



## Note

## Synthesis, crystal and molecular structure of gold(I) thiophenolate with 4'-ferrocenyl[1,1']biphenylisocyanides

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## ABSTRACT

The syntheses of ferrocenylbiphenylisocyanide gold(I) thiophenolato complexes are described. The preparative route starts from ferrocenylphenylbromide and proceeds in six steps to yield the desired gold(I) complexes, (thiophenolato)gold{(4'-ferrocenyl[1,1']biphenyl-4-yl)isocyanide} (**11**) and (thiophenolato)gold{(4'-ferrocenyl-3,5-dimethyl[1,1']biphenyl-4-yl)isocyanide} (**12**) in good yields. The synthetic pathways were developed as a first step toward realizing the goal of preparing metallomesogens based on ferrocenyl-polyphenylenes coordinated to gold(I) thiophenolates, in which long chain alkoxy groups are substituted *para* to sulfur on the phenyl ring. The crystal structures of (chloro)gold{(4'-ferrocenyl[1,1']biphenyl-4-yl)isocyanide} (**9**) and **12** are reported. Complex **9** crystallizes in the space group  $P2_1/c$  and **12** crystallizes in  $P2_1/n$ . Complexes **9** and **12** show short intermolecular Au–Au contacts of 3.3765(7) Å and 3.3334(3) Å, respectively.

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## 1. Introduction

In our previous papers we reported on the design and synthesis of new “calamitic” liquid crystals (LC) based on ferrocenyl-polyphenylenes of type **I** (Scheme 1) [1,2]. The “bridging” –O–C(=O)– moiety in molecules of type **I** can be replaced, in principle, with certain gold(I) containing fragments. The presence of gold in molecules of this type may provide an additional factor to assist formation of supramolecular aggregates due to the well-known “aurophilicity” of gold [3]. In this regard, isocyanide complexes of gold thiolates are promising because gold forms stable bonds with sulfur, and the linear isocyanide ligands will not disturb a calamitic structure of the proposed mesogen of type **II**, which are gold-containing analogs of type **I** molecules (Scheme 2).

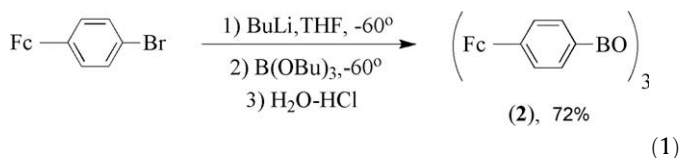
Here we report on the development of synthetic pathways for complexes of type **III** (Scheme 3) as a first step for synthesis of type **II** mesogens. There are only a handful of reports of isocyanide complexes of gold thiolates in the literature [4–7]. We have prepared a stable complex of gold thiophenolate with 2,6-dimethylphenylisocyanide; this work will be reported separately. In this case, stabil-

ization of the complex can be explained by formation of dimers due to close intermolecular contacts between the sulfur atom and the carbon atom of nearby isocyanide ligands. The presence of methyl groups in the isocyanide ligand is anticipated to increase the solubility of the complexes.

## 2. Results and discussion

## 2.1. Synthesis

The synthesis of complexes of type **III** begins with preparation of the corresponding ferrocenyl substituted polyphenylene isocyanides. The Suzuki reaction was used for the construction of biphenyl fragments of type **III** molecules, as described previously [8]. A modified procedure for preparation of *tris*(4-ferrocenylphenyl)boroxine, **2**, is described here (Eq. (1) and Section 2).



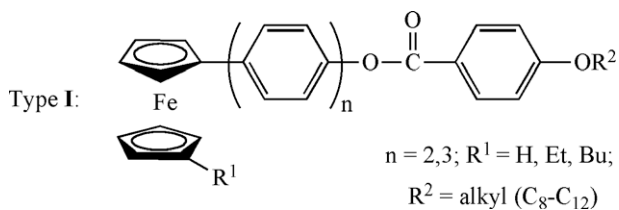
(1)

The cross-coupling reactions of boroxine **2** with 4-iodoanilines and with 4-iodo(bromo)formanilides were investigated. For iodo-

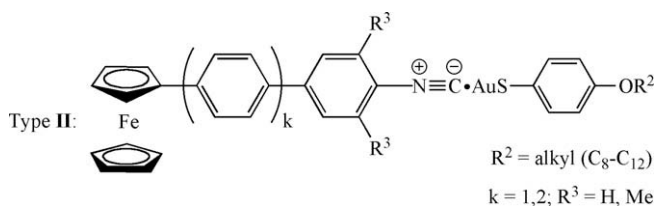
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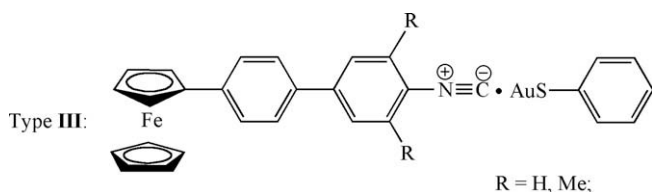
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Scheme 1.



