COMMUNICATIONS

DOI: 10.1002/adsc.201200086

Gold-Catalyzed Synthesis of Dibenzopentalenes – Evidence for Gold Vinylidenes

A. Stephen K. Hashmi,[a,]* Marcel Wieteck,[a] Ingo Braun,[a] Pascal Nösel,[a]
Linda Jongbloed,[a] Matthias Rudolph,[a] and Frank Rominger[a,b]

[a] Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: (+49)-6221-54-4205
(http://www.hashmi.de); e-mail: hashmi@hashmi.de
[b] Crystallographic investigation

Received: December 20, 2011; Revised: February 1, 2012; Published online: February 23, 2012

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201200086.

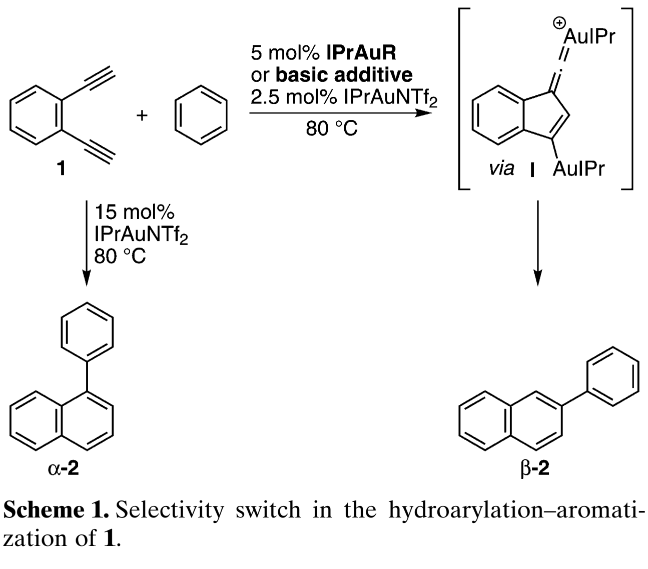
Abstract: A series of easily accessible arene-1,2-diynes, bearing one aryl substituent on one of the alkynyl groups, is readily converted to dibenzopentalenes in good yields by gold(I) catalysts. The participation of gold acetylides could be proven by the direct conversion to the corresponding *gem*-diaurated dibenzopentalenes with a gold catalyst. From an experiment with a gold acetylide complex and stoichiometric amounts of the gold "catalyst" the corresponding *gem*-diaurated complex of a dibenzopentalene could be obtained and characterized by X-ray crystal structure analysis. Labelling studies with deuterated alkynes show the expected deuteration of the two remaining positions of the pentalene core. All this provides evidence for a dual activation mode of the reaction and gold(I) vinylidene complexes as intermediates of the catalytic cycle.

Keywords: alkynes; dibenzopentalenes; digold compounds; extended π-systems; gold catalysis; gold vinylidenes; vinylgold intermediates

In the highly active field of homogeneous gold-catalyzed reactions,[1] only recently, have diynes been employed as starting materials. The general reactivity pattern of the reactions is based on an initial attack of an intra- or intermoleculary offered nucleophile onto one of the triple bonds. The so-formed intermediate en-yne systems then undergo further transformations that lead to highly complex molecular structures.[2]

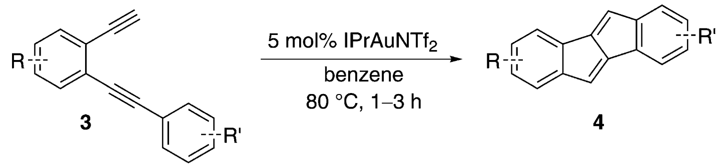
We have just contributed a new hydroarylating aromatization of arene-diynes (Scheme 1).[3] This reaction is mechanistically highly interesting as it proves that the participation of gold acetylides can induce completely different selectivities in gold-catalyzed reactions. It also proves a double activation by the gold catalyst. By using basic additives or organo-gold compounds, the gold acetylide formation could be enforced and instead of the expected α-phenylnaphthalenes α-**2**, we observed the *exclusive* formation of isomeric β-phenylnaphthalene β-**2**. The results from that very complex mechanistic study indicate that so far only scarcely mentioned gold vinylidene species are involved in the reaction mechanism.[4]

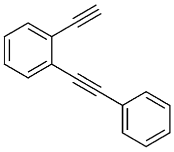
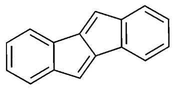
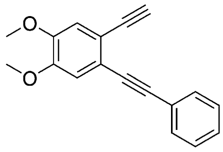
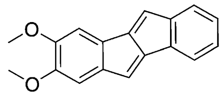
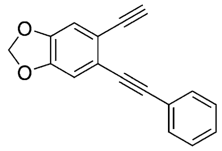
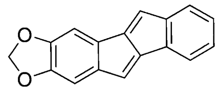
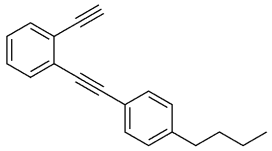
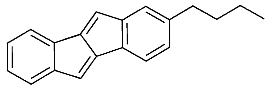
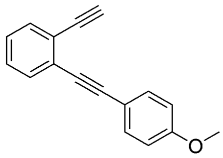
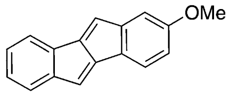
Here we report another exciting aspect of this completely new type of gold-catalyzed conversion. When we investigated arene-diynes possessing one terminal and one aryl-substituted alkyne, completely different products were obtained. No incorporation of the aro-



Scheme 1. Selectivity switch in the hydroarylation–aromatization of **1**.

Table 1. Gold-catalyzed dibenzopentalene synthesis.



