

The direct cycloauration of 6-(2''-thienyl)-2,2'-bipyridine

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Abstract

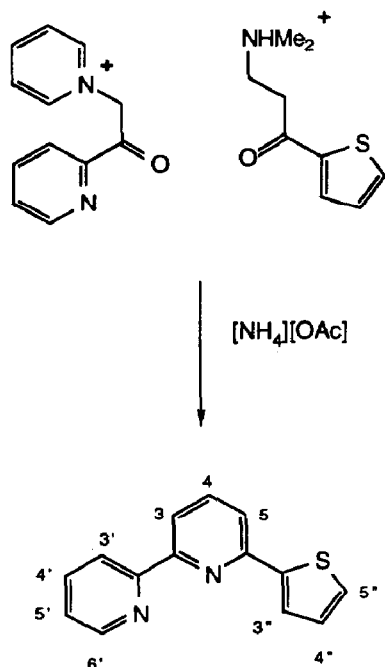
The potentially terdentate *N,N,S*-donor 6-(2''-thienyl)-2,2'-bipyridine (**HL**) reacts with $\text{Na}[\text{AuCl}_4]$ to form the complex $[\text{Au}(\text{HL})\text{Cl}_3]$ in which the ligand acts as a monodentate *N*-donor. This complex is converted into the cycloaurated compound $[\text{Au}(\text{L})\text{Cl}_2]$ upon warming. This is the first example of a direct cycloauration reaction of this type, and can be ascribed to non-bonded interactions of the ligand with the metal in $[\text{Au}(\text{HL})\text{Cl}_3]$.

Introduction

Although organometallic derivatives of gold are well-known [1–3], examples of cycloaurated complexes are rare. Cycloaurated derivatives of azobenzene [4–8] and *N,N'*-dimethylaminomethylbenzene [9,10] have been prepared by transmetallation or organomercurial intermediates, but cannot be obtained from direct reactions of the ligands with $[\text{Au}_2\text{Cl}_6]$ or $[\text{AuCl}_4]^-$. We have recently investigated the coordination chemistry of 6-(2''-thienyl)-2,2'-bipyridine with a view to enhancing thiophene coordination by chelation. We report here the facile cycloauration of 6-(2''-thienyl)-2,2'-bipyridine by direct reaction with $\text{Na}[\text{AuCl}_4]$.

Results and discussion

The compound 6-(2''-thienyl)-2,2'-bipyridine (**HL**) has been known since 1976 [11], but despite its obvious potential as a terdentate ligand, no coordination compounds containing it have been reported. The ligand is readily prepared in good yield by the Kröhnke pyridine synthesis [11]. The reaction of 2-(2-pyridyl)-2-oxoethylpyridinium iodide with *N*-{3-(2-thienyl)-3-oxopropyl}-*N,N*-dimethylammonium chloride and ammonium acetate in acetic acid gives a dark solution, from which **HL** can be obtained as pale yellow needles (75%) after the addition of aqueous methanol. The ^1H NMR spectrum of a solution of **HL** in CDCl_3 confirms the proposed structure. Chemical shift data are presented in Table 1, but the most



pertinent feature is the AMX pattern for the thiophene ring, with H(4'') as the highest field resonance (δ 7.13, $J_{3'',4''}$ 3.7, $J_{5'',4''}$ 5.5 Hz).

The addition of a solution of **HL** in acetonitrile to an aqueous solution of Na[AuCl₄] at 45 °C gives a precipitate of an orange microcrystalline solid, formulated as {Au(**HL**)Cl₃} on the basis of elemental analysis. The presence of **HL** rather than a metallated form of the ligand is confirmed by the presence of ten non-equivalent resonances in the aromatic region of the ¹H NMR spectrum of the complex. The AMX system of the thiophene ring is clearly seen in the COSY spectrum (Fig. 1a). The most likely structures for the complex are [Au(**HL**)Cl₂]Cl (**HL** as a bidentate *N,N'*-donor) or [Au(**HL**)Cl₃] (**HL** as a monodentate *N*-donor through the terminal or central pyridine ring). The complex is not sufficiently soluble in dichloromethane to allow a conductivity determination, but its insolubility in water argues against the first structure. This is supported by the infra-red spectrum