Scheme 2.

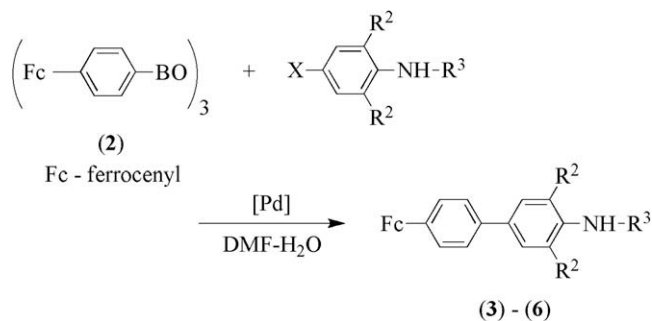


Scheme 3.

derivatives, the yield of the cross-coupling product is significantly higher in the case of the corresponding formilide (Table 1). The yields of cross-coupling products are also higher for the Pd(0) complex, which is typical for this type of reaction.

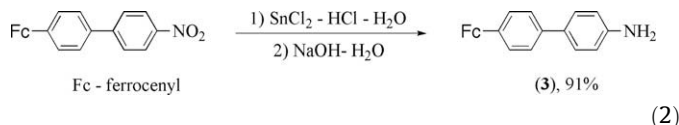
Ferrocenyl-biphenylamine, **3**, was also prepared by reduction of the corresponding nitro-derivative (Eq. (2)). Formylation of aryl amines was carried out by the action of acetic formic anhydride by a modified procedure (Eq. (3)) [9]. The next step in preparing the target ferrocenylbiphenyl ligands was dehydration of the substituted formilides, which was carried out by the action of

**Table 1**  
 Synthesis of ferrocenylbiphenylamines by Suzuki reaction.

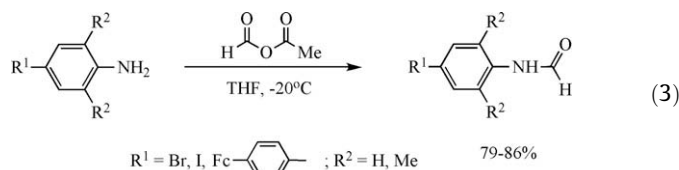


X	R <sup>2</sup>	R <sup>3</sup>	Ferrocenyl-biphenyl	Yield of ferrocenylbiphenyl (%)	
				[Pd] = (Ph <sub>3</sub> P) <sub>2</sub> PdCl <sub>2</sub>	[Pd] = (Ph <sub>3</sub> P) <sub>4</sub> Pd
I	H	H	<b>3</b>	–	68
Br	H	C(O)H	<b>4</b>	–	70
I	Me	H	<b>5</b>	55	65
I	Me	C(O)H	<b>6</b>	76	85

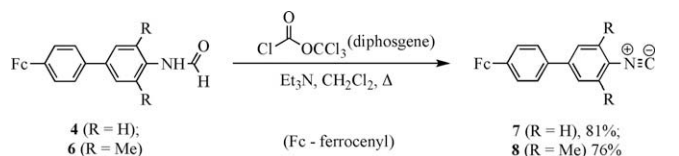
diphosgene in the presence of base [10]. This method is convenient in comparison with other known methods and the preparation of ferrocene containing isocyanides proceeds with good, reproducible yields (Eq. (4)).



(2)

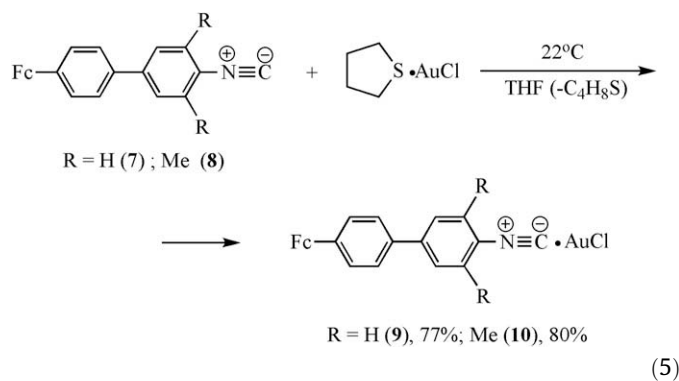


(3)

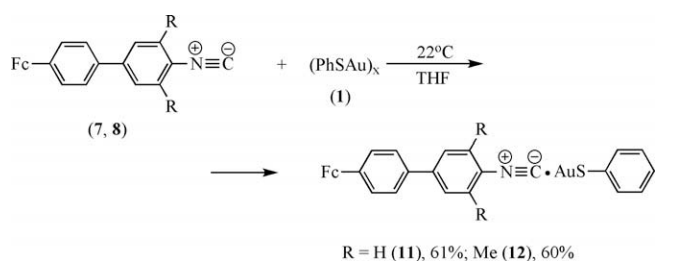


(4)

