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Investigating Direct Alkynylation at the Bridgehead of Bicyclic Cages Using Silver(I) Acetylides

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Silver(I) acetylides facilitate direct carbon–carbon bond formation at the bridgehead position of adamantane, and in some instances related systems such as carborate anions and bicyclo[2.2.2]octanes. Substrate constraints along with attempts to further understand the underlying mechanism are presented.

Introduction

Direct acetylenic carbon–carbon bond formation at the bridgehead position of bicyclic cages is an area of synthetic methodology increasingly in demand fuelled by the rapidly growing field of nanotechnology, for example, AFM tips (e.g. **1**),[1] molecular rotors (e.g. **2**),[2] nanoporous architecture (e.g. **3**),[3] molecular connectors (e.g. **4**),[4] and polymeric nanomaterials[5] (Figure 1).

Not surprisingly, however, this type of direct methodology is poorly represented[6] in the chemical literature and even procedures which perform this task over multiple synthetic steps are limited.[7] It is in this context that we initiated a program aimed at addressing this deficiency in synthetic methodology, results of which are disclosed herein.[8]

In the view that silver(I) salts, such as silver acetate, have been used for converting adamantyl halides, e.g. **5**, to the corresponding acetates[9] **6**, and that silver(I) acetylides of type **7** react readily with methyl iodide to give methylated acetylenes like **8**[10] (Scheme 1), we reasoned that silver(I) acetylides, e.g. **7**, may well facilitate alkynylation at a bridgehead position, affording products of type **9**.

Organosilver(I) compounds are generally considered unstable to air and water, and often decompose to the corresponding organic dimer. Silver(I) acetylides, however, are an exception to this rule,[11] and are readily synthesised as air- and water-stable solids.[12] Surprisingly, investigations into this class are limited only to a handful of synthetic applications, for example, addition to aldehydes,[13] ketones,[13] acid chlorides,[12,14] pyridines[15] and nucleosides.[16]

The reaction of silver(I) phenylacetylide (**11**) with 1-bromoadamantane (**10**) was investigated in the first instance. The choice of solvent was found to be crucial as most silver(I) acetylides are notoriously insoluble in most organic solvents and require strongly coordinating aprotic solvents, such as, dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA) or pyridine for reaction. The use of either DMSO or HMPA as the solvent afforded gross mixtures, whereas pyridine at 100 °C gave, after 24–48 h, low yields of the desired product[17] **12** (Scheme 1). Substituting 1-bromoadamantane (**10**) with 1-iodoadamantane (**13**) increased the yield to 35%, although it was obvious that many side reactions involving pyridine were occurring. Attempts to prevent these side reactions with related solvents, such as lutidine and picoline, failed to improve the outcome. The use of triethylamine and tetramethylethylenediamine as the solvent gave no product, but *N*-methylmorpholine (NMM) increased the yield of **12** to 68%. It should be noted that triphenylphosphane–silver(I) phenylacetylide[18] gave no improvement, and copper(I) acetylide[19] afforded less than 5% of the product **12**. Gold(I) phenylacetylide was also considered, however, gold substrates do not have the desired stability as compared to those of silver.[20]

1-Iodoadamantane (**13**) was subsequently subjected to a reaction with a range of silver(I) arylacetylides utilizing the optimised conditions (Entries 1–9, Table 1), which afforded the corresponding adamantylalkynes in isolated yields ranging from 20 to 68%.

Disappointingly, silver(I) 4-bromophenylacetylide (Table 1, Entry 4) reacted poorly, affording less than 20% yield. Silver(I) 3-pyridylacetylide (Table 1, Entry 8) did not

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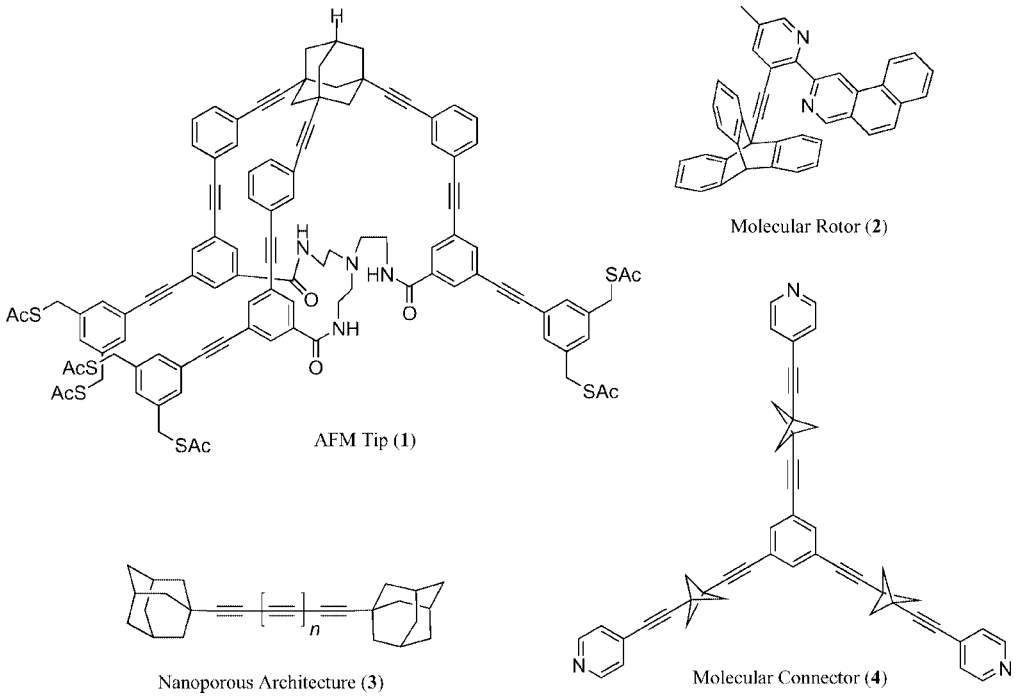
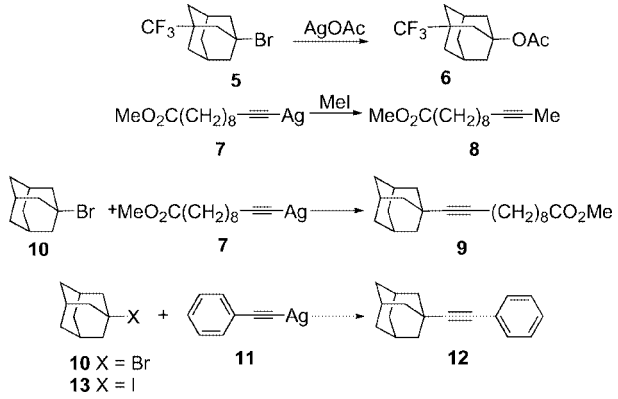


