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Organogold(III) complexes derived from auration reactions of thienyl-substituted pyridine derivatives

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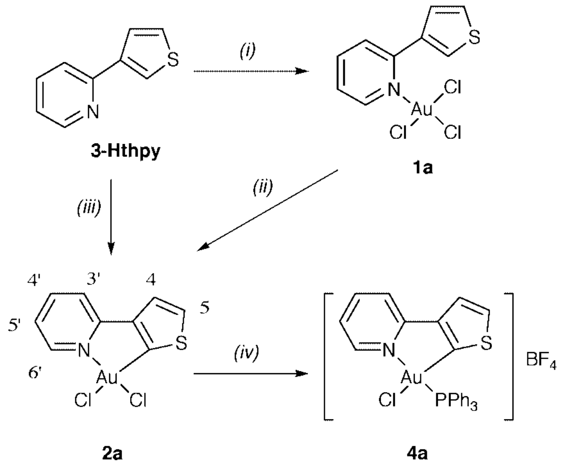
2-(3-Thienyl)pyridine (3-Hthpy) and 2-(2-thienyl)pyridine (2-Hthpy) reacted with $Na[AuCl_4]\cdot 2H_2O$ to afford the adducts $[AuCl_3(3\text{-Hthpy})]$ **1a** and $[AuCl_3(2\text{-Hthpy})]$ **1b**, respectively. The cycloaurated complex $[AuCl_2(3\text{-thpy-}C^2,N)]$ [3-thpy = 3-(2-pyridyl)thiophen-2-yl] **2a** was obtained by warming **1a** at 80 °C in an acetonitrile–water (1 : 5) mixed solvent, whereas the cycloaurated complex $[AuCl_2(2\text{-thpy-}C^3,N)]$ [2-thpy = 2-(2-pyridyl)thiophen-3-yl] **2b** was produced by the reaction of **1b** with silver(I) tetrafluoroborate in refluxing dichloromethane. Moreover, when **1b** was heated at reflux in dichloromethane in the absence of silver(I) tetrafluoroborate, the thiophene-C(5) metallated species $[\{Au(\mu\text{-}Cl)Cl[(2\text{-thpy-}C^5)H]\}_2]Cl_2$ [2-thpy = 2-(2-pyridyl)thiophen-5-yl] **3b** was formed. Thermal degradation of **3b** in aqueous acetonitrile yielded 2-(5-chloro-2-thienyl)pyridine and 5,5′-bis(2-pyridyl)-2,2′-bithienyl. X-Ray structural analyses of $[AuCl(3\text{-thpy-}C^1,N)(PPh_3)]BF_4$ **4a** and $[AuCl(3\text{-thpy-}C^1,N)(PPh_3)]BF_4$ **4b**, which were obtained by the reactions of **2a** and **2b** with triphenylphosphine, have been performed.

Cyclometallation has been receiving much interest in organometallic chemistry from the viewpoint of C–H bond activation by transition metal compounds.[1] Although gold(III) is isoelectronic with palladium(II) and platinum(II) (d^8), its chemistry of cyclometallation is still only poorly explored.[2] Moreover, to date, cyclometallation with gold(III) (cycloauration) has been limited to 2-substituted pyridine derivatives with the condition that the metallation sites are benzene ring-carbons.[2] Concerning metallation sites other than benzene ring-carbons, metallations at thiophene,[3] pyrazole,[4] pyrrole,[5] pyridine[6] and furan ring-carbons[7] have been established in cyclometallation with Ru^{II}, Rh^{III}, Ir^{III}, Pd^{II} and Pt^{II} species.

We have been studying cycloauration of 2-substituted pyridine derivatives in recent years and have reported the successful synthesis of new cycloaurated complexes derived from 2-benzoyl-, 2-anilino-, 2-phenoxy- and 2-(phenylsulfanyl)pyridine.[8] Developing our research interest in cycloauration chemistry, we have studied the cycloauration of 2-(3-thienyl)- and 2-(2-thienyl)-pyridine, both of which are potential ligands to form a C–N chelate ring composed of thiophene ring-carbon and pyridine nitrogen atoms. Concerning the reaction of 2-(2-thienyl)pyridine with gold(III) compounds, Constable and Sousa[9] reported that isolable products from this reaction were the addition complex $[AuCl_3(2\text{-Hthpy})]$, 2-(5-chloro-2-thienyl)pyridine and 5,5′-bis(2-pyridyl)-2,2′-bithienyl. However, our reinvestigation of the above reaction revealed that auration at C^3 (cycloauration) and C^5 of the thienyl group in 2-(2-thienyl)pyridine takes place depending upon the reaction conditions. Here we describe the above results and the novel cycloauration reaction of 2-(3-thienyl)pyridine as well.