Table 1

¹H NMR data for gold(III) complexes of pyridine and **HL**. All assignments were made on the basis of phase-sensitive double quantum filtered COSY experiments

Compound	H(6')	H(5')	H(4')	H(3')	H(3)	H(4)	H(5)	H(3'')	H(4'')	H(5'')
HL ^a	8.67	7.31	7.85	8.57	8.29	7.81	7.75	7.65	7.13	7.41
[Au(HL)Cl ₃] ^a	9.14	8.07	8.60	8.67	8.33	8.07	7.96	7.96	7.24	7.59
[Cu(L)Cl ₂] ^b	9.22	8.05	8.05	8.41	8.10	8.05	7.96		6.92	7.68
py ^a	8.50	7.06	7.46	7.06						
[Au(py)Cl ₃] ^a	8.89	7.74	8.17	7.74						

^a CDCl₃. ^b CD₃SOCD₃.

of the complex which exhibits a single $\nu(\text{Au}-\text{Cl})$ stretch at 364 cm^{-1} . The complex $[\text{Au}(\text{bipy})\text{Cl}_2]^+$ exhibits two infra-red active $\nu(\text{Au}-\text{Cl})$ modes at 368 and 255 cm^{-1} whereas $[\text{Au}(\text{py})\text{Cl}_3]$ exhibits a single band at $363\text{--}366\text{ cm}^{-1}$ [12–14]. The ^1H NMR spectrum of the complex also supports its structure. Upon coordination to the gold, the resonances assigned to $\text{H}(3'')$, $\text{H}(4'')$ and $\text{H}(5'')$ of the thiophene, and $\text{H}(3)$, $\text{H}(4)$ and $\text{H}(5)$ of the central pyridine ring undergo very slight downfield shifts of $+0.04\text{--}+0.21\text{ ppm}$. In contrast, the resonances of $\text{H}(3')$, $\text{H}(4')$, $\text{H}(5')$ and $\text{H}(6')$ of the terminal pyridine ring shows much greater downfield shifts. This strongly suggests that $[\text{Au}(\text{HL})\text{Cl}_3]$ contains a monodentate HL ligand bonded to the AuCl_3 unit through the nitrogen atom of the terminal pyridine ring. This is further