Figure 1. Examples of an AFM tip (**1**), molecular rotor (**2**), nanoporous architecture (**3**) and a molecular connector (**4**) containing bridgehead acetylenic bonds.



Scheme 1.

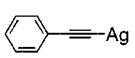
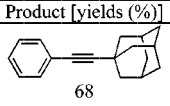
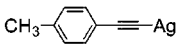
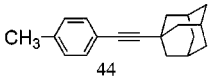
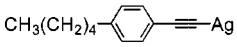
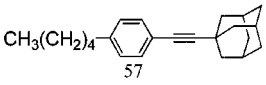
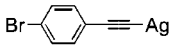
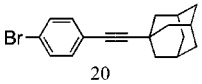
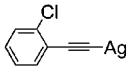
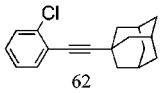
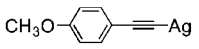
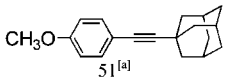
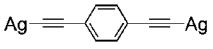
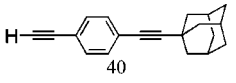
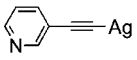
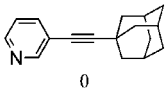
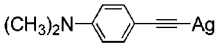
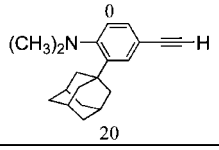
react, most likely due to the nitrogen donor group causing aggregation leading to oligomerisation. Silver(I) [4-(dimethylamino)phenyl]acetylide (**14**) (Table 1, Entry 9) did not effect bridgehead alkynylation but instead underwent electrophilic aromatic substitution (Entry 9) affording **15** as determined by X-ray crystallographic analysis (Figure 2).

This unexpected result raised the question as to whether the [4-(dimethylamino)phenyl]acetylene had actually been converted into the silver(I) derivative **14**. Conceivably either a silver nitrate complex of the acetylene (e.g. **16**) or silver(I) acetylide (**17**) (Figure 3) could have been formed instead which may well have facilitated the electrophilic aromatic substitution. That is, not producing a nucleophile in the case of **16** or perturbing nucleophilicity in the case of **17**.

In answer to this concern, selected silver(I) arylacetylides, including **14**, were subjected to elemental analysis and produced results within 10% of theoretical (Table 4, Exp. Sect.). This level of accuracy allows the structure of the derivative **14** to be depicted as shown, eliminating **16** and **17** as significant contributors to the reaction (Figure 3). IR data obtained from previously reported silver(I) acetylides are consistent with the literature.[19,21] Therefore, considering electrophilic arylation of adamantyl halides is well known,[22] we are inclined to propose that in the case of **14** the electron-rich aromatic ring prefers to undergo electrophilic aromatic substitution with 1-iodoadamantane (**13**), giving **18**, followed by hydrogen iodide induced deargentation affording **15** (Scheme 2).

Aliphatic and silylated silver(I) acetylides also react with adamantyl iodide under these conditions (Entries 1–4, Table 2) but much higher temperatures were required and the yields were found to be lower in these cases as compared to the arylacetylides. In the case of the silylated acetylide (Entry 4, Table 2) the resulting low yield is perhaps not surprising, as silver salts are known to deprotect silylated acetylenes.[23] It is not clearly understood, however, why the remaining silver(I) acetylides (Entries 1–3, Table 2) react poorly in comparison to the silver(I) arylacetylides. A possible explanation could be that at these elevated temperatures the silver(I) acetylides are undergoing deargentation affording the starting acetylene and not a dimer (Scheme 3) as increased dimer formation was not observed. Evidence for this unusual deargentation process was provided in the reaction of silver(I) (cyclohexenyl)acetylide (**19**) with adamantyl iodide (Entry 3, Table 2), which in addition to the

Table 1. Reaction of adamantyl iodide (**13**) with silver(I) arylacetylides.

Entry	Reactant	Product [yields (%)]
1		 68
2		 44
3		 57
4		 20
5		 62
6		 51[a]
7		 40
8		 0
9		 20

[a] Reaction performed at 90 °C.

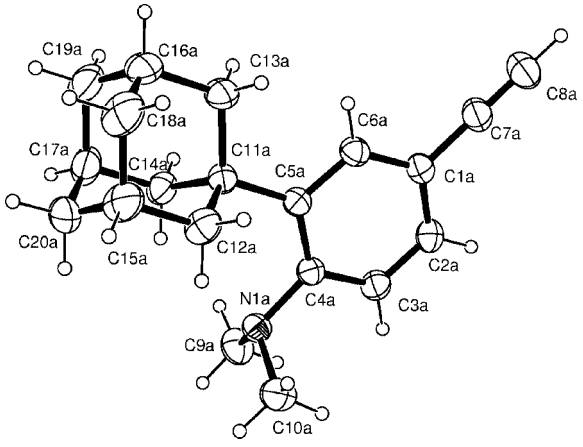


Figure 2. ORTEP3 drawing of compound **15** (30% probability ellipsoids).