Results and discussion

The methods for preparation of the new gold(III) complexes derived from 2-(3-thienyl)pyridine (3-Hthpy) and 2-(2-thienyl)pyridine (2-Hthpy) are shown in Scheme 1 and 2, respectively. Assignment of the ^1H NMR spectra was performed with the aid of ^1H–^1H correlation spectroscopy (COSY) and the data are summarized in Table 1.



Scheme 1 (*i*) $Na[AuCl_4]\cdot 2H_2O$; (*ii*) CH_3CN–H_2O (1 : 5); (*iii*) $Na[AuCl_4]\cdot 2H_2O$ in CH_3CN–H_2O (1 : 5); (*iv*) PPh_3, $NaBF_4$.

Auration of 3-Hthpy and 2-Hthpy and characterization of the resulting gold(III) complexes

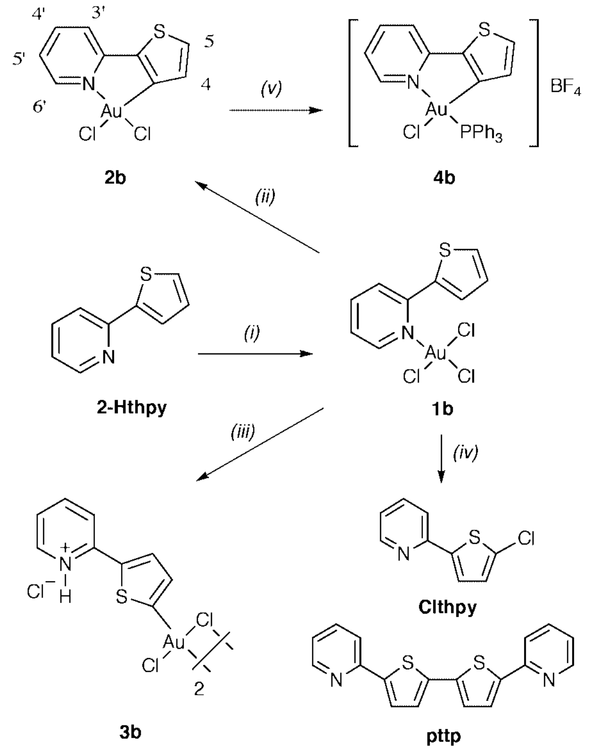
At room temperature 2-(3-thienyl)pyridine (3-Hthpy) and 2-(2-thienyl)pyridine (2-Hthpy) reacted with an equimolar amount of $Na[AuCl_4]\cdot 2H_2O$ in an acetonitrile–water (1 : 1) mixed solvent to give the adducts $[AuCl_3(3\text{-Hthpy})]$ **1a** and $[AuCl_3(2\text{-Hthpy})]$ **1b**, respectively, in nearly quantitative yields. In their far-IR spectra, adducts **1a** and **1b** showed only one strong band each, at 367 and 368 cm^{-1}, respectively, attributable to the overlapping ν(Au–Cl) frequencies *trans* to the pyridine-nitrogen and chloro ligand.[10] The absence of the characteristic band due to ν(Au–Cl) frequencies of the bond *trans* to sulfur (around 310 cm^{-1})[11] excludes the possibility of thiophene-sulfur coordination in **1a** and **1b**.