Entry	Substrate		Product		Yield
1		**3a**		**4a**	54%
2		**3b**		**4b**	68%
3		**3c**		**4c**	62%
4		**3d**		**4d**	60%
5		**3e**		**4e**	80%

matic solvent into the product was detected. Instead the second aromatic system serves as nucleophile which allows the fast synthesis of symmetrical and unsymmetrical dibenzopentalenes. The starting materials for our substrates were obtained *via* an efficient two-step synthesis from 2-bromobenzaldehydes.[5] Together with the new gold-catalyzed protocol this offers an extremely straightforward access towards this interesting class of molecules which are of interest in the context of materials science (especially for those that are unsymmetrical).[6]

The results are summarized in Table 1. Simple 1-ethynyl-2-(phenylethynyl)benzene could be transformed into dibenzopentalene **4a**, and only traces of intermolecular benzene addition products were detected *via* GC-MS (entry 1). The reason for the only moderate yield is based on the low solubility of the resulting product. Thin layer chromatography and *in situ* ^{1}H NMR spectroscopy of the reaction indicated a clean conversion, but a part of the sensitive material was obviously lost during the purification by column chromatography. Most fortunately, we were able to collect crystals that were suitable for an X-ray crystal structure analysis.[7] Figure 1 shows the solid state structure which unambiguously confirms the dibenzopentalene architecture. Substitutions at the central ar-

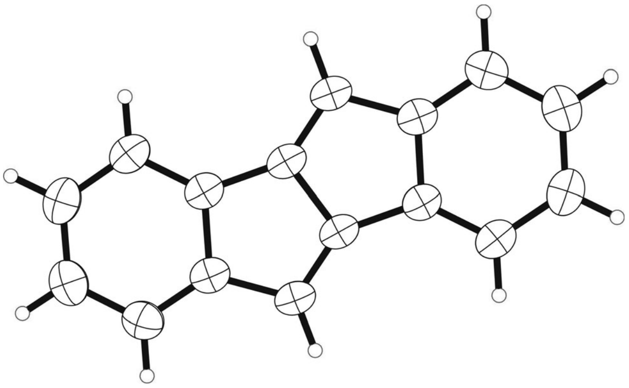


Figure 1. Solid state molecular structure of **4a**.

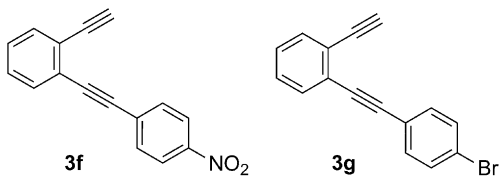
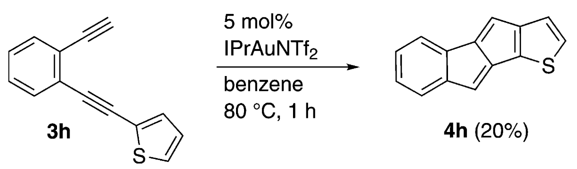


Figure 2. Non-reacting substrates.



Scheme 2. Reaction of the thiophene-containing substrate **3h**.

omatic system of the starting diynes were also tolerated (entries 2 and 3) and the yields for the unsymmetrical dibenzopentalenes **4b** and **4c** were also acceptable. Next we investigated a differently substituted aromatic system at the non-terminal alkyne. While electron-rich systems delivered selective conversions and good yields (entries 4 and 5), no conversions were observed for the electron-deficient compounds **3f** and **3g** (Figure 2). A first example for a heterocyclic system could also be obtained (Scheme 2). The thiophene-substituted alkyne **3h** delivered product **4h**, but due to the sensitivity of the product the yield was low.

In addition to systems with mono-cyclic aromatic nucleophiles, we also tested an anthracene moiety in the substrate (**5**, Scheme 3). Now the *ortho*-positions at the central ring are blocked, but the *peri*-positions can serve as nucleophiles. This conversion was very slow, which can be explained by the shielded environment of the non-terminal alkyne. An unselective reaction was observed, the intermolecular benzene addition pathway was favoured and 24% of β-naphthalene **6** could be separated from several ill-defined by-products. The certain structural assignment of product **6** was possible by an X-ray solid state structure analysis (Figure 3).[7] In addition to the benzene addition, minute amounts of another crystalline compound were also isolated. An X-ray crystal structure analysis of a single crystal revealed an astonishing dimer of **7** with an interesting helical distortion (Figure 4).[7] Mechanistically, at this moment it remains unclear how this product of an oxidative coupling was formed, but indeed attack of the *peri*-position of the anthracene moiety onto the intermediate gold vinylidene must have taken place. Then dimerization of the resulting gold species and reduction of the gold might furnish dimer **8**.[8]

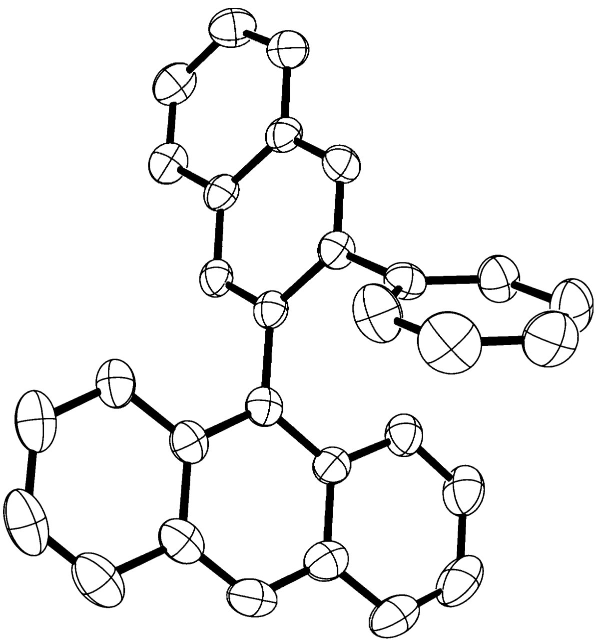
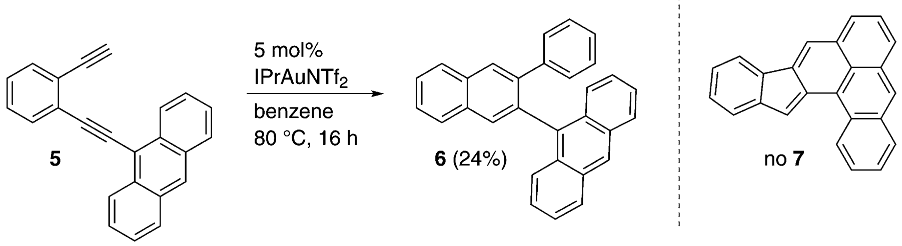


Figure 3. Solid state molecular structure of **6**.