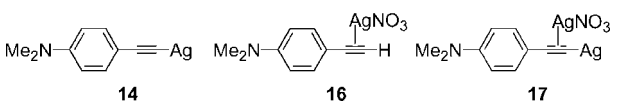
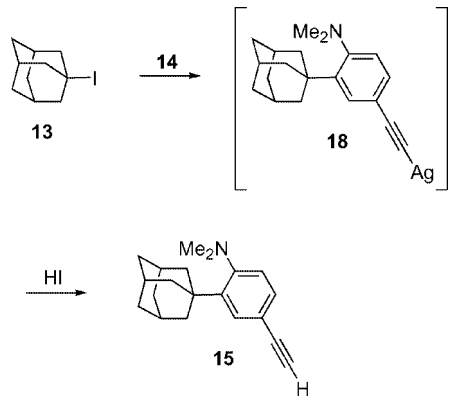


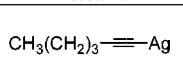
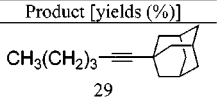
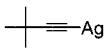
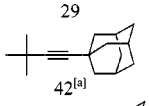
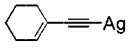
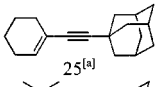
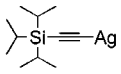
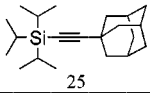
Figure 3. Possible complexes arising from the reaction of [4-(dimethylamino)phenyl]acetylene and silver nitrate.



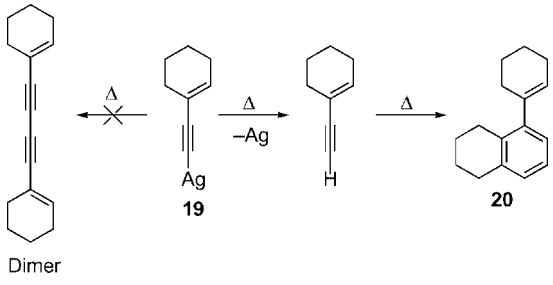
Scheme 2.

desired product afforded the tetrahydronaphthalene **20**. The tetrahydronaphthalene **20** is readily obtained from the known oligomerisation of (cyclohexenyl)acetylene[24] suggesting the presence of (cyclohexenyl)acetylene in our system. This can only occur through deargentation as no cyclohexenyl acetylene was present in the starting silver(I) (cyclohexenyl)acetylide (**19**) (Scheme 3).

Table 2. Reaction of adamantyl iodide with silver(I) aliphatic acetylides.

Entry	Reactant	Product [yields (%)]
1		 29
2		 42[a]
3		 25[a]
4		 25

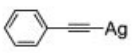
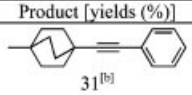
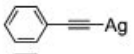
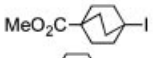
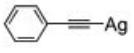
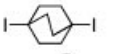
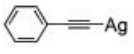
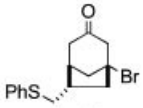
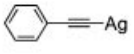
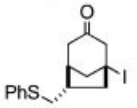
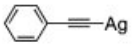
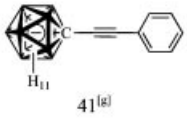
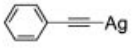
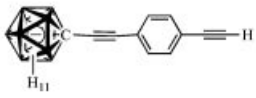
[a] Reaction conducted at 150–170 °C (pressure vessel).



Scheme 3.

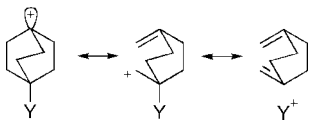
Three bicyclo[2.2.2]octane iodides were treated (Entries 1–3, Table 3) with silver(I) phenylacetylide. Only in the case of Entry 1 (Table 3) was product formation observed. This

Table 3. Reaction of bicyclic cage systems with silver(I) arylacetylides.[a]

Entry	Silver(I) arylacetylide	Bicyclic cages	Product [yields (%)]
1			 31[b]
2[c]			N/R
3[d]			N/R
4[e]			decomposition
5[e]			decomposition
6[f]			 41[g]
7[f]			N/R
8[f]			 <10[h]

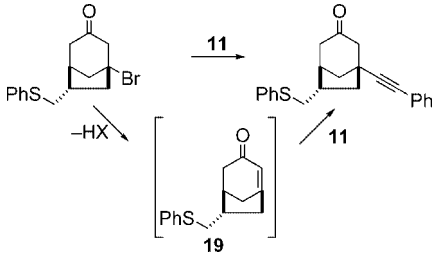
[a] Reactions performed in refluxing *N*-methylmorpholine. [b] Reaction conducted at 160 °C in pyridine. [c] 1-Iodo-4-methylcarbonylbicyclo[2.2.2]octane was synthesised according to Adcock.[32] [d] 1,4-Diiodobicyclo[2.2.2]octane was synthesised according to Kopecky.[33] [e] Bicyclo[3.2.1]octanes used in Entries 4 and 5 were prepared using the method of Kraus.[34] [f] Carborate anions used in Entries 6–8 were prepared according to the method of Michl.[35] [g] After the first reaction the crude material was subjected to two repeats. [h] Reaction mixture could not be purified by HPLC. Yield is estimated using decoupled ^{11}B NMR spectroscopy.

is consistent with the reaction proceeding through an electron-deficient intermediate; the extent of hyperconjugative stabilisation by the substituent at the 4-position is crucial and is demonstrated in Scheme 4. This shows the canonical structures which may contribute below for a carbocation intermediate. The same interaction can be readily envisaged for the equivalent radical but stabilisation would be greater for the carbocation. Importantly, the extent of hyperconjugative stabilisation in these systems has been shown to increase in the order $CO_2Me < I < CH_3 < H$, initially using ^{19}F NMR chemical shifts,[25–27] though it has only been recently that quantification of some of these parameters has been proposed.[28]



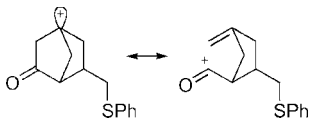
Scheme 4.