Isocyanides **7** and **8** form stable complexes with gold(I) chloride and with gold(I) thiophenolate. Chloro-complexes **9** and **10** can be prepared starting from (tetrahydrothiophene)gold chloride (Eq. (5)). Polymeric gold(I) thiophenolate (**1**) interacts with isocyanides **7** and **8** in THF solution producing stable complexes **11** and **12** (Eq. (6)). As we anticipated, the methyl-substituted complex **12** is more soluble in organic solvents in comparison with complex **11**, which does not contain alkyl groups on the aromatic moiety. Isocyanides **7** and **8** do not form any stable complexes with gold(I) decylthiolate, i.e. (C<sub>10</sub>H<sub>21</sub>SAu)<sub>x</sub> under the same conditions.



(5)



(6)

## 2.2. Molecular structures of gold(I) complexes

The crystal and molecular structure of complex **12** was established by X-ray and <sup>1</sup>H NMR spectroscopy. The X-ray structure

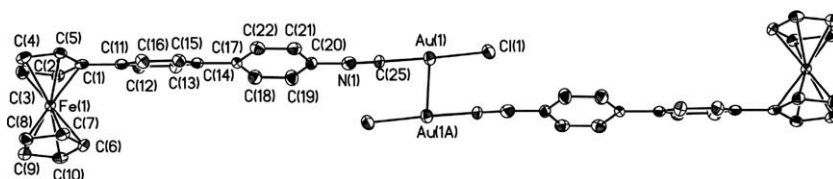
**Table 2**  
The principal bond lengths (Å) and angles (°) in complexes **9** and **12**.

Complex	<b>9</b>	<b>12</b>
Au··Au	3.3765(7)	3.3334(3)
NC··S	–	3.467(5)
Au–S	–	2.2734(9)
Au–C	1.918(10)	1.954(4)
NCAu	179.3(11)	173.9(3)
CAuX	177.3(3)	175.0(1)

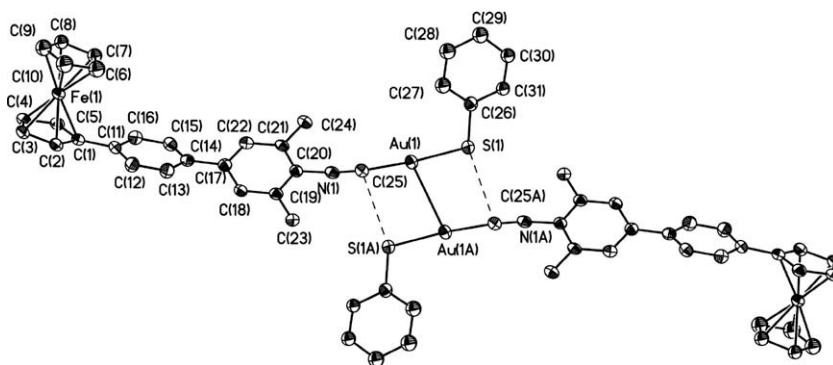
determination of the corresponding complex of gold(I) chloride, **9**, was carried out for comparison.

The X-ray structure investigations of **9** and **12** reveal sub-van-der-Waals contacts between gold atoms [11], which leads to the formation of centrosymmetric dimers for both complexes (Table 2 and Figs. 1 and 2). Short intermolecular Au··Au contacts are characteristics of gold(I) complexes and are usually explained by “*aur-*

