which was identified by NMR spectral comparison to literature data [14], as an equal mixture of **1** and **2** (135 mg, corresponding to ~ 32% yield of each); (c) a red solid, **7** (91 mg, 32%). ^{1}H NMR (500 MHz, $CDCl_3$) *atom numbering as in the X-ray structure*: δ 8.40 (1H, s, H_{10}), 8.07 (2H, m, H_1,H_8), 7.99 (2H, m, H_4,H_5), 7.79 (1H, s, H_{11}), 7.46 (2H, m, H_2,H_7), 7.44 (2H, m, H_3, H_6), 0.41 (9H, s, C=C-Si*Me*$_3$), -0.30 (9H, s, C≡C-Si*Me*$_3$). ^{13}C NMR (125 MHz): δ 144.4 (C_{11}), 132.8 (C_{12}), 132.6 (C_9), 131.2 (C_{4a},C_{8b}), 128.7 (C_{8a},C_{9a}), 128.5 (C_4,C_5), 126.8 (C_{10}), 126.5 (C_1,C_8), 125.1 (C_2,C_7), 125.0 (C_3,C_6), 105.1 (C_{14}), 105.0 (C_{13}), -0.4 (C≡C-Si*Me*$_3$), -1.65 (C=C-Si*Me*$_3$).

*4.3 X-ray crystal determination for **7***

A sample of **7** suitable for X-ray crystallography was obtained by slow evaporation of a cyclohexane-dichloromethane solution. Crystal data were collected at 100K using a Bruker SMART APEX CCD area detector diffractometer. A full sphere of reciprocal space was scanned by phi-omega scans. Pseudo-empirical absorption correction based on redundant

reflections was performed by the program SADABS [31]. The structures were solved by direct methods using SHELXS-97 [32] and refined by full matrix least-squares on F^2 for all data using SHELXL-97 [32]. Hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic thermal displacement parameters were fixed to 1.2 times (1.5 times for methyl groups) the equivalent one of the parent atom. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. CCDC 1866057 contains the supplementary crystallographic data for this paper. These data may be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This project emanated from research conducted with the financial support of the Synthesis and Solid State Pharmaceutical Centre (SSPC), funded by Science Foundation Ireland (SFI) under grant number 12/RC/2275. We also thank the UCD School of Chemistry and the Centre for Synthesis and Chemical Biology (CSCB) for the use of analytical facilities, and the reviewers for their helpful comments.

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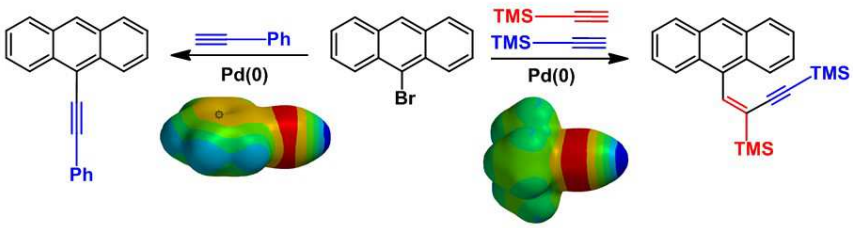
Graphical abstract



Coupling of bromoanthracene and substituted acetylenes using copper-free palladium catalysis conditions leads to unexpected diverse products: phenylacetylene yields a Sonogashira-type product (left), but the more electron-rich trimethylsilylacetylene gives, in two steps, an insertion product (right).

Highlights

- Sonogashira coupling of 9-bromoanthracene and TMS-acetylene yields three products
- They were identified as an alkyne, an aceanthrylene and an enyne
- Yields are very sensitive to reaction conditions and the identity of the catalyst
- The products are formed competitively, not consecutively
- A mechanistic rationale is offered to account for all the products