When **1a** was heated at 80 °C in an acetonitrile–water (1 : 5) mixed solvent, the cycloaurated complex $[AuCl_2(3\text{-thpy-}C^2,N)]$ [3-thpy = 3-(2-pyridyl)thiophen-2-yl] **2a** was isolated in 81% yield. Complex **1b** was also obtained directly from the reaction

Table 1 Proton NMR spectra of the organogold(III) complexes derived from 3-Hthpy and 2-Hthpy^{a}

Complex	2-Pyridyl moiety^{b} $H^{6'}$	Other protons		Thienyl moiety^{b} H^4 or H^5	PPh_3
1a [$AuCl_3$(3-Hthpy)]	8.88 (1H, dd)^{c}	7.73 (1H, dt, $H^{5'}$)^{d} 8.20 (1H, dt, $H^{4'}$)^{e}	7.88 (1H, dd, $H^{3'}$)^{e}	7.61 (1H, dd, H^4)^{f} 7.69 (1H, dd, H^5)^{g} 8.13 (1H, dd, H^2)^{h}	—
2a [$AuCl_2$(3-thpy-C^2,N)]	9.25 (1H, dd)^{d}	7.63 (1H, t, $H^{5'}$)^{i} 8.35 (1H, dt, $H^{4'}$)^{e}	8.13 (1H, dd, $H^{3'}$)^{e}	7.86 (1H, d)^{j} 7.88 (1H, d)^{j}	—
2b [$AuCl_2$(2-thpy-C^3,N)]	9.29 (1H, dd)^{d}	7.62 (1H, dt, $H^{5'}$)^{e} 8.29 (1H, dt, $H^{4'}$)^{e}	8.01 (1H, dd, $H^{3'}$)^{e}	7.32 (1H, d)^{j} 7.99 (1H, d)^{j}	—
3b [{Au(μ-Cl)Cl[(2-thpy-C^5)H]}$_2$]Cl_2	8.50 (1H, d)^{i}	7.26 (1H, d, $H^{5'}$)^{e}	7.85 (2H, $H^{3'}$, $H^{4'}$)^{l}	6.96 (1H, d)^{j} 7.70 (1H, d)^{j}	—
4a [AuCl(3-thpy-C^1,N)(PPh_3)]BF_4	9.27 (1H, br)^{k}	8.20 (1H, d, $H^{3'}$)^{i} 7.55–8.0 (1H, $H^{4'\text{ or }5'}$)^{l}	8.37 (1H, t, $H^{4'\text{ or }5'}$)^{i}	7.55–8.0 (2H)^{l}	7.55–8.00 (15H)^{l}
4b [AuCl(2-thpy-C^3,N)(PPh_3)]BF_4	8.9 (1H, br)	7.85 (1H, br, $H^{4'\text{ or }5'}$) 7.3–7.7 (2H, $H^{4'\text{ or }5}$, $H^{3'}$)^{l}		6.57 (1H, d)^{j} 7.3–7.7 (1H)^{l}	7.3–7.7 (15H)^{l}

[a] Measured in DMSO-d_6, except for **1a** (CD_3CN) at 270 MHz and 23 °C; δ in ppm with respect to $SiMe_4$; s = singlet, d = doublet, t = triplet, br = broad, dd = double doublet, dt = double triplet. [b] For numbering see Scheme 1 and 2. [c] ^3J(HH) = 5.9 Hz, ^4J(HH) = 1.0 Hz. [d] ^3J(HH) = 5.9 Hz, ^4J(HH) = 1.5 Hz. [e] ^3J(HH) = 7.8 Hz, ^4J(HH) = 1.5 Hz. [f] ^3J(HH) = 5.1 Hz, ^4J(HH) = 1.5 Hz. [g] ^3J(HH) = 5.1 Hz, ^4J(HH) = 2.9 Hz. [h] ^3J(HH) = 2.9 Hz, ^4J(HH) = 1.5 Hz. [i] ^3J(HH) = 7.8 Hz. [j] ^3J(HH) = 5.4 Hz. [k] Apparent triplet. [l] Overlapping signals.



Scheme 2 (*i*) Na[$AuCl_4$]·$2H_2O$; (*ii*) $AgBF_4$ in dichloromethane; (*iii*) dichloromethane; (*iv*) CH_3CN–H_2O (4 : 3); (*v*) PPh_3, $NaBF_4$.

between 3-Hthpy and Na[$AuCl_4$]·$2H_2O$ in an acetonitrile–water (1 : 5) mixed solvent at 80 °C. In contrast, as shown by Constable and Sousa[9] under the same reaction conditions adduct **1b** did not afford the cycloaurated complex [$AuCl_2$(2-thpy-C^3,N)] [2-thpy = 2-(2-pyridyl)thiophen-3-yl] **2b** and only the starting material was recovered from the reaction. However, we found that the 2-(2-thienyl)pyridine ligand in **1b** cyclometallated with gold when **1b** was heated at reflux in dichloromethane with silver(I) tetrafluoroborate (yield of **2b**, 46%). Interestingly, the above reaction performed in the absence of silver(I) tetrafluoroborate gave another metallation product, [{Au(μ-Cl)Cl[(2-thpy-C^5)H]}$_2$]Cl_2 [2-thpy = 2-(2-pyridyl)thiophen-5-yl] **3b**, where the C(5) of the thiophene moiety is metallated.