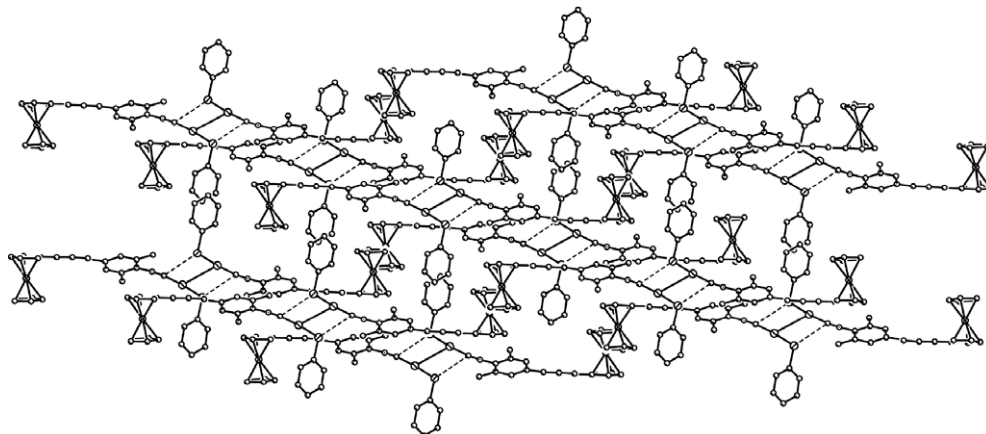
*ophilic*” interactions [3]. The shortest contacts are found in gold complexes with tertiary phosphines (2.50–3.24 Å). [12] In the thiophenolate complex (**12**), in addition to *aurophilic* interactions between dimers, there are shortened contacts between the sulfur atom of the thiophenolate ligand and the carbon atom of the isocyanide ligand (3.467(5) Å). This additional contact, which can be attributed to charge transfer from the sulfur electron lone pair to the  $\pi^*$  bond of the CN group, leads to a slight deviation in the expected linear Au–C–N angle to 173.9°. The attractive character of the PhS··CN contact can be further confirmed by the value of the C(6)S(1)C(25) angle that is equal to 131°, which is close to the expected position of the sulfur electron lone pair. At the same time, we cannot exclude some contribution for dimer stabilization due to a Au··S intermolecular contact that is equal to 3.74 Å. In contrast, in the chloride complex (**9**), the Au–C–N angle is 179.4° and there is no evidence for additional shortened interactions. Complex **12** packs in the crystal to form infinite ladder-like ribbons (Fig. 3).



**Fig. 1.** Centrosymmetric dimers formed by chloro complex **9** in representation of atoms by thermal ellipsoids ( $p = 50\%$ ).



**Fig. 2.** Centrosymmetric dimers formed by thiophenolato complex **12** in representation of atoms by thermal ellipsoids ( $p = 50\%$ ). The minor positions of the disordered Cp-ring and phenyl rings are omitted for clarity.



**Fig. 3.** Infinite ladder-like ribbons formed by complex **12**.

The “*aurophilic*” interactions in **9** and **12** are longer and weaker in comparison to phosphine complexes of gold. We hypothesize that the *aurophilic* interactions in **9** and **12** will be strong enough to promote formation of mesophases but not so strong as to exclude mobility of the intermolecular aggregates, which is necessary for mesophase existence. We are proceeding with the next step in the synthesis of molecules of type **II**, i.e. substituting long chain alkoxy groups in the *para* position of the thiophenylate ligands in order to design gold-containing liquid crystals based on ferrocenyl-polyphenyleneisocyanides.

### 3. Experimental

Acetic formic anhydride [13], 4-iodoaniline [14], and 4-iodo-2,6-dimethylaniline [15] were prepared according to published procedures. Diphosgene (chloroformic acid trichloromethylester) was prepared by photochemical chlorination of chloroformic acid methylester according to a published procedure [10]. All cross-coupling reactions were carried out according to established procedures [2] by using molar ratios of boroxine (**3**):aryliodide(bromide):K<sub>2</sub>CO<sub>3</sub>:catalyst ≈ 1:3:9:0.1. Anhydrous THF and dry chloroform were used in all experiments.

#### 3.1. 4-Bromoformanilide

A solution of 4-bromoaniline (2.00 g; 0.011 mol) in THF (15 ml) was added with stirring to a cold (−20 °C) solution of acetic formic anhydride (2.75 g; 0.031 mol) in THF (5 ml). The reaction mixture was stirred at −20 °C for 30 min. The solvent was removed *in vacuo* and the residue was recrystallized from an ethanol–water mixture (ca. 2:1). Yield: 1.90 g (86%), m.p. 110–112 °C, cf. [16]: m.p. 117 °C.

#### 3.2. 4-Iodo-2,6-dimethylformanilide

A solution of 4-iodo-2,6-dimethylaniline (3.00 g; 0.012 mol) in 15 ml of THF was added with stirring to a cold (−20 °C) solution of acetic formic anhydride (2.75 g; 0.031 mol) in THF (5 ml). The reaction mixture was stirred at −20 °C for 15 min. A precipitate of 4-iodo-2,6-dimethylformanilide was separated by suction filtration and air-dried. Yield: 2.87 g (87%), m.p. 234–236 °C, decomp. Anal. Calc. for C<sub>9</sub>H<sub>10</sub>INO: C, 39.30; H, 3.66; N, 5.10. Found: C, 39.45; H, 3.53; N, 5.18%. <sup>1</sup>H NMR (chloroform-d, δ): 2.19 (s, 6H); 7.46 (m, 2H); 8.02 (s, 0.5H; NH); 8.04 (s, 0.5H; NH); 8.35 (s, 1H).