Next we focussed on mechanistic insights. We prepared mono-acetylide complex **9** and subjected it to stochiometric amounts of activated catalyst (Scheme 4). Interestingly, the formation of a *gem*-diaurated species from the mono-aurated diyne was detected. This *gem*-diaurated compound **10** precipitated quickly. During purification by recrystallization from benzene/DCM, we were able to obtain single crystals suitable for a X-ray structure analysis.[7] The solid state structure proves that the two gold atoms are positioned at the benzylic carbon of the non-aromatic double bond of the dibenzopentalene system



Scheme 3. Intermolecular benzene addition pathway of **5**.

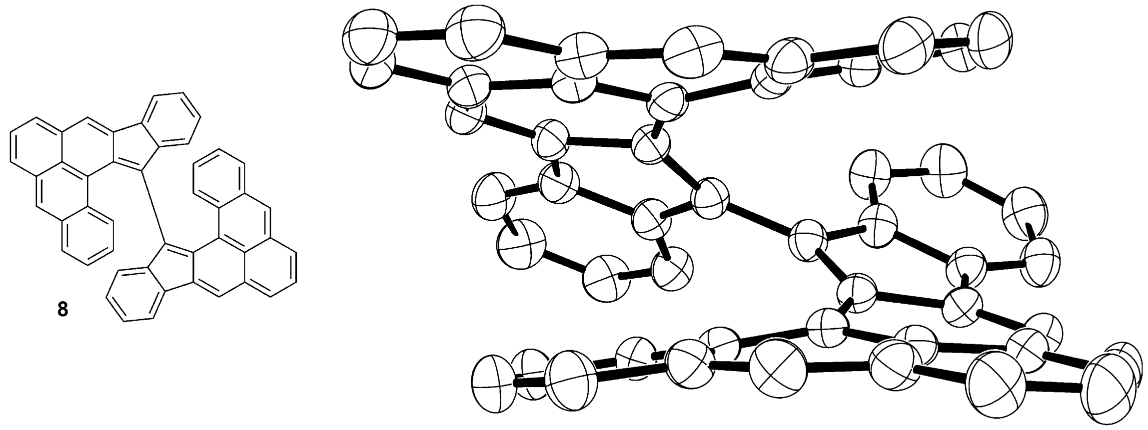
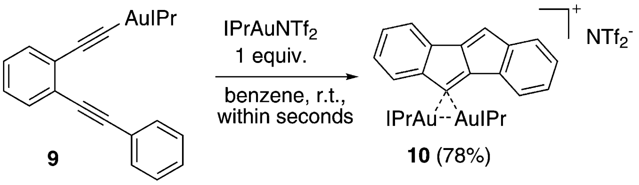


Figure 4. Homo-coupled dimer **8** and its solid state molecular structure.



Scheme 4. Synthesis of *gem*-diaurated compound **10**.

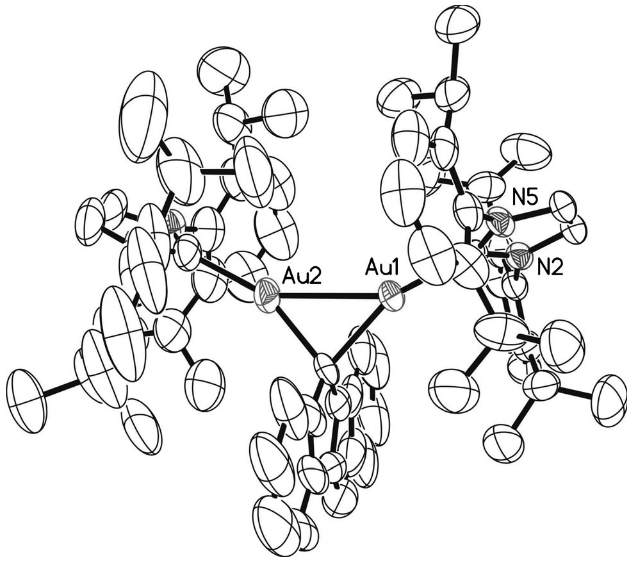
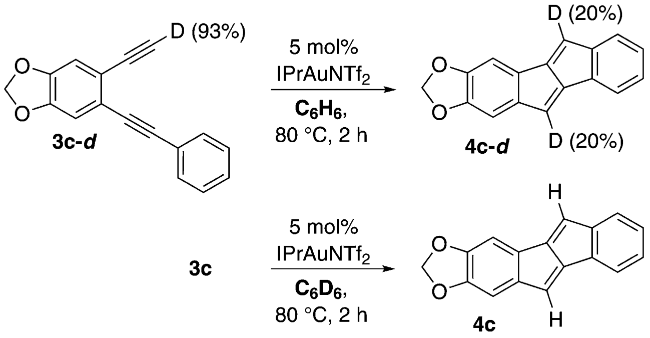


Figure 5. Solid state molecular structure of **10**.

