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First examples of a covalent bond between gold and selenophene

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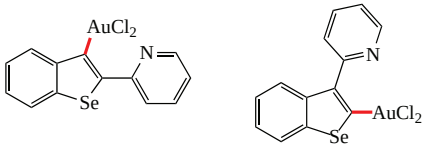
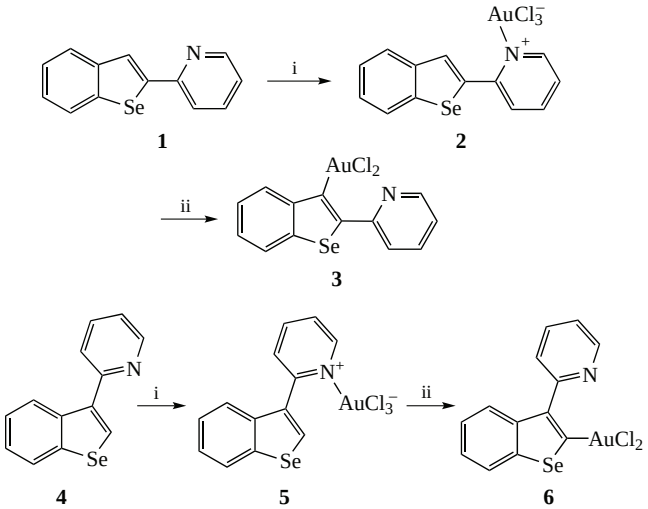
2(3)-Dichloroauryl-3(2)-(pyridin-2-yl)benzo[*b*]selenophenes bearing covalent bond with gold(III) were synthesized by the treatment of (pyridin-2-yl)benzoselenophenes with sodium tetrachloroaurate. Molecular structures were unambiguously confirmed by X-ray analysis.



Keywords: gold compounds, organogold compounds, organoselenium compounds, selenophenes, X-ray.

Organogold chemistry is booming in recent years due to high potential of such derivatives in medicine,[1–4] catalysis[5–10] and materials chemistry.[11–14] On the other hand, incorporation of heavy chalcogens (selenium and tellurium) in new materials,[15–19] especially OLEDs,[20–23] can be considered as a prospective research direction. Recently, we have reported a new series of iridium-containing benzoselenophene derivatives which showed red emission color deeper than the corresponding NTSC (National Television System Committee) standard.[24] Besides, phosphorescent platinum complexes bearing 2- and 3-positioned (2-pyridyl)benzo[*b*]selenophenes can be used as phosphorescent dopants for hybrid solution-processable OLEDs.[25] Inspired by prospective impact of the incorporation of selenium in phosphorescent emitter structure we would like to report our findings in the synthesis of benzoselenophenylpyridine gold complexes (Scheme 1).

2-(Benzo[*b*]selenophen-2-yl)pyridinium trichloroaurate **2** was obtained by treatment of pyridine derivative **1**[24] with $NaAuCl_4$ in MeCN–H_2O mixture (see Scheme 1). The formation of orange precipitate started after half an hour and the reaction was complete in 3 h yielding desired betain **2** in 86% yield. The orange substance was then suspended in MeCN and refluxed for 5 h. After cooling, bright yellow solid was formed being the desired [2-(pyridin-2-yl)benzo[*b*]selenophen-3-yl]gold(III) chloride **3** (36% yield). Similarly, isomeric derivative **5** was obtained from **4**,[25] and further reflux afforded organogold compound **6**.¶ All new compounds showed very low solubility.



Scheme 1 *Reagents and conditions*: i, $NaAuCl_4$ (0.8 equiv.), MeCN/water, room temperature, 3 h; ii, MeCN, reflux, 5 h.