The ^1H NMR spectrum of the adduct **1b** in CD_3CN was identical with that reported,[9] but in DMSO-d_6 it showed the same spectrum as that of free 2-Hthpy. Moreover, signals due to free 3-Hthpy were observed in the ^1H NMR spectrum of the adduct **1a** in DMSO-d_6. These results indicated that the co-ordinated 2-Hthpy or 3-Hthpy ligand readily dissociates in DMSO. Concerning the cycloauration of complexes **2a** and **2b**, their ^1H NMR spectra both showed only six aromatic protons and their far-IR spectra each exhibited two bands characteristic of ν(Au–Cl) frequencies of bonds *trans* to a pyridyl nitrogen atom [366 (**2a**) and 362 cm^{-1} (**2b**)] and a thienyl carbon atom [283 (**2a**) and 281 cm^{-1} (**2b**)],[10] as expected from the cycloaurated structures. The lower field shifts of $\delta(H^{6'})$ resonances (for the numbering scheme, see Scheme 1) in the spectra of **2a** (δ 9.06) and **2b** (δ 9.17) compared with those of the free ligands [3-Hthpy (δ 8.59) and 2-Hthpy (δ 8.52)] and the adducts [**1a** (δ 8.88) and **1b** (δ 8.95)[10] in CD_3CN] are also observed in other cycloaurated complexes containing pyridine ligands.[2] This shift was ascribed to the proximity of the $H^{6'}$ proton to chloride ligand,[12] and can be used as a good indicator of cycloauration. The two protons in the thiophene ring of **2b** appeared as a well-separated AB pattern at δ 7.32 and 7.99, while those of **2a** were observed at nearly equal chemical shifts, δ 7.86 and 7.88.

The C(5) metallated species **3b** showed two bands at 364 and 300 cm^{-1} in its IR spectrum assignable to ν(Au–Cl) frequencies due to the bonds *trans* to chloride and carbon, respectively.[10] Moreover, bands assignable to ν(NH) and $\nu(C{=}N^+)$ frequencies were observed at 3230 and 1600 cm^{-1} indicating the presence of a pyridinium moiety. The ^1H NMR spectrum of this complex exhibited six protons in the aromatic region with chemical shifts quite different from those observed in **2b**. The FAB mass spectrum of **3b** gave a parent peak at *m*/*z* 893 attributable to $[M - Cl]^+$. On the basis of these results and elemental analysis, **3b** was tentatively assigned to have the structure shown in Scheme 2. However, the conductivity of **3b**, measured in acetone (Λ_M 137 S cm^2 mol^{-1}) and DMSO (68.0 S cm^2 mol^{-1}), showed lower values than might be expected for a 2 : 1 electrolyte,[13] implying that in solution **3b** exists to a considerable degree as the zwitterionic species [Au^-Cl_3{(2-thpy-C^5)H}$^+$]. Similar lower molar conductivity (Λ_M 85 S cm^2 mol^{-1} in acetone) has been observed for [$AuCl_2$(L)·HCl] (HL = 1-phenylpyrazole) formed by the C(4) metallation of 1-phenylpyrazole by anhydrous $AuCl_3$.[14] Such thiophene-C(5) metallated species have been reported by Constable *et al.*[15] from the reaction between Na[$AuCl_4$] and 6-(2-thienyl)-2,2′-bipyridine. Both our results and those of Constable indicate that gold(III) species are apt to attack upon the most electrophilic C(5) site rather than C(3) of the thiophene moiety which leads to formation of a cycloaurated complex. Moreover, it was found that by thermal degradation of **3b** at 84 °C in aqueous acetonitrile 2-(5-chloro-2-thienyl)pyridine (Clthpy) and 5,5′-bis(2-pyridyl)-2,2′-bithienyl (pttp) were produced in 8 and 18% yields, respectively. Considering the previous observation by Constable and Sousa,[9]