#### 3.3. Gold(I) thiophenolate (**1**)

Thiophenol (2.26 g; 20.5 mmol) was added with stirring to a solution of hydrogen tetrachloroaurate (HAuCl<sub>4</sub>·3H<sub>2</sub>O) (2.10 g; 5.33 mmol) in methanol (61 ml) and water (12 ml). The reaction mixture was stirred for 10 min. A white precipitate of gold thiophenolate (**1**) was separated by filtration, washed with methanol (10 ml), acetone (10 ml), then ether (10 ml) and dried in air. Gold thiophenolate (**1**), 1.60 g (98%) was obtained as a white powder; decomp. above 178 °C. Anal. Calc. for C<sub>6</sub>H<sub>5</sub>AuS: C, 23.54; H, 1.65. Found: C 23.71; H, 1.50%.

#### 3.4. Tris(4-ferrocenylphenyl)boroxine (**2**). Modified procedure [2]

A cold (−6 °C) 1.6 M *n*-BuLi solution (10.5 ml, 16.8 mmol) in hexane was added to a solution of 4-bromophenylferrocene (5.0 g, 14.6 mmol) [2] in a mixture of THF (85 ml) and ether (25 ml) cooled to −60 °C. The reaction mixture was stirred at −60 °C for 50 min. A solution of 4-ferrocenylphenyllithium was obtained (in some experiments this organolithium compound was formed as an orange suspension). Freshly distilled tributyl borate

(5.5 ml, 4.6 g, 20 mmol) was added to the reaction mixture at −60 °C. The solution was allowed to gradually warm to −20 °C with stirring. The cooling bath was removed and stirring was continued at 20 °C for 40 min. The reaction mixture was quenched with water (7 ml), after which a 3% HCl solution (about 38 ml) was added to acidify the solution. The organic layer was separated, washed several times with water until the pH was neutral, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed *in vacuo*. *m*-Xylene (50 ml) was added to the residual orange oil and then removed on a rotary evaporator at a bath temperature of ca. 90 °C (see a note after description of the experiment). The solid residue was extracted with boiling petroleum ether (70/100) (3 × 15 ml) to remove phenylferrocene. Tris(4-ferrocenylphenyl)boroxine (**2**) was obtained as a brick-red powder in a yield of 3.0 g (71%); decomp. above 270 °C. cf. [8]: decomp. above 270 °C. The <sup>1</sup>H NMR spectrum is consistent with published data; (chloroform-d, δ): 4.07 (s, 5H); 4.39, 4.77, 7.62 and 8.18 (all m, 2H each).

*Note:* The reaction usually produces a mixture of **2** and 4-ferrocenylphenylboronic acid. This boronic acid, in contrast to anhydride **2**, is soluble in petroleum ether. The described procedure is intended for conversion of the mixture into boroxine **2** by removal of water by azeotropic distillation with xylene. Benzene or toluene can be used instead of xylene but in these cases the azeotropic distillation of water should be repeated several times.

#### 3.5. 4'-Ferrocenyl [1,1']biphenyl-4-amine (**3**)

A mixture of 1.60 g (4.2 mmol) of 4'-ferrocenyl-4-nitro-[1,1']biphenyl [17], 15 ml of 30% HCl and tin dichloride, SnCl<sub>2</sub>·2H<sub>2</sub>O (6.55 g; 29 mmol) was stirred under reflux for 3 h. After cooling to ambient temperature the reaction mixture was poured into a solution of NaOH (12.0 g; 0.30 mol) in 160 ml water. The product of the reduction reaction was extracted from the resulting suspension with ether (six portions of 20 ml). The combined ether extracts were washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Ether was removed *in vacuo*, the solid residue was dissolved in chloroform and this solution was filtered through a 3 cm layer of silica gel (60 μ). After removal of solvent *in vacuo*, **3** was obtained (1.30 g; 90%), m.p. 162–165 °C (after recrystallization from toluene-petroleum ether 1:10 mixture). Anal. Calc. for C<sub>22</sub>H<sub>19</sub>FeN: C, 74.80; H, 5.42; N, 3.97. Found: C, 74.70; H, 5.59; N, 3.95%. <sup>1</sup>H NMR (chloroform-d, δ): 3.71 (s, 2H); 4.07 (s, 5H); 4.32 (m, 2H); 4.66 (m, 2H); 6.76 (m, 2H); 7.48 (m, 6H).

#### 3.6. N-(4'-Ferrocenyl[1,1']biphenyl-4-yl)formamide (**4**)

A solution of 4'-ferrocenyl[1,1']biphenyl-4-amine (0.40 g; 1.13 mmol) in 3 ml of THF was added with stirring to a cold (−20 °C) solution of acetic formic anhydride (0.26 g; 2.93 mmol) in 4 ml of THF. Stirring was continued for an additional 10 min and solvent was removed *in vacuo*. N-(4'-Ferrocenyl[1,1']biphenyl-4-yl)formamide (**5**) (0.34 g; 79%) was obtained, decomp. above 240 °C. Anal. Calc. for C<sub>23</sub>H<sub>19</sub>FeNO: C, 72.46; H, 5.02; N, 3.67. Found: C, 72.14; H, 4.88; N, 3.78%. <sup>1</sup>H NMR (chloroform-d, δ): 4.06 (s, 5H); 4.33 (m, 2H); 4.66 (m, 2H); 7.38 (m, 9H); 8.57 (broad signal, 1H). IR (nujol, ν, cm<sup>−1</sup>): 1520 (C=O), 1690 (C=O), 3200 (NH).