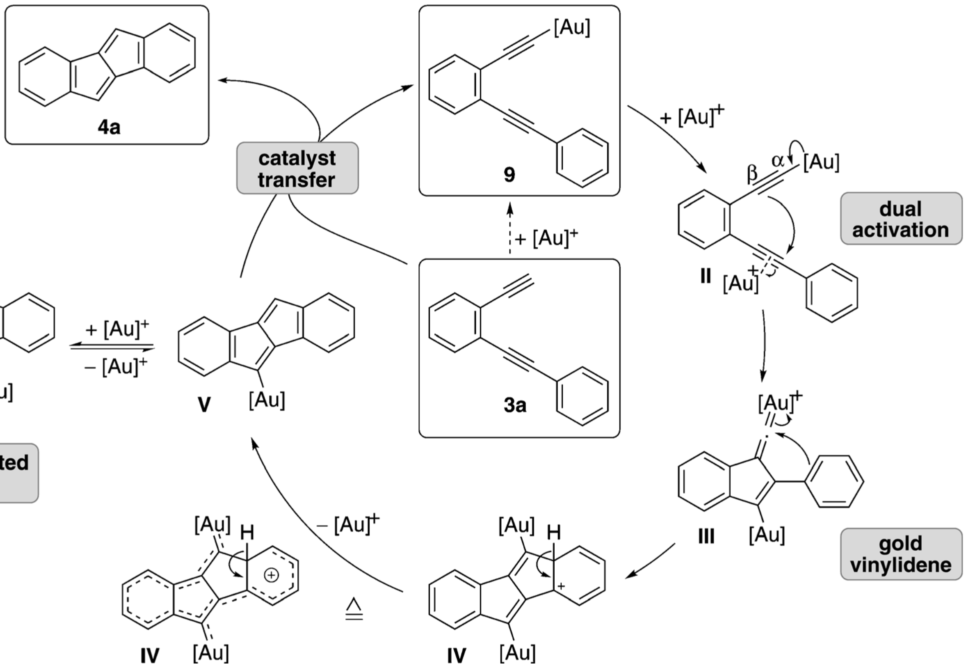


Scheme 5. Isotopic labelling experiments.

(Figure 5). The gold–gold distance of 274.6 pm is slightly shorter than in the case of the corresponding *gem*-diaurated species derived from the intermolecular benzene addition reaction (276.1 pm).[3] This strong aurophilic interaction is well in the range of other reported diaurated species.[9]

To gain further mechanistic insights, the substrate **3c-*d*** with a deuterated alkyne was transformed to the corresponding dibenzopentalene (Scheme 5). The analysis of the NMR spectra showed that part of the deuterium labelling of the terminal alkyne was transferred to the product. Remarkably, both of the central double bonds were partially deuterated. The inverse experiment with undeuterated **3c** in deuterated benzene afforded solely non-deuterated **4c**. This means that the partial loss of deuterium in **4c-*d*** must be derived from traces of water in the solvent, no exchange processes with the solvent benzene are involved.

The suggested mechanism is depicted in Scheme 6. The catalytic cycle starts with the formation of gold acetylide complex **9**. For further transformation the second alkyne must be activated by π-coordination of a molecule of activated gold catalyst (no reaction took place when acetylide **9** was heated in benzene without activated catalyst). This dual σ/π-activation mode initiates the formation of highly reactive gold vinylidene complex **III**. Its formation can be explained by a nucleophilic attack of the β-carbon of gold acetylide **II** onto the π-coordinated alkyne in a 5-*endo-dig* fashion. Gold vinylidene **III** is most probably the same intermediate for the dibenzopentalene reaction as well as for the β-naphthalene pathway.[3] This is indicated by the competing benzene addition which was observed with anthracene derivate **5**.



Scheme 6. Mechanistic rationale.

Furthermore, for some of the reactions, traces of byproducts showing a mass increase of a benzene molecule could be detected *via* GC/MS. If the reaction proceeds *via* the dibenzopentalene pathway, the intramoleculary offered nucleophilic aromatic carbon atom attacks the highly electrophilic *sp*-carbon centre of the vinylidene species. After that, one of the two gold atoms gets proto-demetallated from the proton that is released during rearomatization. In analogy to the organo-gold intermediate of the naphthalene reaction, an equilibrium exists between mono-gold species **V** and *gem*-diaurated species **10**. As *gem*-diaurated species **10** binds the active cationic catalyst, the reaction rates should be strongly dependent on this equilibrium (apart from the need for the dual activation, this might be one reason for the need of elevated reaction temperatures at all). Finally, the last step consists of a catalyst transfer. The final product is released and a new molecule of starting material is activated *via* σ-coordination of a gold atom.[10]

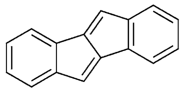
In conclusion, the generation of a reactive gold vinylidene *via* σ/π -dual activation of diyne substrates offers a complete new reactivity pattern which should allow a whole series of valuable gold-catalyzed cyclizations in the future. If one considers the similarities between the intramolecular addition of aromatic substituents that leads to the dibenzopentalene systems and our recently published formation of β-naphthalenes *via* the intermolecular pathway; even if the products are totally different; the elementary reaction steps (acetylide formation, dual activation of the substrate, gold vinylidene formation, nucleophilic trapping, formation of a *gem*-diaurated system and catalyst transfer) for both of the systems are closely related.

Experimental Section

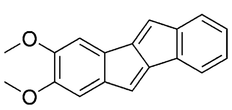
General Procedure for the Gold Catalyzed Conversions

One equivalent of the diyne was dissolved in benzene and the Au catalyst (5 mol%) was added. The reaction mixture was stirred at 80 °C until complete conversion (monitored by TLC). The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography or recrystallized.

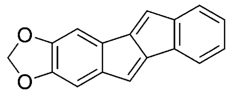
Indeno[2,1-*a*]indene (4a): According to the general procedure IPrAuNTf$_2$ (10.7 mg, 12.4 μmol, 5 mol%) was added to a solution of 1-ethynyl-2-(phenylethynyl)benzene **3a** (50.0 mg, 247 μmol) in benzene (2 mL) and stirred at 80 °C for 2 h. The crude product was purified by flash column chromatography on silica gel (PE) and gave **4a** as a red solid; yield: 27.0 mg (134 μmol, 54%). The ^{1}H NMR data corresponds to that reported in literature.[9]. ^{1}H NMR [(CD$_3$)$_2$SO, 300 MHz]: $\delta = 6.64$ (s, 2 H), 6.87–6.91 (m, 4 H), 6.94–6.98 (m, 2 H), 7.10–7.15 (m, 2 H).