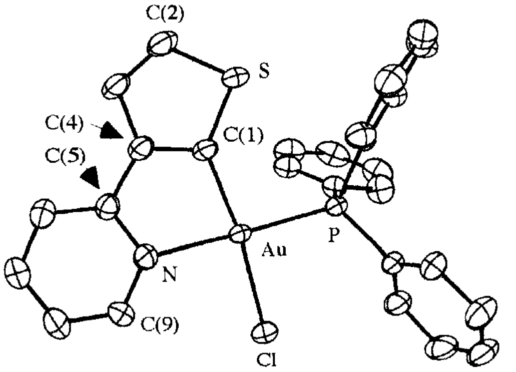


Fig. 1 An ORTEP view of [AuCl(3-thpy-C^1,N)(PPh$_3$)]BF$_4$·CH$_2$Cl$_2$ [3-thpy = 3-(2-pyridyl)thiophen-2-yl] **4a**·CH$_2$Cl$_2$. Hydrogen atoms and the tetrafluoroborate anion are omitted for clarity.

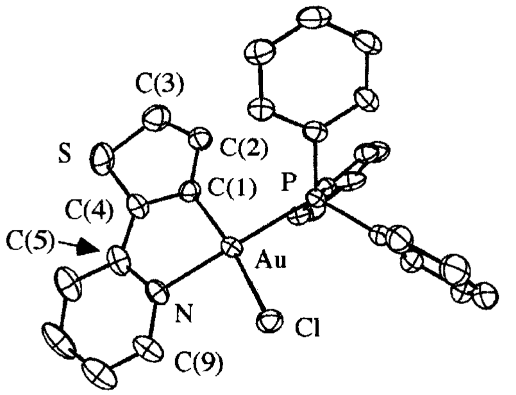


Fig. 2 An ORTEP view of [AuCl(2-thpy-C^3,N)(PPh$_3$)]BF$_4$ [2-thpy = 2-(2-pyridyl)thiophen-3-yl] **4b**. Hydrogen atoms and the tetrafluoroborate anion are omitted for clarity.

where Clthpy and pttp were obtained by warming the adduct **1b** at 80 °C in aqueous acetonitrile, it is reasonable to regard **3b** as an intermediate for the formation of Clthpy and pttp.

Synthesis and X-ray structural analysis of [AuCl(3-thpy-C^1,N)(PPh$_3$)]BF$_4$ and [AuCl(2-thpy-C^1,N)(PPh$_3$)]BF$_4$

In the presence of NaBF$_4$, complexes **2a** and **2b** reacted with an equimolar amount of PPh$_3$ to give cationic complexes **4a** (Λ_M 145 S cm^2 mol^{-1} in acetone) and **4b** (Λ_M 128 S cm^2 mol^{-1} in acetone), respectively. The IR spectra of both complexes exhibited a strong band due to BF$_4^-$ at 1055 cm^{-1} and only one band assignable to the ν(Au–Cl) frequency *trans* to a phenylene group at 327 (**4a**) and 320 cm^{-1} (**4b**).[10] In the ^{1}H NMR spectrum of **4b**, the H^4 signal appeared at considerably higher field (δ 6.57) which is caused by the ring current of the adjacent benzene ring of the triphenylphosphine ligand co-ordinated *cis* to the C–Au bond. On the basis of these data together with elemental analyses, **4a** and **4b** were identified as the cationic four-coordinate complexes [AuCl(3-thpy-C^1,N)(PPh$_3$)]BF$_4$ and [AuCl(2-thpy-C^1,N)(PPh$_3$)]BF$_4$, respectively.

Table 2 Crystallographic data for complexes **4a** and **4b**

	4a·CH$_2$Cl$_2$	**4b**
Formula	C$_{28}$H$_{23}$AuBCl$_3$F$_4$NPS	C$_{27}$H$_{21}$AuBCl$_3$F$_4$NPS
M	826.67	741.73
T/K	293(1)	193(1)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	10.473(3)	13.585(3)
b/Å	11.501(3)	9.3107(9)
c/Å	13.235(4)	20.572(5)
α/°	99.45(2)	90
β/°	107.93(1)	93.65(1)
γ/°	85.49(2)	90
U/Å^3	1495.6(7)	2596.9(9)
Z	2	4
Crystal dimensions/ mm	0.60 × 0.45 × 0.21	0.60 × 0.42 × 0.13
μ(Mo-Kα)/cm^{-1}	53.44	59.42
No. measured reflections	5636	4868
No independent reflections	5052	4293
R	0.026	0.032
R'	0.031	0.037