A search within the Cambridge Structural Database (CSD, Version 5.41, November 2019) indicates that there are no entries containing selenophene derivatives with C–Au bonds. Thus, compounds **3** and **6** are the first such representatives. Scarce reports on benzothiophenes with C–Au bonds indicate that (1-benzothiophen-2-yl)[*N*-(4-methoxyphenyl)cyano]gold[26] contains the shortened C(2)–Au bond (2.018 Å), while in the structure of bis(1-benzothiophen-2-yl)[5-methyl-2-(pyridin-2-yl)phenyl]gold ligands are disordered, the average C(2)–Au bond length being 2.033 Å.[27] The most interesting is cluster complex of (μ_2-1-benzothiophen-2-yl)bis(triphenylphosphine)-digold with Au–Au bond,[28] in which lengths of C(2)–Au(1) and C(2)–Au(2) bonds are 2.107 and 2.142 Å. Two structures of benzothiophenes containing C–Au bond with 3-positioned Au atom, *viz*. dichloro-[2-(pyridin-2-yl)-1-benzothiophen-3-yl]-gold[29] [sulfur isoster of **3**, C(3)–Au, 2.026 Å] and 2-(pyridin-2-yl)-(1-benzothiophen-3-yl)-(1,4,7-trithionane)gold [C(3)–Au, 2.071 Å],[29] were documented.

Molecular structures of products **2**, **3**, **5** and **6** were unambiguously confirmed by X-ray analysis (Figure 1, Table 1).† In the crystal structure of **3**, there is a strong σ-hole intermolecular

† *Crystal data for* **2**. $C_{13}H_9AuCl_3NSe$ (M = 561.51): orthorhombic, space group $Pna2_1$ (no. 33), a = 8.1633(4), b = 29.275(2) and c = 6.1468(4) Å, V = 1468.99(15) Å^3, Z = 4, T = 140.0(1) K, μ(MoKα) = 13.021 mm^{-1}, d_{calc} = 2.5387 g cm^{-3}, 5935 reflections measured ($2\theta \leqslant 65.0°$), 3143 unique (R_{int} = 0.0312, R_σ = 0.0458) which were used in all calculations. The final R_1 was 0.0337 [$I > 2\sigma(I)$] and wR_2 was 0.0842 (all data).

Crystal data for **3**. $C_{13}H_8AuCl_2NSe$ (M = 525.05): triclinic, $P\bar{1}$ (no. 2), a = 7.2208(1), b = 9.0322(2) and c = 11.2166(2) Å, α = 70.068(2)°, β = 74.574(2)°, γ = 87.073(2)°, V = 662.31(2) Å^3, Z = 2, T = 160.0(1) K, μ(MoKα) = 14.235 mm^{-1}, d_{calc} = 2.6326 g cm^{-3}, 25147 reflections measured ($2\theta \leqslant 60.0°$), 4680 unique (R_{int} = 0.0464, R_σ = 0.0278) which were used in all calculations. The final R_1 was 0.0182 [$I > 2\sigma(I)$] and wR_2 was 0.0442 (all data).

Crystal data for **5**. $C_{13}H_9AuCl_3NSe$ (M = 561.51): orthorhombic, space group $P21/n$, a = 8.0131(2), b = 16.2569(4) and c = 11.6467(2) Å, V = 1516.47(6) Å^3, Z = 4, T = 160.0(2) K, μ(MoKα) = 12.613 mm^{-1}, d_{calc} = 2.459 g cm^{-3}, 20035 reflections measured ($2\theta \leqslant 65.0°$), 5683 unique (R_{int} = 0.0342, R_σ = 0.0848) which were used in all calculations. The final R_1 was 0.0425 [$I > 2\sigma(I)$] and wR_2 was 0.0885 (all data).

