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Gold Catalysis: First Applications of Cationic Binuclear Gold(I) Complexes and the First Intermolecular Reaction of an Alkyne with a Furan

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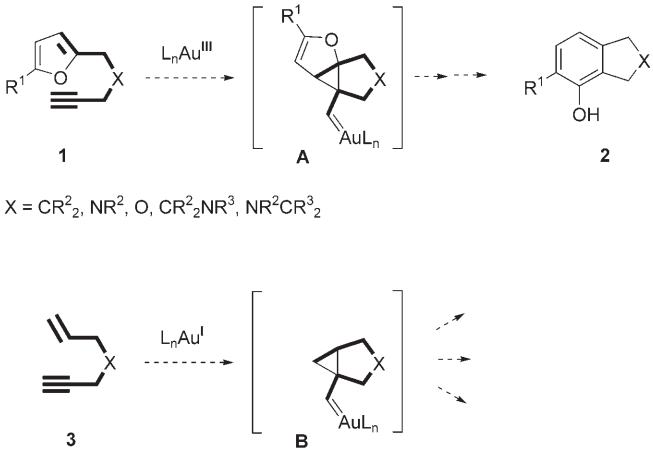
Abstract: Reaction of the cationic binuclear gold(I) complex $[(Ph_3PAu)_2Cl]BF_4$ with ω-alkynylfurans furnished phenols as the major product and anellated furans as the side-products. The analogous trimesitylphosphane complex $[(Mes_3PAu)_2Cl]BF_4$ selectively afforded only the phenols. The latter catalyst then enabled the first intermolecular gold-catalyzed phenol synthesis.

Keywords: alkynes; arenes; furans; gold; homogeneous catalysis



Scheme 1. The analogy of the gold-catalyzed phenol synthesis and the gold-catalyzed enyne cyclization.

The first step of the gold-catalyzed phenol synthesis,[1] an isomerization reaction transforming an ω-alkynylfuran **1** to an anellated phenol **2** by breaking four bonds and forming four new bonds, is the intramolecular reaction of the alkyne-gold complex with the olefin part of the furan ring to form intermediate **A**, as later demonstrated by most elegant work of Echavarren.[2,3]

The 1,n-enyne substructure of **1** (shown in bold in Scheme 1) underlines the analogy to the beautiful extension of the 1,n-enyne cycloisomerization chemistry subsequently developed by Echavarren[4] and others[5] on the basis of gold catalysts; the first step to the cyclopropylcarbene complex **B** is in complete analogy to the formation of **A**, the reaction pathways divert only in the subsequent steps.

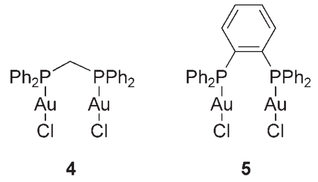
While the phenol synthesis so far was only reported to be catalyzed by gold(III)[1,2] and related d^8-complexes,[1b,1e,2] the enyne cyclization was reported to proceed with gold(I) complexes.[4] Due to the similarity of the first step this is difficult to understand, especially since many other gold-catalyzed reactions can be induced by complexes in both oxidation states[6] and theoretical calculations for other gold-catalyzed reactions indicated that the barriers of activation do not differ much for both oxidation states.[7]

Specifically, $AuCl_3$,[1,2] Au^{III}-pyridine complexes (the latter being the most efficient catalysts for this transformation known so far)[1e] and a number of other d^8-complexes of other transition metals[1b,1e,2] were reported to catalyze this transformation, but with gold(I) in the form of $Et_3PAuCl/AgBF_4$ we had initially only observed a slow, sluggish and unselective reaction, which might have been based on traces of Au^{III}.[1a] Thus we decided to investigate the possibility of a gold(I)-catalyzed phenol synthesis more closely.