Bicyclo[3.2.1] systems were also investigated (Entries 4 and 5, Table 3), however, both substrates failed to yield product and no starting material could be recovered. This was somewhat unexpected as product can arise, mechanistically speaking, either from direct reaction at the bridgehead [carbocation, $S_{RN}1$ (see below)] or through elimination of HX to give the anti-Bredt system[29] (i.e. **19**) which could react with the silver(I) acetylide by a Michael-type addition[30] (Scheme 5). It should be stated, however, that when anti-Bredt enones are formed they usually undergo dimerisation to the cyclobutane[29,31] and this was not observed in our case. The presence of a ketone at this position may limit the extent of hyperconjugative stabilisation of an electron-deficient system (such as a carbocation) as demonstrated by canonical forms illustrated in Scheme 6.



Scheme 5.

In stark contrast to the bicyclo[2.2.2] and bicyclo[3.2.1] systems the carborate anion ($1\text{-I-}CB_{11}H_{12}^-$), which, other than containing a bridgehead position, is electronically different from adamantane,[36] was found to undergo slow but smooth reaction with silver(I) phenylacetylide. Although,



Scheme 6.

this was not observed for the more hindered permethylated derivative. Disilver(I) 4-phenyldiacetylide (**20**) also reacted with the carborate anion but only afforded the monosubstituted product in low yield as a mixture (Entry 8, Table 3). Considering this result was identical to that of the adamantyl iodide case (Entry 7, Table 1), that is monosubstitution, we questioned the validity of our material (**20**) but it was identical in all aspects to that reported.[19] This implies a deargentation process is occurring [discussed above (Scheme 3)] in contrast to the possibility that **21** might be the reactant (Figure 4).

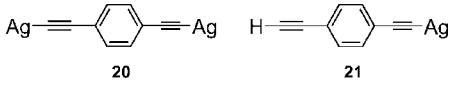
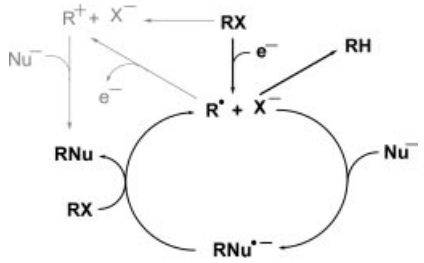


Figure 4. Bis- and mono silver(I) phenylacetylides of (4-ethynylphenyl)acetylene.

Initially it was considered that the addition of silver(I) acetylides to adamantyl halides proceeded through an $S_{RN}1$ mechanism [see Scheme 7 (part in black)],[37] which has been found to operate in the substitution of bridgehead halides.[38–44]



Scheme 7.

However, in order to gain a greater appreciation of the mechanism, the outcome of the reaction [silver(I) phenylacetylide with 1-iodoadamantane (**13**)] was observed (GCMS) under conditions that are known to affect radical pathways (i.e. photostimulation,[42,43,45–47] radical traps (e.g. TEMPO[48]), reversible electron acceptors [e.g. *p*-dinitrobenzene (DNB)][44,46,48]).

Both TEMPO and DNB increased the proportion of product (and decreased the extent of formation of the reduction product, adamantane) indicating a radical component to the reaction.[49] However, both these results also support the presence of a competing silver(I)-assisted carbocationic mechanism [see Scheme 7 (part in grey)].[6c,50] As TEMPO and DNB would be anticipated to have no effect on both the heterolysis of the adamantyl halide and the nucleophilic addition, the increase in the proportion of the substitution product suggests that the initiation of the radical process may be inhibited, resulting in reaction proceeding to a greater extent through the carbocationic pathway. (A nitrone, 2-phenyl-5,5-dimethyl-1-pyrroline 1-oxide, was also examined, but no useful information was obtained.) The reaction was also carried out in the presence of iron(II) bromide ($S_{RN}1$ stimulant[45,47]), which decreased the amount of coupled product and afforded 1-bromoadamantane (**10**) (ca. 35%) presumably, from reaction of bromide with the adamantyl radical. Conversely, dimethoxybenzene (DMB) (radical sensitiser[51]) increased the amount of the desired product **12**, while the amount of the reduction product stayed approximately the same.

Irrespective of the relative rates of the different processes discussed and the proportion of the substitution product **12** that arises through each of the mechanisms, both radical and polar processes are contributing to the outcome. This is consistent with the previous observations that there can be a fine balance between polar and radical pathways for bridgehead substitutions, as exemplified by the trimethylstannylation of bridgehead dihalogenated polycyclic alkanes.[52–56]