#### 3.7. 4'-Ferrocenyl[1,1']biphenyl-4-amine (**3**) – typical procedure

To boroxine **2** (1.80 g; 0.2 mmol) in an argon purge were sequentially added: 4-iodoaniline (0.140 g; 0.64 mmol), K<sub>2</sub>CO<sub>3</sub> (0.220 g; 1.72 mmol), dimethylformamide (5 ml), water (3 ml) and tetrakis(triphenylphosphine)palladium (0.230 g; 0.02 mmol). The reaction mixture was stirred in an argon purge at 65–75 °C for 3 h and then poured into water (50 ml). The product was

extracted from the resulting suspension with chloroform (three portions of 10 ml). The combined extracts were washed with several portions of water, dried with Na<sub>2</sub>SO<sub>4</sub> and then chloroform was removed *in vacuo*. The residue was subjected to column chromatography on silica gel with methylene chloride as the eluent. After removal of the solvent *in vacuo*, 0.15 g (68%) of **3** was obtained, m.p. 162–165 °C. <sup>1</sup>H NMR (chloroform-d, δ): 3.71 (s, 2H); 4.07 (s, 5H); 4.32 (m, 2H); 4.66 (m, 2H); 6.76 (m, 2H); 7.48 (m, 6H).

### 3.8. *N*-(4'-Ferrocenyl-3,5-dimethyl[1,1']biphenyl-4-yl)formamide (**4**)

The reaction was carried out with boroxine **2** (1.44 g; 1.7 mmol), 4-bromoformanilide (1.00 g; 5.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.93 g; 14 mmol), dimethylformamide (45 ml), water (25 ml) and tetrakis(triphenylphosphine)palladium (0.20 g; 0.17 mmol). After chromatography on silica gel (eluent, 1:1 chloroform:ether mixture) 1.34 g (70%) of **4** was obtained, decomp. above 240 °C. <sup>1</sup>H NMR and IR spectra are consistent with spectra of an authentic sample (see above).

### 3.9. 4'-Ferrocenyl-3,5-dimethyl[1,1']biphenyl-4-amine (**5**)

#### 3.9.1. Catalyst – Pd(PPh<sub>3</sub>)<sub>4</sub>

The reaction was carried out with boroxine **2** (0.1640 g; 0.19 mmol), 4-iodo-2,6-dimethylaniline (0.1400 g; 0.57 mmol), K<sub>2</sub>CO<sub>3</sub> (0.2200 g; 1.72 mmol), dimethylformamide (5 ml), water (3 ml) and tetrakis(triphenylphosphine)palladium (0.0230 g; 0.02 mmol). After chromatography on silica gel (eluent, chloroform) 0.14 g (65%) of **5** was obtained, m.p. 152–154 °C. Anal. Calc. for C<sub>24</sub>H<sub>23</sub>FeN: C, 75.60; H, 6.08; N, 3.67. Found: C, 75.70; H, 6.11; N, 3.65%. <sup>1</sup>H NMR (chloroform-d, δ): 2.26 (s, 6H); 3.62 (s, 2H); 4.06 (s, 5H); 4.31 (m, 2H); 4.65 (m, 2H); 7.23 (s, 2H); 7.47 (m, 6H).

#### 3.9.2. Catalyst – (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>

The reaction was carried out as described in the previous experiment. From boroxine **2** (0.52 g; 0.6 mmol) and 4-iodo-2,6-dimethylaniline (0.44 g; 1.8 mmol), compound **5** 0.38 g (55%) was obtained, m.p. 152–154 °C.

### 3.10. *N*-(4'-Ferrocenyl-3,5-dimethyl[1,1']biphenyl-4-yl)formamide (**6**)

#### 3.10.1. Catalyst – Pd(PPh<sub>3</sub>)<sub>4</sub>

The reaction was carried out with boroxine **2** (1.04 g; 1.2 mmol), 4-iodo-2,6-dimethylformanilide (0.99 g; 3.6 mmol), K<sub>2</sub>CO<sub>3</sub> (1.32 g; 9.6 mmol), dimethylformamide (25 ml), water (15 ml) and tetrakis(triphenylphosphine)palladium (0.14 g; 0.12 mmol). After chromatography on silica gel (eluent, 1:1 chloroform:ether mixture) 1.21 g (85%) of **6** was obtained, m.p. 170–171 °C. Anal. Calc. for C<sub>25</sub>H<sub>23</sub>FeNO: C, 73.36; H, 5.67; N, 3.42. Found: C, 73.46; H, 5.76; N, 3.42%. <sup>1</sup>H NMR (chloroform-d, δ): 2.34 (s, 3H); 2.38 (s, 3H); 4.06 (s, 5H); 4.34 (m, 2H); 4.67 (m, 2H); 7.36 (m, 2H); 7.48 (m, 4H); 8.13 (s, 0.5H: NH); 8.16 (s, 0.5H: NH); 8.45 (s, 1H: CHO).