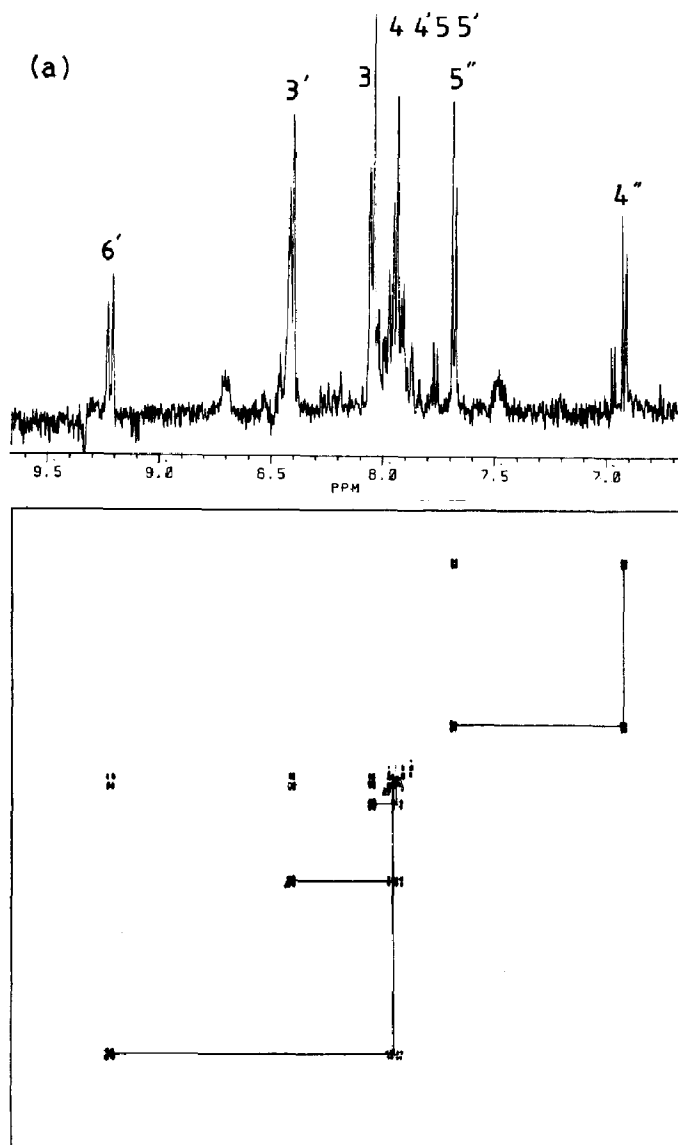


Fig. 1. The double quantum filtered phase sensitive COSY spectra of (a) $[\text{Au}(\text{HL})\text{Cl}_3]$ in CDCl_3 and (b) $[\text{Au}(\text{L})\text{Cl}_2]$ in CD_3SOCD_3 .

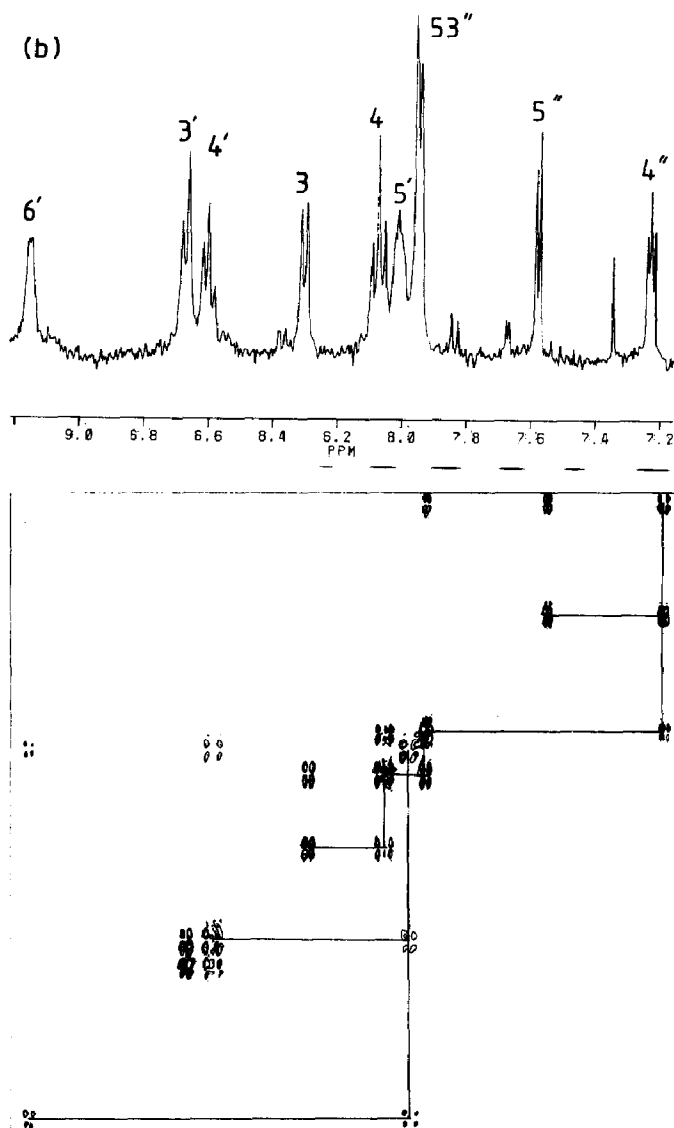


Fig. 1 (Continued).

supported by a comparison of the chemical shift changes ($\Delta\delta$) occurring upon coordination in the ligands in $[\text{Au}(\text{py})\text{Cl}_3]$ and $[\text{Au}(\text{HL})\text{Cl}_3]$ (Table 1). The down-field shifts observed for H(6'), H(5') and H(4') in $[\text{Au}(\text{HL})\text{Cl}_3]$ ($\Delta\delta$ +0.47, +0.76 and +0.75 respectively) are very similar to those observed for H(2,6), H(3,5) and H(4) in $[\text{Au}(\text{py})\text{Cl}_3]$ ($\Delta\delta$ +0.39, +0.68 and +0.71 respectively). The resonance assigned to H(3') in HL is only slightly shifted in $[\text{Au}(\text{HL})\text{Cl}_3]$ ($\Delta\delta$ +0.10), and this may be ascribed to a conformational change in the ligand upon coordination.