Conclusion

A novel carbon–carbon bond-forming protocol is reported for direct one-step alkynylation of the adamantyl ring system, which is also applicable to certain bicyclo[2.2.2]octane and carborate anions. It is our hope that this newly developed methodology will both aid those synthesising organic based nanotechnological devices, and encourage others to develop new procedures for this rapidly developing field.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV300 (300.13 MHz; 75.47 MHz), AV400 (400.13 MHz; 100.62 MHz) and a DRX500 (500.13 MHz; 125.77 MHz) in deuteriochloroform ($CDCl_3$) unless otherwise stated. Coupling constants are given in Hz and chemical shifts are expressed as δ values in ppm. ^{11}B shifts were referenced to $BF_3{\cdot}Et_2O$ [$B(OMe)_3$ at δ = 18.1 ppm] with an external reference contained in a capillary within the sample tube. High- and low-resolution EI mass spectroscopic data were obtained with a KRATOS MS 25 RFA. Electrospray negative and positive ion mass spectra were measured in methanol solution using a Hewlett Packard 5989 API/ES/MS instrument for carborane related compounds. Microanalyses were performed by the University of Queensland Microanalytical Service. Column chromatography was undertaken on silica gel (Flash Silica gel 230–400 mesh), with distilled solvents. *N*-Methylmorpholine was distilled from calcium hydride under argon and stored with predried sodium hydroxide pellets. Melting points were determined with a Fischer Johns Melting Point apparatus and are uncorrected. Acetylenes were purchased from the Aldrich Chem. Co. Silver(I) acetylides were stored in the freezer in the absence of light and generally lasted for many months. An HPLC system employing a reverse-phase C_{18} column (250 × 4.6 mm, 5 m) with methanol/water (containing a 1% AcOH/

0.7% Et_3N buffer) as the mobile phase was used for monitoring reactions, while larger columns of the same phase were used for semi-preparative separations.

Preparation of Silver(I) Acetylides: The method of Davis[12] was used (Table 4).

Table 4. Microanalytical results for selected silver(I) arylacetylides.

Silver(I) arylacetylide	Found (%)			Calculated (%)		
	C	H	N	C	H	N
[4-(Dimethylamino)phenyl]acetylide	44.07	3.81	6.07	47.65	4.00	5.56
Phenylacetylide	45.67	2.34	0	45.98	2.41	–
(1,4-Diethynylphenyl)acetylide	34.61	1.50	1.56	33.34	1.19	–
(4-Pentylphenyl)acetylide	55.97	5.52	0	55.94	5.42	–
(2-Chlorophenyl)acetylide	39.22	1.61	0	39.47	1.66	–
(4-Methoxyphenyl)acetylide	44.84	2.92	0	45.22	2.95	–

Representative Procedure: For Tables 1, 2, and 3: All subsequent reactions involving 1-iodoadamantane were performed on 0.38 mmol (100 mg) scale. Silver(I) phenylacetylide (159 mg, 0.76 mmol) was added to a solution of 1-iodoadamantane (100 mg, 0.38 mmol) in anhydrous *N*-methylmorpholine (3 mL) and the suspension heated at reflux under argon in the dark. After 16–24 h the solvent was removed under high vacuum; the residue diluted with dichloromethane (ca. 3 mL) and passed through celite. The filtrate was then washed with a solution (0.1 M) of sodium azide (20 mL), dried (Na_2SO_4) and the solvents evaporated. Column chromatography [petroleum spirit (40–60 °C)] of the crude on silica gel gave 1-(phenylethynyl)adamantane as a white solid (60 mg, 67%), which was recrystallised from petroleum spirit (colourless needles), m.p. 82–84 °C. ^{1}H NMR: δ = 1.70–1.74 (m, 6 H), 1.93–1.96 (m, 6 H), 1.96–2.03 (m, 3 H), 7.22–7.29 (m, 3 H), 7.36–7.40 (m, 2 H) ppm. ^{13}C NMR: δ = 28.0, 30.0, 36.4, 42.9, 79.3, 98.4, 124.1, 127.3, 128.1, 131.6 ppm. Near IR (neat) $\tilde{\nu}$ 2900, 2219, 1597, 1493, 1451, 753, 695 cm^{-1}. MS (EI): *m*/*z* = 236 (100) [M$^{+\cdot}$], 193 (10), 179 (60), 167 (7), 165 (11), 149 (9), 143 (8), 141 (7), 131 (8), 119 (5), 97 (7). HRMS (EI): [M]$^+$ $C_{18}H_{20}$ calcd. 236.1565, found: 236.1563. $C_{18}H_{20}$ (236.35): calcd. C 91.47, H 8.53; found: C 91.41, H 8.61.

Warning: Silver azide is potentially explosive, although, no instances occurred in our laboratories.

[(4-Methylphenyl)ethynyl]adamantane: Colourless crystals, (42 mg) 44% yield; m.p. 88–89 °C. ^{1}H NMR: δ = 1.68–1.70 (m, 6 H), 1.93–1.94 (m, 6 H), 1.95–1.98 (m, 3 H), 2.30 (s, 3 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR: δ = 21.4, 28.1, 30.0, 36.4, 42.9, 79.3, 97.6, 121.0, 128.8, 131.5, 137.2 ppm. Near IR (neat): $\tilde{\nu}$ = 2908, 2852, 2135, 1503, 1451, 805 cm^{-1}. MS (EI): *m*/*z* = 251 (12), 250 (55) [M$^{+\cdot}$], 194 (5), 193 (22), 178 (6), 156 (6), 115 (5), 91 (6). HRMS (EI): [M]$^+$ $C_{19}H_{22}$ calcd. M$^+$ 250.17215, found: 250.1718. $C_{19}H_{22}$ (250.38): calcd. C 91.14, H, 8.86; found C 91.38, H 9.11.

[(4-Pentylphenyl)ethynyl]adamantane: Colourless crystals, (66 mg) 57% yield; m.p. 71–76 °C. ^{1}H NMR: δ =0.86 (t, *J* = 7.2 Hz, 3 H), 1.24–1.38 (m, 4 H), 1.52–1.60 (m, 2 H), 1.69–1.70 (m, 6 H), 1.93–1.94 (m, 6 H) 1.96–1.97 (m, 3 H), 2.55 (t, *J* = 7.6 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.3 Hz, 2 H) ppm. ^{13}C NMR: δ = 14.0, 22.5, 28.0, 30.0, 31.0, 31.4, 35.7, 36.4, 42.9, 79.3, 97.6, 121.2, 128.2, 131.5, 142.3 ppm. Near IR (neat): $\tilde{\nu}$ = 2901, 2850, 2220, 1509, 1451, 811 cm^{-1}. MS (EI): *m*/*z* = 308 (5), 301 (39), 306 (100) [M$^{+\cdot}$], 250 (19), 249 (74), 193 (6), 179 (8), 178 (7), 165 (6), 155 (7), 153 (6), 141 (5), 128 (5), 115 (7), 91 (9), 79 (9), 43 (17), 41 (10). HRMS (EI): [M]$^+$ $C_{23}H_{30}$ calcd. 306.23475, found: 306.2345. $C_{23}H_{30}$ (306.48): calcd. C 90.13, H 9.87; found C 90.06, H 10.12.