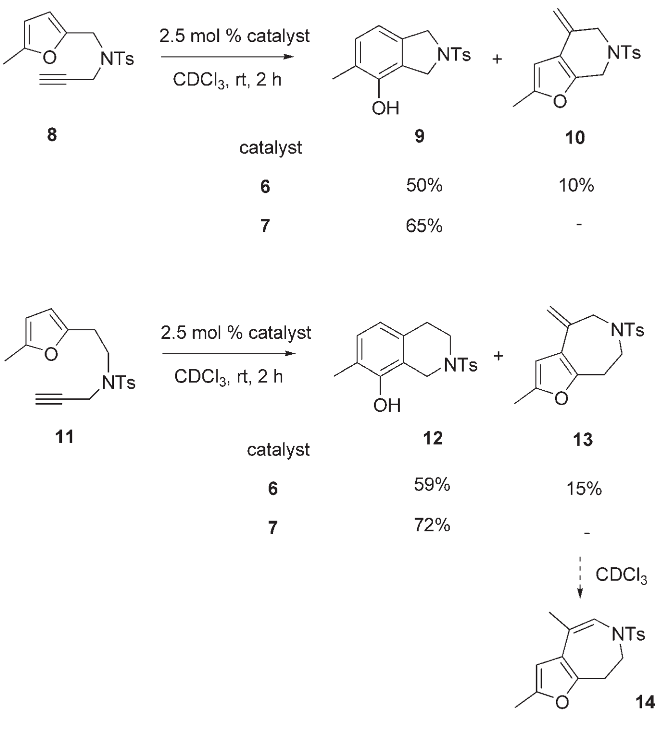
While several new tests with $Et_3PAuCl/AgBF_4$, $Ph_3PAuCl/AgBF_4$, $THTAuCl/AgBF_4$ and dinuclear complexes like **4**[8] or **5**[9,10] (Scheme 2) still gave no acceptable results, first promising experiments with the Uson–Laguna[11] salt $[(Ph_3PAu)_2Cl]BF_4$ (**6**) then led to the use of the Schmidbaur–Bayler[12] salt $[(Mes_3PAu)_2Cl]BF_4$ (**7**), which proved to be superior. It is amazing that $Ph_3PAuCl/AgBF_4$ did not react well while **6** was reactive – both should be a source for the catalyst $[Ph_3PAu]^+$. The difference might be that with $Ph_3PAuCl/AgBF_4$ the formation of $[Ph_3PAu]^+$ is irreversible; once this cation is set free, it can only react with the substrate or enter catalyst deactivating pathways. Salt **6**, on the other hand, sets free $[Ph_3PAu]^+$ in a reversible manner, thus offering the re-formation of **6** as a potential resting state in competition to a possible catalyst deactivation.

While with catalyst **6** and the substrate **8** the conversion was fast but unselective (leading to **9** and **10**), with catalyst **7** only the desired product **9** and no **10** was obtained (Scheme 3). A similar observation was made with substrate **11**, with **6** mainly the tetrahydroisoquinoline **12** was formed, with **7** only **12**. Chloroform was superior to acetone or acetonitrile as solvent, in the latter two the reaction was much slower and small amounts of uncharacterized side-products were observed.

We succeeded to obtain single crystals for a crystal structure analysis of **12** (Figure 1),[13] which provided clear proof for the constitution of that product; in the dihydroisobenzoindoles known so far (like **9**), the NTs group is symmetrically connected with the phenol ring by one methylene group on each side, in **12** this local symmetry is lost. Compound **12** has one methylene tether and one ethylene tether, a safe spectroscopic distinction of the connectivity shown for **12** (CH_2 *ortho* to OH, CH_2CH_2 *meta* to OH; the isomer in accord with the mechanism) from the other conceivable isomer (CH_2CH_2 *ortho* to OH, CH_2 *meta* to OH, not expected) would have needed significantly more effort.



Scheme 2. Unreactive gold(I) complexes **4** and **5**.



Scheme 3. Isomerization of γ- and δ-alkynylfurans with the Uson–Laguna and the Schmidbaur–Bayler salts **6** and **7**.

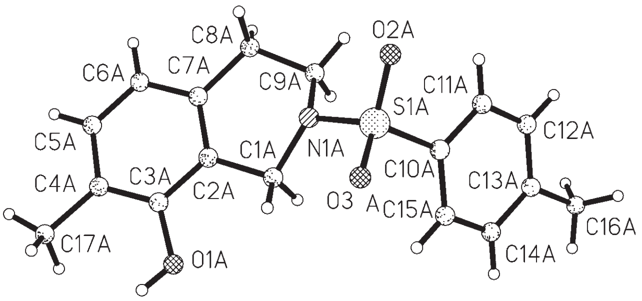


Figure 1. Crystal structure of the tetrahydroisoquinoline **12** as a clear proof of the connectivity.