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **4a**·CH$_2$Cl$_2$

Au–C(1)	2.022(5)	Au–N	2.112(4)
Au–Cl	2.322(1)	Au–P	2.307(1)
C(1)–C(4)	1.379(7)	C(4)–C(5)	1.454(8)
C(5)–N	1.361(7)	C(1)–S	1.711(5)
C(2)–S	1.718(6)	C(2)–C(3)	1.353(9)
C(3)–C(4)	1.428(8)		
C(1)–Au–N	80.0(2)	C(1)–Au–P	97.2(1)
N–Au–P	175.0(1)	P–Au–Cl	90.26(5)
N–Au–Cl	92.2(1)	C(1)–Au–Cl	171.5(2)

Table 4 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex **4b**

Au–C(1)	2.025(8)	Au–N	2.103(6)
Au–Cl	2.349(2)	Au–P	2.304(2)
C(1)–C(4)	1.36(1)	C(4)–C(5)	1.45(1)
C(5)–N	1.35(1)	C(4)–S	1.71(1)
C(3)–S	1.70(1)	C(2)–C(3)	1.36(1)
C(1)–C(2)	1.42(1)		
C(1)–Au–N	80.7(3)	C(1)–Au–P	93.7(2)
N–Au–P	168.8(2)	P–Au–Cl	93.98(7)
N–Au–Cl	93.0(2)	C(1)–Au–Cl	169.2(2)

The structures of **4a** and **4b** were established by X-ray diffraction and ORTEP[16] views of the molecules are shown in Fig. 1 and 2. Crystal data are listed in Table 2, and selected bond distances and angles are presented in Tables 3 and 4. The gold atom in complex **4a** displays square-planar co-ordination with very slight pyramidal distortion: thus the C, N, Cl and P atoms are coplanar (mean deviation from the best plane of 0.0044 Å), with the gold atom lying 0.0769(2) Å below the best plane. On the other hand, in complex **4b** the gold atom displays a distorted square-planar co-ordination, with the Au, C, P and Cl atoms essentially coplanar [maximum deviation from their best plane being +0.0474(80) and −0.0940(3) Å for C and Au, respectively], whereas the N atom is displaced 0.5191(66) Å out of this plane. The dihedral angle between the Au–P–Cl and Au–C–N planes is 12.77(71)°. A similar distortion has been previously found in [Au(L)Cl] [HL = 6-(α,α-dimethyl)benzyl-2,2′-bipyridine], where the dihedral angle between Au–N–N and Au–Cl–C is 11.2(6)°.[2e] The Au–C and Au–P bond distances in **4a** and **4b** are normal for gold(III) complexes.[2b,d,e,8,10,17,18] The bite angles of the cycloaurated ligands are 80.0 (**4a**) and 80.7° (**4b**), values which are comparable to those in five-membered auracycles derived from *N*,*N*-dimethylbenzylamine [82.2(4)°],[19] 4,4-dimethyl-2-phenyl-1,3-oxazoline [81.7(3)°],[17] 4-butyl-*N*-(trimethoxybenzylidene)aniline [81.41(14)°][10] and 4,4′-dimethylazobenzene [80.1(2)°],[20] and smaller than the values found in six-membered auracycles such as [AuCl(C$_6$H$_4$CH$_2$C$_5$H$_4$N-C^1,N)(PPh$_3$)]BF$_4$ [85.8(4)°],[8a] [AuCl$_2$(C$_6$H$_4$CMe$_2$C$_5$H$_4$N-C^1,N)] [85.7(1)°],[2e] [AuCl$_2$(C$_6$H$_4$COC$_5$H$_4$N-C^1,N)] [89.5(3)°],[8a] [AuCl(C$_6$H$_4$NHC$_5$H$_4$N-C^1,N)(PPh$_3$)]BF$_4$ [85.2°],[8b] [AuCl$_2$(C$_6$H$_4$OC$_5$H$_4$N-C^1,N)] [86.6°][8b] and [AuCl$_2$(C$_6$H$_4$SC$_5$H$_4$N-C^1,N)] [88.3°].[8b] The slightly longer Au–Cl [2.322(1) (**2a**) and 2.349(2) Å (**2b**)] and Au–N bond distances [2.112(4) (**2a**) and 2.103(6) Å

(**2b**)] are caused by the greater *trans* influences of the carbon donor and phosphine ligand, respectively.