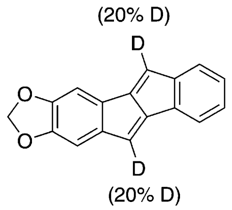
2,3-Dimethoxyindeno[2,1-*a*]indene (4b): According to the general procedure IPrAuNTf$_2$ (8.25 mg, 9.53 μmol, 5 mol%)



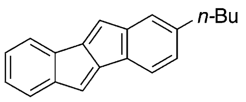
was added to a solution of 1-ethynyl-4,5-dimethoxy-2-(ethynylphenyl)benzene **3b** (44.0 mg, 168 μmol) in benzene (2 mL) and stirred at 80 °C for 1 hour. The crude product was purified by flash column chromatography on silica gel (PE/EA = 20:1) and gave **4b** as a beige solid; yield: 30.0 mg (114 μmol, 68%); decomp.: 280 °C; R_f (PE/EA = 2:1) = 0.35. IR (KBr): $\tilde{\nu}$ = 2946, 1633, 1481, 1288, 1216, 1102, 1031, 855, 756 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 3.83 (s, 3H), 3.84 (s, 3H), 6.20 (s, 1H), 6.23 (s, 1H), 6.48 (s, 1H), 6.67 (s, 1H), 6.77–6.81 (m, 3H), 6.89–6.96 (m, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 56.1 (q), 56.2 (q), 107.6 (d), 108.1 (d), 121.5 (d), 122.9 (d), 125.3 (d), 126.1 (d), 127.1 (d), 127.9 (s), 127.9 (d), 135.3 (s), 143.5 (s), 148.3 (s), 148.4 (s), 149.1 (s), 149.9 (s), 150.3 (s); MS (EI+, 70 eV): m/z (%) = 263 (21) [M+H]$^+$, 262 (100) [M]$^+$, 247 (27), 219 (29), 218 (12), 204 (13), 176 (15), 162 (6), 151 (8), 131 (7), 113 (5), 88 (8); HR-MS (EI+, 70 eV): m/z = 262.0974 [C$_{18}$H$_{14}$O$_2$]$^+$, calcd. for C$_{18}$H$_{14}$O$_2$ (262.30): 262.0994.



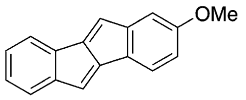
Indeno[2′,1′:1,2]indeno[5,6-*d*][1,3]dioxole (4c): According to the general procedure IPrAuNTf$_2$ (8.79 mg, 10.2 μmol, 5 mol%) was added to a solution of of 5-ethynyl-6-(ethynylphenyl)-1,3-benzodioxole **3c** (50.0 mg, 203 μmol) in benzene (2 mL) and stirred at 80 °C for 1 hour. The crude product was purified by flash column chromatography on silica gel (PE/EA = 20:1) and gave **4c** as a bronze solid; yield: 30.0 mg, (122 μmol, 60%); decomp.: 230 °C; R_f (PE/EA = 10:1) = 0.48. IR (KBr): $\tilde{\nu}$ = 2960, 2924, 1610, 1494, 1467, 1432, 1363, 1205, 1129, 1043, 934, 861, 748 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 5.24 (s, 2H), 5.66 (d, J = 1.7 Hz, 1H), 5.72 (d, J = 1.7 Hz, 1H), 6.17 (s, 1H), 6.44 (s, 1H), 6.52–6.57 (m, 1H), 6.62–6.69 (m, 2H), 6.75–6.80 (m, 1H); MS (EI+, 70 eV): m/z (%) = 247 (17) [M+H]$^+$, 246 (100) [M]$^+$, 190 (5), 189 (12), 188 (18), 187 (20), 162 (5), 151 (8), 123 (8), 113 (5), 94 (6); HR-MS (EI+, 70 eV): m/z = 246.0698 [C$_{17}$H$_{10}$O$_2$]$^+$, calcd. for C$_{17}$H$_{10}$O$_2$ (246.26): 246.0681.



Indeno[2′,1′:1,2]indeno[5,6-*d*][1,3]dioxole (4c-*d*): According to the general procedure IPrAuNTf$_2$ (8.79 mg, 10.2 μmol, 5 mol%) was added to a solution of of 5-ethynyl-6-(ethynylphenyl)-1,3-benzodioxole **3c-*d*** (50.0 mg, 203 μmol) in benzene (2 mL) and stirred at 80 °C for 1 hour. The crude product was purified by flash column chromatography on silica gel (PE/EA = 20:1) and gave **4c-*d*** as a bronze solid; yield: 30.0 mg (122 μmol, 60%). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ = 5.23 (s, 2H), 5.64–5.66 (m, 0.8H), 5.70–5.73 (m, 0.8H), 6.17 (s, 1H), 6.43 (s, 1H), 6.52–6.56 (m, 1H), 6.63–6.67 (m, 2H), 6.75–6.79 (m, 1H).