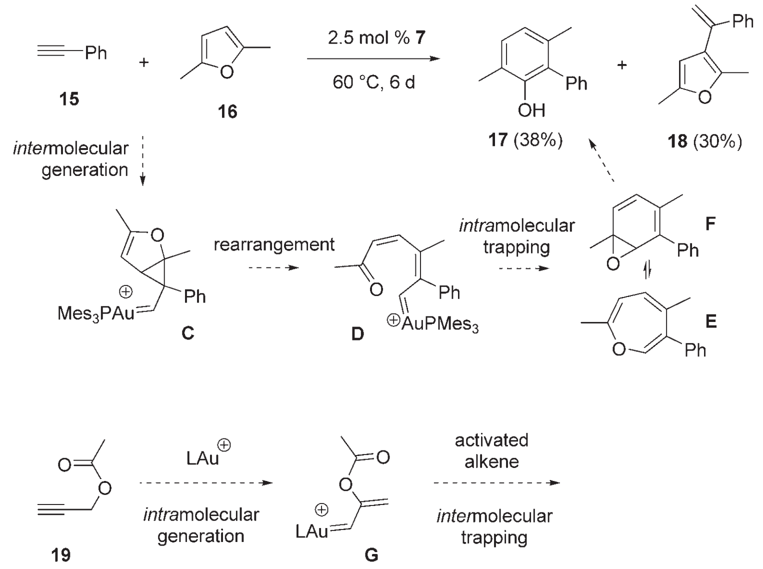
It was also interesting to notice that the seven-membered side-product **13** is readily and highly selectively isomerized to **14** in $CDCl_3$ at room temperature without a catalyst, while the six-membered analogue **10** did not show this isomerization under the same conditions.

Thus we have for the first time experimentally proved that, when the proper ligand is chosen, Au^I can selectively and efficiently catalyze the phenol synthesis, too. So both oxidation states Au^{III} and Au^I show a comparable activity, this is experimental evidence for either similar barriers of activation or the *in-situ* conversion of one oxidation state as a pre-catalyst to the other oxidation state as the catalytically active species.

Finally, we investigated the intermolecular reaction of phenylacetylene **15** and 2,5-dimethylfuran **16**. With the Au^{III} catalysts all previous efforts had failed, while with Au^I in catalyst **7** for the first time a small amount (38%) of the *ortho, ortho*-disubstituted biaryl compound **17** was observed. The hydroarylation[14] product **18** was also obtained (30%, Scheme 4).

A crystal structure analysis[13] of the 1,2,3,4-tetrasubstituted arene in **17** unambiguously proved the sequence of the four substituents to be in accordance with the mechanistic proposal (Figure 2).

This observation is unique, as these reactions proceed *via* the initial formation of a gold carbene,[2,3] it is the first example of a formation of such a gold carbene **C** (the analogue of **A**) by an *inter*molecular reaction. So far only an *inter*molecular trapping of such gold carbenes, themselves generated *in-situ* by *intra*molecular reactions as shown for **B** in Scheme 1[15] or, as shown for **G**, from



Scheme 4. Formation of **17** as evidence for the first generation of gold carbenes by an *inter*molecular alkyne/alkene reaction.

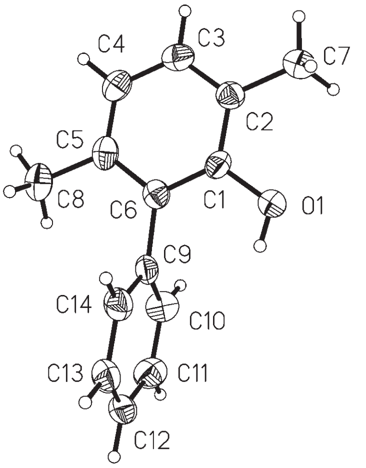


Figure 2. Crystal structure of the 1,2,3,4-tetrasubstitued arene **17**.

compounds of type **19**[16] was successful, their generation by an *inter*molecular alkyne/alkene reaction is unprecedented.

The phenol synthesis can be catalyzed by gold(I) precatalysts of type **6** and **7**, the bulkier phosphane showing a higher selectivity for the phenolic products. Catalyst **7** then enabled the first intermolecular reaction of such a type, which still needs optimization but opens the door to a synthetically promising field.

Experimental Section

Gold-Catalyzed Conversion of 8

To a solution of **8** (150 mg, 495 μmol) in $CDCl_3$ (700 μL)) in an NMR tube, **6** (12.9 mg, 12.4 μmol, 2.5 mol %) was added. The reaction was monitored by ^1H NMR, after two hours the substrate was consumed. The solvent was removed under vacuum and the residue purified by flash chromatography on silica gel (petrol ether/diethyl ether, 8:1) to give known **9**[1a] (yield: 74.5 mg, 50%) and **10** as a yellow oil (yield: 15.3 mg, 10%).