#### 3.10.2. Catalyst – (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>

The reaction was carried out as described in the previous experiment. From boroxine **2** (1.08 g; 1.25 mmol) and 4-iodo-2,6-dimethylformanilide, compound **6** (1.12 g; 76%) was obtained, m.p. 170–171 °C.

### 3.11. (4'-Ferrocenyl[1,1']biphenyl-4-yl)isocyanide (**7**)

A 0.83 M solution of diphosgene in chloroform (0.54 ml, 0.45 mmol of diphosgene) was slowly added with stirring to a refluxing suspension of formamide, **4** in a mixture of dry triethylamine (0.8 ml) and chloroform (3 ml). The reaction mixture was

stirred under reflux for an additional 20 min, then cooled to ambient temperature and washed with a 10% solution of Na<sub>2</sub>CO<sub>3</sub>. The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed on rotary evaporator and the residue was subjected to chromatography on silica gel (eluent, 1:1 petroleum ether:chloroform mixture). Isocyanide **7** was obtained (0.26 g; 81%), m.p. 169–170 °C. Anal. Calc. for C<sub>23</sub>H<sub>17</sub>FeN: C, 76.05; H, 4.72; N, 3.86. Found: C, 76.10; H, 4.71; N, 3.86%. <sup>1</sup>H NMR (chloroform-d, δ): 4.06 (s, 5H); 4.36 (m, 2H); 4.68 (m, 2H); 7.52 (m, 8H).

### 3.12. (4'-Ferrocenyl-3,5-dimethyl[1,1']biphenyl-4-yl)isocyanide (**8**)

A 1.25 M solution of diphosgene in chloroform (1 ml; 1.25 mmol of diphosgene) was slowly added with stirring to a refluxing suspension of formamide **6** (1.00 g; 1.45 mmol) in a mixture of dry triethylamine (2.4 ml) and chloroform (25 ml). The reaction mixture was stirred under reflux for an additional 15 min, then it was worked up as in the case of isocyanide **7**. Isocyanide **8** was obtained (0.73 g; 76%) as dark red powder, m.p. 186–188 °C. Anal. Calc. for C<sub>25</sub>H<sub>21</sub>FeN: C, 76.74; H, 5.41; N, 3.58. Found: C, 76.75; H, 5.46; N, 3.45%. <sup>1</sup>H NMR (chloroform-d, δ): 2.48 (s, 6H); 4.05 (s, 5H); 4.34 (m, 2H); 4.67 (m, 2H); 7.33 (m, 2H); 7.45–7.54 (m, 4H, AA'BB' – system).

### 3.13. (Chloro)gold{(4'-Ferrocenyl[1,1']biphenyl-4-yl)isocyanide} (**9**)

A solution of isocyanide **7** (0.04 g; 0.1 mmol) in 2 ml of THF was added with stirring to a solution of (tetrahydrothiophene)gold(I)chloride (0.035 g; 0.1 mmol) [18] in 3 ml of THF. The reaction mixture was stirred for 5 min then ether (4 ml) was added and solvent was decanted from the precipitate of complex **9**. The precipitate was washed with ether and air-dried.

Complex **9** was obtained (0.51 g; 77%) as an orange powder, decomp. above 220 °C. Anal. Calc. for C<sub>23</sub>H<sub>18</sub>AuClFeN: C, 46.38; H, 2.88; N, 2.35. Found: C, 46.28; H, 2.82; N, 3.00%.

### 3.14. (Chloro)gold{(4'-ferrocenyl-3,5-dimethyl[1,1']biphenyl-4-yl)isocyanide} (**10**)

The experiment was carried out as described for preparation of complex **9**. From isocyanide **8** (0.10 g (0.26 mmol) and (tetrahydrothiophene)gold(I)chloride (0.08 g; 0.26 mmol) complex **10** was obtained (0.13 g; 80%) as an orange powder, decomp. above 220 °C. Anal. Calc. for C<sub>25</sub>H<sub>21</sub>AuClFeN: C, 48.14; H, 3.39; N, 2.25. Found: C, 48.30; H, 3.40; N, 2.34%.