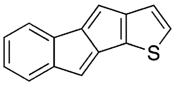


2-Butylindeno[2,1-a]indene (4d): According to the general procedure IPrAuCl (6.21 mg, 10.0 μmol, 5 mol%) and AgPF$_6$ (2.78 mg, 11.0 μmol, 5.5 mol%) were added to a solution of 1-[(4-butylphenyl)ethynyl]-2-ethynyl-benzene **3d** (50.0 mg, 194 μmol) in benzene (2 mL) and stirred at 50 °C for 3 h. The product precipitated, was dissolved in hot benzene and filtrated to remove the silver salt. Evaporation of the solvent gave **4d** as a red solid; yield: 40.0 mg (116 μmol, 60%); decomp.: 230 °C; R_f (PE/EA = 10:1) = 0.58. IR (KBr): $\tilde{\nu}$ = 2958, 2928, 2856, 1455, 1434, 898, 828, 751, 731, 471 cm^{-1}; UV-Vis (DCM): λ_{max} (log ε) = 279 (4.81), 290 (4.92), 394 (4.01), 419 nm (4.11); ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.88 (t, J = 7.3 Hz, 3H), 1.21–1.36 (m, 2H), 1.40–1.53 (m, 2H), 2.33 (t, J = 7.3 Hz, 2H), 5.98 (d, J = 1.5 Hz, 1H), 6.06 (d, J = 1.5 Hz, 1H), 6.53 (s, 1H), 6.57 (d, J = 7.5 Hz, 1H), 6.59–6.53 (m, 1H), 6.66–6.71 (m, 2H), 6.84 (d, J = 7.5 Hz, 1H), 6.85–6.90 (m, 1H); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 14.1 (q), 22.6 (t), 33.6 (t), 36.0 (t), 122.3 (d), 122.4 (d), 123.3 (d), 124.1 (d), 125.6 (d), 126.5 (d), 127.3 (d), 127.4 (d), 128.6 (d), 133.1 (s), 135.5 (s), 143.6 (s), 149.7 (s), 150.0 (s), 151.1 (s), 151.2 (s); MS (EI+, 70 eV): m/z (%) = 259 (17) [M+H]$^+$, 258 (84) [M]$^+$, 251 (19), 215 (100), 201 (25), 151 (53), 113 (39); HRMS (EI+, 70 eV): C$_{20}$H$_{18}$ (258.36), [C$_{20}$H$_{18}$]$^+$ calc.: 258.1409, found: 258.1405.



2-Methoxyindeno[2,1-a]indene (4e): According to the general procedure IPrAuCl (6.83 mg, 11.0 μmol, 5 mol%) and AgPF$_6$ (3.03 mg, 12.0 μmol, 5.5 mol%) were added to a solution of 1-ethynyl-2-[(4-methoxyphenyl)ethynyl]benzene **3e** (50.0 mg, 216 μmol) in benzene (2 mL) and stirred at 80 °C for 2 h. The product precipitated, was washed with petroleum ether and ethyl acetate and dissolved in tetrahydrofuran to remove the silver salt after filtration. Evaporation of the solvent gave **4e** as a brown solid: yield: 40.0 mg (172 μmol, 80%); decomp.: 250 °C; R_f (PE/EA = 10:1) = 0.38. IR (KBr): $\tilde{\nu}$ = 2960, 1602, 1586, 1486, 1431, 1289, 1248, 1225, 1183, 1133, 1036, 855, 819, 751, 729 cm^{-1}; UV-Vis (DCM): λ_{max} (log ε) = 280 (5.14), 296 (5.22), 393 (3.27), 471 nm (3.23); ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 3.26 (s, 3H), 5.91 (s, 2H), 6.21 (dd, J = 8.1, 2.4 Hz, 1H), 6.42 (d, J = 2.4 Hz, 1H), 6.59–6.64 (m, 1H), 6.65–6.74 (m, 2H), 6.82 (d, J = 8.1 Hz, 1H), 6.86–6.91 (m, 1H); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 55.0 (q), 108.1 (s), 110.7 (d), 111.8 (d), 122.4 (d), 123.0 (d), 123.1 (d), 124.4 (d), 125.7 (d), 127.0 (d), 128.8 (d), 135.4 (s), 149.3 (s), 151.2 (s), 152.7 (s), 161.3 (s), one carbon atom not visible; MS (EI+, 70 eV): *m/z* (%) = 233 (19) [M + H]$^+$, 232 (100) [M]$^+$, 217 (32), 189 (46), 187 (9); HR-MS (EI+, 70 eV): *m/z* = 232.0877 [$C_{17}H_{12}O$]$^+$, calcd. for $C_{17}H_{12}O$ (232.28): 232.0888.

Thiopheneindeno[2,1-*a*]indene (4h): According to the general procedure IPrAuCl (7.45 mg, 12.0 μmol, 5 mol%)



and $AgPF_6$ (3.29 mg, 13.0 μmol, 5.5 mol%) were added to a solution of 2-[(2-ethynylphenyl)ethynyl]thiophene **3h** (50.0 mg, 240 μmol) in benzene (2 mL) and stirred at 80 °C for 2 h. The crude product was purified by flash column chromatography on silica gel (PE) and gave **4h** as a yellow solid; yield: (10.4 mg, 50.0 μmol, 20%); decomp.: 230 °C; R_f (PE/EA = 10:1) = 0.51. IR (KBr): $\tilde{\nu}$ = 3070, 1715, 1636, 1456, 1254, 831, 759, 748, 690, 649 cm^{-1}; UV-Vis (DCM): λ_{max} (log ε) = 282 (4.44), 289 (4.44), 393 (3.74), 471 nm (3.69); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.98 (d, *J* = 1.8 Hz, 1 H), 6.06 (d, *J* = 1.8 Hz, 1 H), 6.50 (d, *J* = 4.8 Hz, 1 H), 6.61–6.72 (m, 4 H), 6.91 (d, *J* = 4.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.1 (d), 121.3 (d), 122.1 (d), 123.7 (d), 128.0 (d), 128.6 (d), 128.8 (d), 136.6 (s), 145.0 (s), 150.3 (s), 152.1 (s), 157.0 (s), 2 carbon atoms not visible; MS (EI+, 70 eV): *m/z* (%) = 209 (17) [M + H]$^+$, 208 (100) [M]$^+$, 164 (8), 163 (16), 151 (8), 113 (7); HR-MS (EI+, 70 eV): *m/z* = 208.0361 [$C_{14}H_8S$]$^+$, calcd. for $C_{14}H_8S$ (208.28): 208.0347.

Acknowledgements

LJ is grateful to the EU for an Erasmus fellowship. The authors thank Umicore AG & Co. KG for the generous donation of gold salts.