[(4-Bromophenyl)ethynyl]adamantane: White solid, (24 mg) 20% yield; m.p. 78–80 °C. ^{1}H NMR: δ = 1.70 (br. t, *J* = 3.0 Hz, 6 H), 1.92 (m, 6 H), 1.97 (br. s, 3 H), 7.21 (d, *J* = 8.6 Hz, 2 H), 7.37 (d, *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR: δ = 28.0, 30.1, 36.4, 42.7, 78.4, 99.6, 121.4, 123.1, 131.3, 133.1 ppm. Near IR (neat) $\tilde{\nu}$ 2907, 2851, 2221, 1743, 1485, 1451, 1066, 1008, 819 cm^{-1}. MS (EI): *m*/*z* =(GCMS) 317 (24) [M$^{+\cdot}$], 316 (87), 315 (23), 314 (100), 259 (29), 257 (31), 222 (12), 220 (14), 193 (15), 192 (15), 191 (11), 180 (10), 179 (29), 178 (69), 167 (11), 165 (24), 152 (23), 141 (12), 139 (10), 126 (12), 115 (14), 96 (11), 94 (22), 93 (14), 91 (15), 89 (21), 82 (11), 79 (31), 79 (31), 77 (16), 44 (27), 41 (25), 39 (33). HRMS (EI): [M]$^+$ $C_{18}H_{19}Br$ calcd. 314.0670; found: 314.0681.

[(2-Chlorophenyl)ethynyl]adamantane: Colourless crystals, (64 mg) 62% yield; m.p. 63–64 °C. ^{1}H NMR: δ = 1.71 (br. s, 6 H), 1.98 (br. s, 9 H), 7.13–7.16 (m, 2 H) 7.33–7.35 (m, 1 H), 7.39–7.40 (m, 1 H) ppm. ^{13}C NMR: δ = 28.0, 30.4, 36.4, 42.7, 76.3, 104.0, 123.9, 126.2, 128.3, 129.0, 133.1, 135.8 ppm. Near IR (neat): $\tilde{\nu}$ = 2903, 2850, 2226, 1509, 1452, 751 cm^{-1}. MS (EI): *m*/*z* = 272 (39), 271 (23), 270 (100) [M$^{+\cdot}$], 227 (13), 215 (13), 213 (38), 179 (12), 178 (26), 165 (17), 115 (11), 94 (14), 93 (16), 91 (23), 86 (27), 84 (29), 80 (20), 79 (24), 77 (20), 55 (16), 51 (21), 49 (58), 44 (11), 41 (27), 40 (16), 39 (14). HRMS (EI): [M]$^+$ $C_{18}H_{19}Cl$ calcd. 270.1175, found: 270.1180. $C_{18}H_{19}Cl$ (270.80): calcd. C 79.84, H 7.07; found C 79.82, H 7.12.

[(4-Methoxyphenyl)ethynyl]adamantane: Reaction performed at 90 °C. Colourless crystals (52 mg), 51% yield; m.p. 112–114 °C. ^{1}H NMR: δ = 1.68–1.70 (m, 6 H), 1.92–1.93 (m, 6 H), 1.95–1.97 (m, 3 H), 3.77 (s, 3 H), 6.77 (d, *J* = 6.8 Hz, 2 H), 7.27 (d, *J* = 6.8 Hz, 2 H) ppm. ^{13}C NMR: δ = 28.0, 30.0, 36.4, 43.0, 55.2, 79.0, 96.8, 113.7, 116.2, 132.9, 158.9 ppm. Near IR (neat): $\tilde{\nu}$ 2906, 2849, 2139, 1604, 1508, 1452, 1244, 1087, 1026, 927, 824, 809 cm^{-1}. MS (EI): *m*/*z* = 267 (42), 266 (100) [M$^{+\cdot}$], 223 (8), 210 (14), 209 (61), 194 (7), 172 (10), 165 (9), 145 (6), 133 (6), 121 (7), 115 (6), 91 (9), 79 (6), 77 (6), 41 (8), 39 (5). HRMS (EI): [M]$^+$ $C_{19}H_{22}O$ calcd. 266.1671; found: 266.1673. $C_{19}H_{22}O$ (266.38): calcd. C 85.67, H 8.32; found C 85.74, H 8.53.

[(4-Ethynylphenyl)ethynyl]adamantane: Pale yellow oil, (20 mg, yield based on 2 equiv. 1-iodoadamantane) 40% yield. ^{1}H NMR: δ = 1.69–1.70 (m, 6 H), 1.92–1.94 (m, 6 H), 1.96–1.98 (m, 3 H), 3.10 (s, 1 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.36 (d, *J* = 8.5 Hz, 2 H) ppm. ^{13}C NMR: δ = 27.9, 30.1, 36.3, 42.7, 78.3, 79.0, 83.5, 100.6, 120.8, 124.7, 131.5, 131.8 ppm. Near IR (neat): $\tilde{\nu}$ 3206, 2907, 2853, 2361, 2221, 774 cm^{-1}. MS (EI): *m*/*z* = 261 (22), 260 (100) [M + 100], 204 (16), 203 (47), 202 (48), 189 (14), 166 (16), 165 (13), 151 (10), 139 (15), 115 (13), 91 (15). HRMS (EI): [M]$^+$ $C_{20}H_{20}$ calcd. 260.1565; found: 260.1564.