Experimental

General

The IR spectra were measured on a JASCO FT/IR-420 spectrophotometer, and ^{1}H NMR spectra were recorded on a JEOL JNM-GX-270 spectrometer using tetramethylsilane as an internal standard. Melting points were determined on a Yanaco MP-500D micro melting-point apparatus and are uncorrected. Conductivity measurements were carried out at 25 °C on a Toa Electronics CM-20E conductometer. FAB mass spectra were recorded on a JEOL-SX102A mass spectrometer. 2-(2-Thienyl)pyridine was prepared according to the literature.[21] Other reagents were obtained commercially and used without further purification.

Syntheses

[AuCl$_3$(3-Hthpy)] 1a. An acetonitrile solution (5 cm^3) of 3-Hthpy (0.223 g, 1.38 mmol) was added to a water solution (5 cm^3) of Na[AuCl$_4$]·2H$_2$O (0.501 g, 1.32 mmol), and the resulting mixture was stirred at room temperature. After 2 h, the precipitated orange solids were filtered off and washed with water and diethyl ether to give **1a** (0.572 g, 94%); mp 215 °C (decomp.) (Found: C, 23.5; H, 1.6; N, 3.05. $C_9H_7AuCl_3NS$ requires C, 23.25; H, 1.5; N, 3.0%); ν_{max}/cm^{-1} (KBr) 367 (Au–Cl); Λ_M (1.0 × 10^{-3} mol dm^{-3}, acetone) 1.52 S cm^2 mol^{-1}.

[AuCl$_3$(2-Hthpy)] 1b. This complex was obtained in a similar manner as described for **1a** as brick-red microcrystals in 96% yield and was identified as [AuCl$_3$(2-Hthpy)] on the basis of comparisons with the reported data.[9]

[AuCl$_2$(3-thpy-*C*^{2},*N*)] 2a. *Method (a).* An acetonitrile–water suspension (1 : 5, 6 cm^3) containing the adduct [AuCl$_3$(3-Hthpy)] **1a** (0.100 g, 0.215 mmol) was heated at 80 °C for 2 h. The resulting mixture was filtered off and washed successively with water and diethyl ether to give orange-brown solids. These solids were further washed with a dichloromethane–hexane mixed solvent (5 : 2, 7 cm^3) to afford complex **2a** (0.074 g, 81%); mp 226 °C (decomp.) (Found: C, 25.55; H, 1.45; N, 3.3. $C_9H_6AuCl_2NS$ requires C, 25.25; H, 1.4; N, 3.25%); ν_{max}/cm^{-1} (KBr) 366, 283 (Au–Cl); Λ_M (0.5 × 10^{-3} mol dm^{-3}, DMSO) 1.91 S cm^2 mol^{-1}.

Method (b). An acetonitrile solution (3 cm^3) of 3-Hthpy (0.050 g, 0.309 mmol) was added to a water solution (15 cm^3) of Na[AuCl$_4$]·2H$_2$O (0.102 g, 0.270 mmol), and the resulting mixture was heated at 80 °C for 7 h. After a work-up similar to that described in method (a), complex **2a** was obtained in 83% yield.

[AuCl$_2$(2-thpy-*C*^{3},*N*)] 2b. Silver(I) tetrafluoroborate (0.132 g, 0.679 mmol) was added to a dichloromethane suspension (150 cm^3) of **1b** (0.300 g, 0.646 mmol), and then the resulting mixture was refluxed for 2 h. After filtration, the filtrate was evaporated to dryness and the residue was washed with acetonitrile to remove silver salts, giving **2b** (0.127 g, 46%); mp 240 °C (decomp.) (Found: C, 25.35; H, 1.4; N, 3.35. $C_9H_6AuCl_2NS$ requires C, 25.25; H, 1.4; N, 3.25%); ν_{max}/cm^{-1} (KBr) 362, 281 (Au–Cl); Λ_M (0.5 × 10^{-3} mol dm^{-3}, DMSO) 1.97 S cm^2 mol^{-1}.