References

[1] a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; b) E. Jiménez-Núnez, A. M. Echavarren, *Chem. Commun.* **2007**, 333–346; c) R. Skouta, C.-J. Li, *Tetrahedron* **2008**, *64*, 4917–4938; d) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; e) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; f) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; g) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766–1775; h) S. Sengupta, X. Shi, *ChemCatChem* **2010**, *2*, 609–619; i) C. Nevado, *Chimia* **2010**, *64*, 247–251; j) A. Corma, A. Leyva-Pérez, M. J. Sabater, *Chem. Rev.* **2011**, *111*, 1657–1712; k) A. S. K. Hashmi, M. Rudolph, *Chem. Commun.* **2011**, *47*, 6536–6544.

[2] a) T. Shibata, R. Fujiwara, D. Takano, *Synlett* **2005**, *13*, 2062–2066; b) A. Odedra, C.-J. Wu, T. B. Pratap, C.-W. Huang, Y.-F. Ran, R.-S. Liu, *J. Am. Chem. Soc.* **2005**, *127*, 3406–3412; c) C. H. Oh, A. Kim, W. Park, D. I. Park, N. Kim, *Synlett* **2006**, *17*, 2781–2784; d) J. Zhao, C. O. Hughes, F. D. Toste, *J. Am. Chem. Soc.* **2006**, *128*, 7436–7437; e) J.-J. Lian, P.-C. Chen, Y.-P. Lin, H.-C. Ting, R.-S. Liu, *J. Am. Chem. Soc.* **2006**, *128*, 11372–11373; f) C. H. Oh, A. Kim, *New J. Chem.* **2007**, *31*, 1719–1721; g) J.-J. Lian, R.-S. Liu, *Chem. Commun.* **2007**, 1337–1339; h) A. Das, H.-K. Chang, C.-H. Yang, R.-S. Liu, *Org. Lett.* **2008**, *10*, 4061–4064; i) H.-S. Yeom, J.-E. Lee, S. Shin, *Angew. Chem.* **2008**, *120*, 7148–7151; *Angew. Chem. Int. Ed.* **2008**, *47*, 7040–7043; j) C. Zhang, D.-M. Cui, L.-Y. Yao, B.-S. Wang, Y.-Z. Hu, T. Hayashi, *J. Org. Chem.* **2008**, *73*, 7811–7813; k) J.-M. Tang, T.-A. Liu, R.-S. Liu, *J. Org. Chem.* **2008**, *73*, 8479–8483; l) C. H. Oh, A. Kim, *Synlett* **2008**, *5*, 777–781; m) S. Md. A. Sohel, R.-S. Liu, *Chem. Soc. Rev.* **2009**, *38*, 2269–2281; n) C. Sperger, A. Fiksdahl, *Org. Lett.* **2009**, *11*, 2449–2452; o) J. Meng, Y.-L. Zhao, C.-Q. Ren, Y. Li, Z. Li, Q. Liu, *Chem. Eur. J.* **2009**, *15*, 1830–1834; p) Y. Odabachian, X. F. Le Goff, F. Gagosz, *Chem. Eur. J.* **2009**, *15*, 8966–8970; q) C. H. Oh, S. Karmakar, *J. Org. Chem.* **2009**, *74*, 370–374; r) S. Kramer, J. L. H. Madsen, M. Rottländer, T. Skrydstrup, *Org. Lett.* **2010**, *12*, 2758–2761; s) C. A. Sperger, A. Fiksdahl, *J. Org. Chem.* **2010**, *75*, 4542–4553; t) D.-M. Cui, Y.-N. Ke, D.-W. Zhuang, Q. Wang, C. Zhang, *Tetrahedron Lett.* **2010**, *51*, 980–982; u) A. S. K. Hashmi, M. Bührle, M. Wölfle, M. Rudolph, M. Wieteck, F. Rominger, W. Frey, *Chem. Eur. J.* **2010**, *16*, 9846–9854; v) K. Hirano, Y. Inaba, T. Watanabe, S. Oishi, N. Fujii, H. Ohno, *Adv. Synth. Catal.* **2010**, *352*, 368–372; w) C. Sperger, L. H. S. Strand, A. Fiksdahl, *Tetrahedron* **2010**, *66*, 7749–7754; x) Y. Chen, G. Li, Y. Liu, *Adv. Synth. Catal.* **2011**, *353*, 392–400; y) P. Nun, S. Dupuy, S. Gaillard, A. Poater, L. Cavallo, S. P. Nolan, *Catal. Sci. Technol.* **2011**, *1*, 58–61; z) A. S. K. Hashmi, T. Häffner, M. Rudolph, F. Rominger, *Chem. Eur. J.* **2011**, *17*, 8195–8201; aa) K. Hirano, Y. Inaba, N. Takahashi, M. Shimano, S. Oishi, N. Fujii, H. Ohno, *J. Org. Chem.* **2011**, *76*, 1212–1227; ab) D.-H. Zhang, L.-F. Yao, Y. Wie, M. Shi, *Angew. Chem.* **2011**, *123*, 2631–2635; *Angew. Chem. Int. Ed.* **2011**, *50*, 2583–2587.

[3] A. S. K. Hashmi, I. Braun, M. Rudolph, F. Rominger, *Organometallics* **2012**, *31*, 644–661.

[4] a) V. Mamane, P. Hannen, A. Fürstner, *Chem. Eur. J.* **2004**, *10*, 4556–4575; b) E. Soriano, M. Contelles, *Organometallics* **2006**, *25*, 4542–4553; c) I. V. Seregin, V. Gevorgyan, *J. Am. Chem. Soc.* **2006**, *128*, 12050–12051; d) V. Lavallo, G. D. Frey, S. Kouzar, B. Donnadieu, G. Bertrand, *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 13569–13573; e) I. V. Seregin, A. W. Schammel, V. Gevorgyan, *Tetrahedron* **2008**, *64*, 6876–6883; f) Y. Xia, A. S. Dudnik, Y. Li, V. Gevorgyan, *Org. Lett.* **2010**, *12*, 5538–5541.