1-Adamantyl-2-dimethylamino-5-ethynylbenzene (15): Pale yellow crystals, (21 mg) 20% yield; m.p. 70–71 °C. ^{1}H NMR: δ = 1.73–1.74 (m, 6 H), 2.03–2.05 (m, 3 H), 2.12–2.14 (m, 6 H) 2.56 (s, 6 H), 2.99 (s, 1 H), 7.26 (d, *J* = 8.1 Hz, 1 H), 7.31 (dd, *J* = 8.1, 2.0 Hz, 1 H), 7.42 (d, *J* = 2.0 Hz, 1 H) ppm. ^{13}C NMR: δ = 29.2, 37.0, 37.5, 41.3, 47.2, 76.0, 84.3, 119.1, 125.4, 130.4, 131.2, 147.6, 156.5. MS (EI): *m*/*z* = 249 (7), 240 (6), 169 (8), 168 (40), 158 (7), 156 (6), 155 (7), 144 (7), 135 (5), 115 (6), 91 (6), 79 (6), 77 (6), 41 (9) ppm. HRMS (EI): [M]$^+$ $C_{20}H_{25}N$ calcd. 279.1987; found: 279.1989. $C_{20}H_{25}N$ (279.42): calcd. C 85.97, H 9.02, N 5.01; found: C 85.96, H 9.14, N 4.80.

1-Adamantyl-1-hexyne: Colourless oil, (24 mg) 29% yield. ^{1}H NMR: δ = 0.88 (t, *J* = 7.2 Hz, 3 H), 1.34–1.45 (m, 4 H), 1.64–1.65 (m, 6 H), 1.80–1.81 (m, 6 H), 1.91 (m, 3 H), 2.14 (t, *J* = 7.1 Hz, 2

H) ppm. ^{13}C NMR: δ = 13.6, 18.4, 21.8, 28.1, 29.4, 31.4, 36.4, 43.4, 78.8, 89.0 ppm. MS (EI): *m*/*z* = 217 (8), 216 (49) [M$^{+\cdot}$], 201 (38), 188 (6), 176 (6), 175 (26), 174 (10), 161 (5), 160 (26), 149 (6), 145 (10), 136 (10), 135 (100), 133 (7), 132 (5), 131 (15), 129 (5), 121 (10), 119 (10), 118 (7), 117 (25), 115 (8), 107 (7), 106 (7), 105 (13), 95 (8), 94 (10), 93 (18), 92 (9), 91 (35), 85 (5), 81 (17), 80 (13), 79 (27), 77 (14), 69 (6), 67 (11), 65 (6), 57 (10), 55 (14), 53 (7), 43 (9), 41 (24), 39 (11). HRMS (EI): [M]$^+$ $C_{16}H_{24}$ calcd. 216.1878; found: 216.1875.

1-Adamantyl-3,3-dimethyl-1-butyne: Colourless oil, (35 mg) 42% yield. ^{1}H NMR: δ = 1.15 (s, 9 H), 1.63–1.65 (m, 6 H), 1.77–1.79 (m, 6 H), 1.88–1.90 (m, 3 H) ppm. ^{13}C NMR: δ = 27.1, 28.2, 29.2, 31.6, 36.5, 43.5, 87.2, 87.5 ppm. MS (EI): *m*/*z* = 217 (6), 216 (28) [M$^{+\cdot}$], 202 (17), 201 (100), 173 (7), 160 (5), 159 (22), 145 (24), 143 (74), 121 (19), 119 (18), 117 (23), 115 (16), 109 (7), 108 (8), 107 (23), 106 (7), 105 (33), 103 (7), 95 (15), 94 (10), 93 (35), 92 (11), 91 (66), 81 (20), 80 (10), 79 (57), 63 (6), 57 (14), 55 (25), 53 (23), 52 (5), 51 (12). HRMS (EI): [M]$^+$ $C_{16}H_{24}$ calcd. 216.1878; found: 216.1878.

1-Adamantyl-2-(cyclohex-1-enyl)ethyne: Pale yellow oil, (23 mg) 25% yield. ^{1}H NMR: δ = 1.50–1.62 (m, 4 H), 1.65–1.67 (m, 6 H), 1.83–1.85 (m, 6 H), 1.91–1.93 (m, 3 H), 2.02–2.08 (m, 4 H), 5.97–5.99 (m, 1 H) ppm. ^{13}C NMR: δ = 21.6, 22.4, 25.6, 28.1, 29.8, 29.8, 36.4, 43.1, 80.9, 95.7, 120.9, 133.2 ppm. Near IR (neat) $\tilde{\nu}$ 2908, 2852, 2206, 1450, 773 cm^{-1}. MS (EI): *m*/*z* = 241 (8), 240 (38) [M$^{+\cdot}$], 212 (8), 183 (7), 141 (5), 135 (24), 129 (7), 128 (5), 115 (6), 105 (7), 93 (6), 91 (12), 79 (10), 77 (8), 67 (5), 55(6), 41 (10), 38 (7), 36 (24). HRMS (EI): [M]$^+$ $C_{18}H_{24}$ calcd. 240.1878; found: 240.1879.

1-Adamantyl-2-(triisopropylsilyl)ethyne: Opaque oil, (30 mg) 25% yield. ^{1}H NMR: δ = 0.96–1.04 (m, 3 H), 1.02 (d, *J* = 7.0 Hz, 18 H), 1.65–1.66 (m, 6 H), 1.85–1.86 (m, 6 H), 1.89–1.93 (m, 3 H) ppm. ^{13}C NMR (C_6D_6): δ = 11.7, 19.1, 28.4, 30.8, 36.7, 43.5, 78.0, 118.8 ppm. MS (EI): *m*/*z* = 316 (1) [M$^{+\cdot}$], 274 (9), 273 (38), 203 (11), 74 (23). HRMS (EI): [M]$^+$ $C_{21}H_{36}Si$ calcd. 316.2586; found: 316.2583.