Product **10**: R_f (petrol ether/diethyl ether, 5:3) = 0.38; IR (film): ν = 2923, 2359, 1656, 1347, 1162, 1090, 949, 836, 708, 660 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz): δ = 2.20 (s, 3H), 2.39 (s, 3H), 3.96 (s, 2H), 4.30 (s, 2H), 4.92 (s, 1H), 5.00 (s, 1H), 6.09 (s, 1H), 7.35 (d, $^3J_{H,H}$ = 8.1 Hz, 2H), 7.67 (d, $^3J_{H,H}$ = 8.1 Hz, 2H); ^{13}C NMR (acetone-d_6, 500 MHz): δ = 13.3 (q), 21.4 (q), 44.3 (t), 50.1 (t), 102.8 (d), 106.8 (t), 119.9 (s), 128.5 (d, 2C), 130.4 (d, 2C), 134.4 (s), 135.4 (s), 144.6 (s), 146.7 (s), 153.2 (s); MS [DCI (+)]: m/z (%) = 332 (5), 318 (5), 304.1 (100) [M^+], 147 (55), 91 (5); HR-MS (70 eV): m/z = 304.0999; calcd. for $C_{16}H_{18}NO_3S$ (M^+ + H): 304.1008.

Gold-Catalyzed Conversion of 11

In an NMR tube a solution of **11** (112 mg, 353 μmol) and **6** (9.2 mg, 8.8 μmol, 2.5 mol %) in $CDCl_3$ (700 μL) was prepared. The reaction was monitored by ^1H NMR, after two hours the starting material had been consumed and the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (petrol ether/diethyl ether, 8:1) to give **12** (yield: 66.5 mg, 59%) as colourless crystals and the **13** (yield: 17.0 mg, 15%) as colourless oil.

By evaporation from petrol ether/ethyl acetate/dichloromethane single crystals of **12** suitable for a crystal structure analysis were obtained. Mp 155–156 °C; R_f (petrol ether/ethyl acetate/dichloromethane, 10:0.5:3) = 0.10; IR (film): ν = 3493, 3496, 2914, 1582, 1495, 1458, 1443, 1431, 1375, 1353, 1332, 1320, 1297, 1255, 1127, 1205, 1192, 1155, 1108, 1016, 989, 951, 874, 815, 796, 757, 729, 654, 606 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.20 (s, 3H), 2.42 (s, 3H), 2.88 (t, J = 5.7 Hz, 2H), 3.31 (t, J = 5.7 Hz, 2H), 4.23 (s, 2H), 5.01 (bs, 1H), 6.59 (d, J = 7.7 Hz, 1H), 6.91 (d, J = 7.7 Hz, 1H), 7.32 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 16.69$ (q), 22.95 (q), 30.26 (t), 44.86 (t), 44.99 (t), 120.44 (s), 121.18 (d), 121.94 (s), 129.20 (d, 2C), 130.00 (d), 131.12 (d, 2C), 133.91 (s), 134.85 (s), 145.00 (s), 151.72 (s); MS (70 eV): *m/z* (%) = 347 (24) [M$^+$], 161 (100), 134 (54), 91 (22); anal. calcd. for $C_{17}H_{19}NO_3S$ (317.41): C 64.33, H 6.03, N 4.41; found: C 64.23, H 6.02, N 4.42.

Product **13**: R_f (petrol ether/diethyl ether, 5:3) = 0.39; IR (film): $\nu = 2923$, 2360, 1608, 1305, 1098, 1069, 958, 814, 707, 582 cm^{-1}; ^{1}H NMR (acetone-d_6, 500 MHz): $\delta = 2.17$ (s, 3H), 2.40 (s, 3H), 2.92 (t, $^3J_{H,H} = 5.9$ Hz, 2H), 3.58 (t, $^3J_{H,H} = 5.9$ Hz, 2H), 4.18 (s, 2H), 5.02 (s, 1H), 5.15 (s, 1H), 6.08 (s, 1H), 7.37 (d, $^3J_{H,H} = 8.1$ Hz, 2H), 7.72 (d, $^3J_{H,H} = 8.2$ Hz, 2H); ^{13}C NMR (acetone-d_6, 500 MHz): $\delta = 13.1$ (q), 21.4 (q), 29.8 (t), 48.2 (t), 56.4 (t), 106.6 (d), 111.9 (t), 122.1 (s), 127.9 (d, 2C), 130.5 (d, 2C), 138.5 (s), 138.7 (s), 144.0 (s), 149.5 (s), 151.0 (s); MS (EI): *m/z* (%) = 317 (65) [M$^+$], 253 (5), 162 (100), 133 (45), 120 (30), 105 (25), 91 (50), 77 (20); HRMS (70 eV): *m/z* = 317.1085; calcd. for $C_{17}H_{19}NO_3S$: 317.1086.