[{Au(μ-Cl)Cl[(2-thpy-*C*^{5})H]}$_2$]Cl$_2$ 3b. A dichloromethane solution (80 cm^3) of **1b** (0.501 g, 1.078 mmol) was heated under reflux for 24 h. The resulting precipitates were collected and washed with dichloromethane to give **3b** as yellow microcrystals (0.210 g, 42%), mp 204 °C (decomp.) (Found: C, 23.35; H, 1.5; N, 3.0. $C_{18}H_{12}Au_2Cl_4N_2S_2$ requires C, 25.25; H, 1.4; N, 3.25%); ν_{max}/cm^{-1} (KBr) 364, 300 (Au–Cl); Λ_M 137 S cm^2 mol^{-1} (1.0 × 10^{-3} mol dm^{-3}, acetone), 68.0 S cm^2 mol^{-1} (5.0 × 10^{-4} mol dm^{-3}, DMSO).

2-(5-Chloro-2-thienyl)pyridine (Clthpy) and 5,5′-bis(2-pyridyl)-2,2′-bithienyl (pttp). An acetonitrile–water (4 : 3) suspension (7 cm^3) containing **3b** (0.185 g, 0.199 mmol) was heated at 84 °C for 2 d, and the resulting mixture was filtered while hot. The filtered solution was cooled to ambient temperature and the precipitated solids were collected. The ^{1}H NMR spectrum showed that these solids were composed of two compounds. These two compounds were identified as Clthpy and pttp by comparing the ^{1}H NMR spectrum in acetone-*d*$_6$ (for Clthpy) or DMSO-*d*$_6$ (for pttp).[9] The yields of Clthpy (8%) and pttp (18%) were determined using 2-methylpropan-2-ol as an internal standard.

[AuCl(3-thpy-*C*^{2},*N*)(PPh$_3$)]BF$_4$ 4a. Triphenylphosphine (0.194 g, 0.738 mmol) and then sodium tetrafluoroborate (0.387 g, 3.521 mmol) were added to a dichloromethane solution (30 cm^3) of **2a** (0.300 g, 0.701 mmol). The resulting solution was stirred for 1 d and then filtered. The filtrate was evaporated to dryness under reduced pressure and the residue was extracted with acetonitrile. The extract was concentrated and diluted with diethyl ether to yield yellow microcrystals of **4a** (0.435 g, 84%); mp 185 °C (decomp.) (Found: C, 43.65; H, 2.9; N, 2.05. $C_{27}H_{21}AuBClF_4NPS$ requires C, 43.7; H, 2.85; N, 1.9%); ν_{max}/cm^{-1} (KBr) 1055 (BF$_4^-$), 327 (Au–Cl); Λ_M(1.0 × 10^{-3} mol dm^{-3}, acetone) 145 S cm^2 mol^{-1}.

[AuCl(2-thpy-*C*^{3},*N*)(PPh$_3$)]BF$_4$ 4b. This complex was prepared similarly as described for **4a** as yellow microcrystals in 82% yield; mp 187 °C (decomp.) (Found: C, 46.25; H, 3.1; N, 1.75. $C_{27}H_{21}AuBClF_4NPS$ requires C, 43.7; H, 2.85; N, 1.9%); ν_{max}/cm^{-1} (KBr) 1055 (BF$_4^-$), 320 (Au–Cl); Λ_M (1.0 × 10^{-3} mol dm^{-3}, acetone) 128 S cm^2 mol^{-1}.

X-Ray crystallography

Suitable crystals of [AuCl(3-thpy-*C*^{1},*N*)(PPh$_3$)]BF$_4$·CH$_2$Cl$_2$ **4a**·CH$_2$Cl$_2$ and [AuCl(2-thpy-*C*^{3},*N*)(PPh$_3$)]BF$_4$ **4b** were grown from dichloromethane–diethyl ether and chloroform–diethyl ether, respectively. Each crystal was sealed in a glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. Crystal data and details of the data collection are given in Table 2. Intensity data were collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects and absorption. The structure was solved by direct methods and the computer program MolEN[22] was used for structure solution and refinement. All the non-hydrogen atoms were treated anisotropically. The hydrogen atoms were inserted in their calculated positions and fixed at these positions. The weighing scheme, $w = 1/[\sigma^2(|F_o|) + (0.02|F_o|)^2 + 1.0]$, was employed.

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