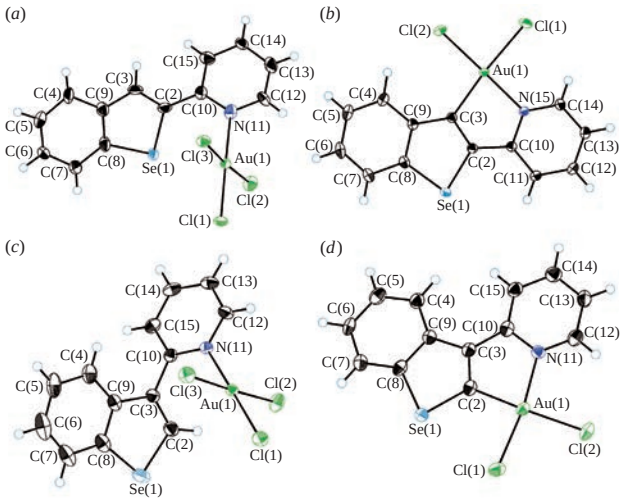


Figure 1 Molecular structures of compounds (*a*) **2**, (*b*) **3**, (*c*) **5** and (*d*) **6** with the atoms presented as thermal ellipsoids with 50% probability.

Table 1 Selected bond lengths (Å) for organogold compounds **2**, **3**, **5** and **6**.

Compound	Au–C	Au–N	Au–Cl
2	–	2.047(3)	2.269(1), 2.275(1), 2.288(1)
3	2.037(2)	2.054(2)	2.2622(6), 2.3673(6)
5	–	2.042(7)	2.286(2), 2.293(2), 2.269(2)
6	1.987(5)	2.044(4)	2.264(1), 2.351(1)

interaction between chlorine Cl(2) and selenium Se(1) atoms with Se(1)···Cl(2) distance of 3.443(1) Å [Se(1)···Cl(2)–Se(1) angle is 166.6(1)°]. Chlorine atom Cl(1) participates in a weak intermolecular hydrogen bond of CH···Cl type with C(13)–H(13) group [C(13)···Cl(1), 3.540(2) Å; H(13)···Cl(1), 2.96 Å; C(13)–H(13)···Cl(1), 122°]. Thus, in the crystal structure atoms Cl(1) and Cl(2) are characterized by different environment; this explains the difference in the lengths of Au–Cl bonds [Au(1)–Cl(1), 2.3673(6) Å; Au(1)–Cl(2), 2.2622(6) Å]. By means of the intermolecular σ-hole interactions and hydrogen bonds, the molecular layers are formed in the crystal structure. These layers are parallel to crystallographic plane (101). In the molecular layers, the π–π stacking interactions occur: the distance between neighboring layers is 3.589(4) Å. Besides, no strong σ-hole interactions were detected in the crystal structure of **6**. Only a weak intermolecular hydrogen bond of CH···Cl type is formed between chlorine atom Cl(1) and C(4)–H(4) group [C(4)···Cl(1), 3.384(6) Å; H(4)···Cl(1), 2.90 Å; C(4)–H(4)···Cl(1), 114°]. However, in the crystal structure the molecules form stacks along crystallographic parameter *a* (see Figure 1). The π–π stacking interactions are stronger than those in **3**; the distance between neighboring molecules in the stack is 3.544(7) Å.

To sum up, we have synthesized first benzoselenophenes containing Au–C bond. Based on X-ray analysis data, its length was estimated as 2.037(2) and 1.987(5) Å. Our further research will be connected with attempts to obtain electroluminescent derivatives containing these moieties.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.006.

Crystal data for **6**. $C_{13}H_8AuCl_2NSe$ (M = 525.05): monoclinic, space group $I2/a$ (no. 15), a = 16.377(1), b = 3.9513(2) and c = 39.309(2) Å, β = 94.799(5)°, V = 2534.8(3) Å^3, Z = 8, T = 150.0(1) K, μ(CuKα) = 28.788 mm^{-1}, d_{calc} = 2.7515 g cm^{-3}, 11647 reflections measured ($2\theta \leqslant 155.0°$), 2651 unique (R_{int} = 0.0474, R_σ = 0.0234) which were used in all calculations. The final R_1 was 0.0341 [$I > 2\sigma(I)$] and wR_2 was 0.0996 (all data).

CCDC 1946871, 1946957, 1946958 and 1984610 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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