Isomerization of 13 to 14

Compound **13** (31.9 mg, 1.01 μmol) was dissolved in $CDCl_3$ (700 μL), after one day a complete isomerization to **14** had occurred. R_f (petrol ether/diethyl ether, 5:3) = 0.39; IR (film): $\nu = 2923$, 2360, 1184, 1096, 1044, 910, 814, 743, 617, 572 cm^{-1}; ^{1}H NMR (acetone-d_6, 300 MHz): $\delta = 1.95$ (d, $^4J_{H,H} = 1.2$ Hz, 3H), 2.20 (s, 3H), 2.42 (s, 3H), 2.95 (t, $^3J_{H,H} = 5.2$ Hz, 2H), 3.61 (t, $^3J_{H,H} = 5.2$ Hz, 2H), 6.04 (d, $^4J_{H,H} = 0.9$ Hz, 1H), 5.15 (s, 1H), 6.45 (d, $^4J_{H,H} = 1.1$ Hz, 1H), 7.42 (d, $^3J_{H,H} = 7.9$ Hz, 2H), 7.77 (d, $^3J_{H,H} = 8.3$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 250 MHz): $\delta = 13.3$ (q), 20.1 (q), 21.5 (q), 30.5 (t), 43.7 (t), 105.6 (d), 115.6 (s), 119.3 (s), 122.0 (d), 126.8 (d, 2C), 129.8 (d, 2C), 143.6 (s), 148.8 (s), 149.8 (s); MS (EI): *m/z* (%) = 317 (30) [M$^+$], 162 (100), 118 (10), 91 (20); HR-MS (70 eV): *m/z* = 317.1080; calcd. for $C_{17}H_{19}NO_3S$: 317.1086.

Intermolecular Gold-Catalyzed Conversion of 15 with 16

To a mixture of **15** (186 mg, 1.82 mmol) and **16** (175 mg, 1.82 mmol) the catalyst **7** was added (58.9 mg, 45.5 μmol, 2.5 mol %). This reaction mixture was stirred at 60 °C and monitored by TLC until most of the starting material was consumed (6 days). Then the volatiles were removed under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane, 100:1:0.5). Thus **17** (yield: 137 mg, 38%) was obtained as a colourless solid and **18** (yield: 108 mg, 30%) was isolated as an colourless oil.

Product **17**: R_f (petrol ether/ethyl acetate/dichloromethane, 10:1:0.5) = 0.57; IR (film): $\nu = 3558$, 2922, 2852, 1732, 1600, 1489, 1259, 1092, 1025, 801, 702, 646 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 2.03$ (s, 3H), 2.25 (s, 3H), 4.75 (s, 1H), 6.76 (d, $^3J_{H,H} = 7.6$ Hz, 1H), 7.03 (d, $^3J_{H,H} = 7.6$ Hz, 1H), 7.29 (m, 2H), 7.42 (tt, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 1.4$ Hz, 1H), 7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 500 MHz): $\delta = 16.0$ (q), 20.2 (q), 121.3 (d), 121.5 (s), 127.6 (q), 128.1 (d), 129.5 (d, 2C), 129.8 (d), 130.3 (d, 2C), 134.4 (q), 135.6 (q), 150.8 (q); MS (EI): *m/z* (%) = 198 (100) [M$^+$], 183 (45), 165 (25), 83 (20); HR-MS (70 eV): *m/z* = 198.1044; calcd. for $C_{14}H_{14}O$: 198.1045.

Product **18**: R_f (petrol ether/ethyl acetate/dichloromethane, 10:1:0.5) = 0.70; IR (film): $\nu = 2358$, 2338, 1577, 1492, 1445, 1217, 890, 778, 698, 641, 627, 579 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 2.08$ (s, 3H), 2.25 (s, 3H), 5.21 (d, $^2J_{H,H} = 1.5$ Hz, 1H), 5.41 (d, $^2J_{H,H} = 1.5$ Hz, 1H), 5.86 (s, 1H), 7.33 (m, 5H); ^{13}C NMR (acetone-d_6, 300 MHz): $\delta = 13.0$ (q), 13.3 (q), 108.6 (d), 114.1 (t), 122.4 (s), 128.3 (d, 2C), 128.7 (d), 129.2 (d, 2C), 142.2 (s), 143.5 (s), 148.2 (s), 150.3 (s); MS (EI): *m/z* (%) = 214 (25), 199 (20) [M$^+$+H], 171 (30), 128 (15), 105 (30), 77 (20), 43 (100), 28 (20); HR-MS (70 eV): *m/z* = 198.1044; calcd. for $C_{14}H_{14}O$: 198.1045.

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[13] CCDC 293003 (**12**) and 293003 (**24**) and contain the supplementary crystallographic data for this paper. These data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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