### 3.15. (Thiophenolato)gold{(4'-ferrocenyl[1,1']biphenyl-4-yl)isocyanide} (**11**)

A solution of isocyanide **7** (0.18 g; 0.5 mmol) in 5 ml of THF was added with stirring to a suspension of gold thiophenolate (**1**) (0.15 g; 0.5 mmol) in THF (10 ml). The reaction mixture was stirred for 20 min. A white precipitate of **1** initially dissolved then an orange precipitate formed. This orange precipitate was separated by filtration, washed with petroleum ether and air-dried. Complex **11** was obtained (0.2 g; 61%) as an orange powder, m.p. 196–198 °C, decomp. Anal. Calc. for C<sub>29</sub>H<sub>22</sub>AuFeNS: C, 52.04; H, 3.31; N, 2.09. Found: C, 52.10; H, 3.33; N, 2.12%.

### 3.16. (Thiophenolato)gold{(4'-Ferrocenyl-3,5-dimethyl[1,1']biphenyl-4-yl)isocyanide} (**12**)

A solution of isocyanide **8** (0.25 g; 0.65 mmol) in 5 ml of THF was added with stirring to a suspension of gold thiophenolate (**1**) (0.25 g; 0.65 mmol) in THF (10 ml). The reaction mixture was stirred for 15 min, an insoluble precipitate was filtered off, and solvent

**Table 3**  
Crystal data and structure refinement parameters for **9** and **12**.

Compound	<b>9</b>	<b>12</b>
Formula	C <sub>23</sub> H <sub>17</sub> AuClFeN	C <sub>31</sub> H <sub>26</sub> AuFeNS
FW	595.64	697.40
T (K)	100	100
Crystal system	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
Z	4 (1)	4 (1)
a (Å)	16.0368(7)	9.5959(9)
b (Å)	10.6479(7)	11.2351(12)
c (Å)	11.4182(9)	23.360(2)
α (°)	90.00	90.00
β (°)	108.9190(10)	98.146(3)
γ (°)	90.00	90.00
V (Å <sup>3</sup> )	1844.4(2)	2493.0(4)
D <sub>calc</sub> (g cm <sup>-3</sup> )	2.145	1.858
μ (cm <sup>-1</sup> )	88.84	65.65
F(0 0 0)	1136	1360
θ Range (°)	58	56
Reflections measured	7150	27 533
Independent reflections	7178	6005
Observed reflections [I > 2σ(I)]	5540	5439
Number of parameters	245	309
Final R(F <sub>hkl</sub> ): R <sub>1</sub>	0.0613	0.0282
wR <sub>2</sub>	0.1962	0.0647
GOF	1.066	1.092
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	2.21, -1.55	1.09, -0.88

was removed *in vacuo*. Complex **12** was obtained (0.27 g; 60%) as a red powder, m.p. 180–183 °C, decomp. Anal. Calc. for C<sub>31</sub>H<sub>26</sub>AuFeNS: C, 53.39; H, 3.76; N, 2.01. Found: C, 53.13; H, 3.80; N, 2.20%. <sup>1</sup>H NMR (chloroform-d, δ): 2.50 (s, 6H); 4.05 (s, 5H); 4.34 (m, 2H); 4.68 (m, 2H); 7.01 (m, 1H); 7.12 (m, 2H); 7.47 (m, 8H).

### 3.17. X-ray structures

Crystals of **9** were grown by gradual addition of ether to a solution of **9** in THF. Crystals of **12** were obtained by crystallization of the complex from hot toluene. All diffraction data were taken using a Bruker SMART APEX II CCD diffractometer [λ(Mo Kα) = 0.71072 Å, ω-scans] (see Table 3). The substantial redundancy in data allows empirical absorption correction to be applied using multiple measurements of equivalent reflections with SADABS. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F<sup>2</sup> in the anisotropic-isotropic approximation.

The results of the index procedure as well as visual inspection of the three-dimensional and rocking curves of spots revealed that the crystal of **9** was a growth twin. All attempts to find a non-twinned sample, even with extremely small dimensions, were unsuccessful since it appears that all crystals were obtained as twins. The collected dataset was indexed using cell\_now software and then intensities of the collected reflections were described as superpositions of two crystal components with a rotation angle equal to 179.5° along the (0 0 1) direction. The frames for **9** were integrated separately for each component and then reflections of

two components were separately included in refinement via HKLF 5 format (BASF is 0.26). All equivalent reflections for **9** were merged using the TWINABS program.

The analysis of the Fourier synthesis of the electron density in **12** revealed that one of the Cp-rings (C(6)–C(10)) and one phenyl ring C(26)–C(31) are disordered over two positions which were refined in the isotropic approximation. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined in the riding model. All calculations were performed using the SHELXTL PLUS 5.0.

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### Appendix A. Supplementary data

CCDC 736698 and 736697 contains the supplementary crystallographic data for **9** and **12**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.09.043](https://doi.org/10.1016/j.jorganchem.2009.09.043).

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