[5] See Supporting Information for the detailed experimental procedures.

[6] For alternative routes towards dibenzopentalenes see: a) K. Brand, *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 3071–3077; b) C. T. Blood, R. P. Linstead, *J. Chem. Soc.* **1952**, 2263–2268; c) M. P. Cava, R. Pohlke, M. J. Mitchell, *J. Org. Chem.* **1963**, *28*, 1861–1863; d) V. E. Müller, K. Munk, P. Ziemek, M. Sauerbier, *Justus Liebigs Ann. Chem.* **1968**, *713*, 40–48; e) V. E. Müller, K. Munk, H.-

G. Fritz, M. Sauerbier, *Justus Liebigs Ann. Chem.* **1969**, *723*, 76–82; f) D. Hellwinkel, H.-J. Hasselbach, F. Lämmerzahl, *Angew. Chem.* **1984**, *96*, 713–714; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 705–706; g) M. Ballester, J. Castañer, J. Riera, O. Armet, *J. Org. Chem.* **1986**, *51*, 1100–1105; h) M. R. Anderson, R. F. C. Brown, K. J. Coulston, F. W. Eastwood, A. Ward, *Aust. J. Chem.* **1990**, *43*, 1137–1150; i) Y. Badrieh, J. Blum, I. Amer, K. P. C. Vollhardt, *J. Mol. Catal.* **1991**, *66*, 295–312; j) Y. Badrieh, A. Greenwald, H. Schumann, J. Blum, *Chem. Ber.* **1992**, *125*, 667–674; k) R. F. C. Brown, F. W. Eastwood, N. R. Wong, *Tetrahedron Lett.* **1993**, *34*, 3607–3608; l) J. Blum, W. Baidossi, Y. Badrieh, R. E. Hoffmann, H. Schumann, *J. Org. Chem.* **1995**, *60*, 4738–4742; m) M. Chakraborty, C. A. Tessier, W. J. Youngs, *J. Org. Chem.* **1999**, *64*, 2947–2949; n) J. Yang, M. V. Lakshmikantham, M. P. Cava, D. Lorcy, J. R. Bethelot, *J. Org. Chem.* **2000**, *65*, 6739–6742; o) D. V. Preda, L. T. Scott, *Org. Lett.* **2000**, *2*, 1489–1492; p) J. K. Kendall, H. Shechter, *J. Org. Chem.* **2001**, *66*, 6643–6649; q) M. Saito, M. Nakamura, T. Tajima, M. Yoshioka, *Angew. Chem.* **2007**, *119*, 1526–1529; *Angew. Chem. Int. Ed.* **2007**, *46*, 1504–1507; r) M. Saito, M. Nakamura, T. Tajima, *Chem. Eur. J.* **2008**, *14*, 6062–6068; s) G. Babu, A. Orita, J. Otera, *Chem. Lett.* **2008**, *37*, 1296–1297; t) T. Kawase, A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, *Chem. Eur. J.* **2009**, *15*, 2653–2661; u) Z. U. Levi, T. D. Tilley, *J. Am. Chem. Soc.* **2009**, *131*, 2796–2797; v) H. Zhang, T. Karasawa, H. Yamada, A. Wakamiya, S. Yamaguchi, *Org. Lett.* **2009**, *11*, 3076–3079; w) J. L. Jeffrey, R. Sarpong, *Tetrahedron Lett.* **2009**, *50*, 1969–1972; x) D. Wang, T. Michinobu, *J. Polym. Sci. Part A* **2010**, *49*, 72–81; y) T.-C. Wu, C.-C. Tai, H.-C. Tiao, M.-Y. Kuo, Y.-T. Wu, *Chem. Eur. J.* **2011**, *17*, 1930–1935. For a review about synthesis and reactions of dibenzopentalenes, see: z) M. Saito, *Symmetry* **2010**, *2*, 950–969.

[7] CCDC 859060 (**4a**), CCDC 859061 (**6**), CCDC 859062 (**8**) and CCDC 859063 (**10**) contain 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.

[8] a) A. S. K. Hashmi, M. C. Blanco, D. Fischer, J. W. Bats, *Eur. J. Org. Chem.* **2006**, 1387–1389; b) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592–597; c) A. S. K. Hashmi, T. D. Ramamurthi, M. H. Todd, A. S.-K. Tsang, K. Graf, *Aust. J. Chem.* **2010**, *63*, 1619–1626.

[9] Au−Au distances for *gem*-diaurated compounds found in the literature: 272.7–284.6 pm. Average value (7 structures): 277.8 pm; a) A. N. Nesmeyanov, E. G. Perevalova, K. I. Grandberg, D. A. Lemenovskii, T. V. Baukova, O. B. Afanassova, *J. Organomet. Chem.* **1974**, *65*, 131–144; b) V. G. Andrianov, Y. T. Struchkov, E. R. Rossinskaya, *J. Struct. Chem.* **1974**, *15*, 65–72; c) H. Schmidbaur, Y. Inoguchi, *Chem. Ber.* **1980**, *113*, 1646–1653; d) R. Usón, A. Laguna, E. J. Fernández, A. Mendia, P. G. Jones, *J. Organomet. Chem.* **1988**, *350*, 129–138; e) K. A. Porter, A. Schier, H. Schmidbaur, *Organometallics* **2003**, *22*, 4922–4927; f) M. Osawa, M. Hoshino, D. Hashizume, *Dalton Trans.* **2008**, 2248–2252; g) G. Seidel, C. W. Lehmann, A. Fürstner, *Angew. Chem.* **2010**, *122*, 8644–8648; *Angew. Chem. Int. Ed.* **2010**, *49*, 8466–8470.

[10] For a detailed discussion of the catalyst transfer step, see ref.[3]