4-Methyl-1-(2-phenylethynyl)bicyclo[2.2.2]octane: 1-Iodo-4-methylbicyclo[2.2.2]octane[57] (100 mg, 0.4 mmol) and silver(I) phenylacetylide (250 mg, 1.2 mmol) were dissolved in anhydrous pyridine (4 mL) under argon. The mixture was heated at 150 °C in the dark for 24 h in a pressure vessel. On cooling the solvent was removed in vacuo, the residue dissolved in dichloromethane, and filtered through a pad of celite. The solvent was removed and the residue purified by silica gel column chromatography (petroleum spirits) affording the title compound as a white solid, (28 mg) 31% yield. M.p. 56–57 °C ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3 H), 1.36–1.41 (m, 6 H), 1.78–1.83 (m, 6 H), 7.21–7.25 (m, 3 H), 7.33–7.36 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.0, 27.3, 28.2, 32.7, 32.9, 80.3, 97.5, 124.1, 127.3, 128.1, 131.6 ppm. Near IR (neat) $\tilde{\nu}$ 2941, 2901, 2856, 2228, 1596, 1454, 754, 692 cm^{-1}. MS (EI): *m*/*z* = 224 (56) [M$^+$], 196 (10), 195 (55), 167 (11), 165 (13), 155 (19), 154 (100), 153 (41), 152 (12), 126 (10), 115 (21), 77 (11). HRMS (EI): [M]$^+$ $C_{17}H_{20}$ calcd. 224.1565; found: 224.1571.

Representative Procedure for Carborate Anions: Silver(I) phenylacetylide (32 mg, 0.15 mmol) was added to a solution of 1-I-$CB_{11}H_{11}^-$ Cs^+ (30 mg, 0.075 mmol) in anhydrous *N*-methylmorpholine (1.5 mL) and the suspension was heated at reflux under argon in the dark. After 16 h the solvent was removed under high vacuum, the residue diluted with dichloromethane (ca. 3 mL) and passed through celite. The solvent was removed under high vacuum and the above procedure was repeated twice. The crude solid was purified by reverse phase HPLC. The white residue was then dissolved in 4 M HCl (25 mL) and extracted with diethyl ether (3 × 15 mL). Water (15 mL) was added to the combined ether layers and the diethyl ether was evaporated. The aqueous solution was filtered and treated with excess tetraphenylphosphonium chloride (ca. 1 equiv.) to yield a white solid precipitate affording tetraphenylphosphonium 1-phenylethynylcarba-*closo*-dodecaborate as an off-white solid (18 mg, 41%).

Note: This product was then converted into the cesium salt by ion exchange to avoid aromatic signal overlap in the NMR spectra.

Cesium 1-Phenylethynylcarba-*closo*-dodecaborate: ^{1}H NMR [Varian Inova-500, $(CD_3)_2CO$]: δ = 7.24 (m, 3 H), 7.42 (m, 2 H) ppm. ^{11}B NMR [Varian VXR-300, $(CD_3)_2CO$]: δ = –6.8 (s, 1 B), –13.21 (s, 5 B), –16.24 (s, 5 B) ppm. ^{13}C NMR [Varian Inova-400, $(CD_3)_2CO$]: δ = 68.2, 78.6, 83.6, 122.6, 128.8, 129.1, 132.1 ppm. Near IR (KBr pellet): $\tilde{\nu}$ 3010, 2945, 2890, 2850, 2250, 1410, 1375, 1292, 908 cm^{-1}. HRMS (ESI) [M$^-$] calcd. 245.2275, found 245.2289.

Cesium [(4-Ethynylphenyl)ethynyl]carba-*closo*-dodecaborate: This product could not be purified from the starting material (1-I-$CB_{11}H_{11}^-$ Cs^+) and the yield is estimated at <10%. Reported spectroscopic data have had starting material resonances removed. ^{11}B NMR [Bruker AV400, $(CD_3)_2CO$]: δ = –6.7 (s, 1 B), –13.2 (s, 5 B), –16.3 (s, 5 B) ppm. HRMS (ESI) [M$^-$] calcd. 269.2276; found: 269.2255.

X-ray Crystallography: Crystallographic data were collected with an Enraf–Nonius CAD4 diffractometer with graphite-monochromatized Mo-K_α radiation, λ = 0.71073 Å operating in the ω-2θ scan mode. Data reduction and corrections for decay and absorption were performed with the WINGX package.[58] Structures were solved by direct methods with SHELXS and refined by full-matrix refinement on F^2 with SHELXL.[59] The molecular structure diagram was produced with the program ORTEP3.[60]

CCDC-615077 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1-Adamantyl-2-dimethylamino-5-ethynylbenzene (15): $C_{20}H_{25}N$, *M* = 279.41, triclinic, space group $P\bar{1}$, *a* = 10.413(4), *b* = 11.300(2), *c* = 22.497(5) Å, α = 78.81(2), β = 79.50(3), γ = 74.69(2)°, *V* = 2481(1) Å^3, *Z* = 6, $D_{calcd.}$ = 1.122 g cm^{-3}, *T* = 293 K, μ = 0.064 mm^{-1}, *F*(000) = 912, colourless prism (0.60 × 0.40 × 0.33 mm); total reflections 9133, unique reflections 8618 (R_{int} = 0.0266). Final refinement: data/restraints/parameters 8618/0/568, goodness-of-fit on F^2 = 1.01, R_1 = 0.0516 [for 3989 obs. reflns $I > 2\sigma(I)$], wR_2 = 0.1667 (all data).

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