When the above procedure was repeated at 100°C , the product was an orange-brown microcrystalline solid. This product was also obtained in near-quantitative yield when a solution of $[\text{Au}(\text{HL})\text{Cl}_3]$ in aqueous acetonitrile was heated to reflux for 6 h. Elemental analysis of the orange-brown product indicated a formulation $[\text{Au}(\text{L})\text{Cl}_2]$. The complex exhibited no detectable $\nu(\text{Au}-\text{Cl})$ modes in its infra-red

spectrum. The ^1H NMR spectrum of a CD_3SOCD_3 solution of the complex exhibits resonances assigned to 9 non-equivalent protons.

The COSY spectrum is shown in Fig. 1b. The most obvious feature is the appearance of an AM pattern for the thiophene ring. This unambiguously confirms the presence of the cyclometallated ligand in the complex. The complex $[\text{Au}(\text{L})\text{Cl}_2]$ is insoluble in water and chlorinated solvents, but readily soluble in dmsO. The chemical shifts of H(6') and H(5') suggest that the terminal pyridine may be coordinated to the metal. We believe that in CD_3SOCD_3 the complex contains a terdentate *N,N',C*-donor cyclometallated ligand. The ^1H NMR spectrum of the CD_3SOCD_3 solution changes with time, possibly as a result of a change from $[\text{Au}(\text{L})\text{Cl}]^+$ to $[\text{Au}(\text{L})(\text{dmsO})]^{2+}$. In the solid state the complex could either be five coordinate with a *N,N',C*-donor ligand or contain a bidentate *N,C*-donor ligand with the terminal pyridine ligand non-coordinated. The ionic structure $[\text{Au}(\text{L})\text{Cl}]\text{Cl}$ may be eliminated on solubility grounds.

The reaction of 6-(2''-thienyl)-2,2'-bipyridine with $[\text{AuCl}_4]^-$ provides the first example of direct cycloauration, and demonstrates the ability of gold(III) to activate arene C–H bonds. The preparation of the 'normal' coordination compound $[\text{Au}(\text{HL})\text{Cl}_3]$ and its facile conversion into the cyclometallated derivative $[\text{Au}(\text{L})\text{Cl}_2]$ provides a very simple route to the organometallic derivatives. The cycloauration reaction involves a considerable rearrangement of the ligand bonding mode. Whilst it is not clear whether the terminal pyridine ring is bonded in the product $[\text{Au}(\text{L})\text{Cl}_2]$, the cyclometallated bonding mode requires the central pyridine ring and the metallated thiophene ring to bond to the metal. This presumably involves a transition state in which there is a π -interaction between the thiophene and the metal. It is of interest to speculate on whether the facile metallation observed in this ligand is due to a pre-organisation in $[\text{Au}(\text{HL})\text{Cl}_3]$ in which the thienyl group is constrained to a position close to the gold. In the absence of further structural data no decision on this can be made.

Experimental

NMR spectra were recorded on Bruker WM250 or AM400 spectrometers in CDCl_3 or CD_3SOCD_3 solution; assignments were made by double-quantum filtered phase-sensitive COSY experiments. Infra-red spectra were recorded with compressed KBr discs and Nujol mulls on Perkin–Elmer 1710 FT or 983 spectrophotometers. 2-Acetylthiophene (Aldrich), 2-acetylpyridine (Aldrich) and $\text{Na}[\text{AuCl}_4]$ (Johnson-Matthey) were used as supplied. 2-(2-Pyridyl)-2-oxoethylpyridinium iodide and *N*-{3-(2-thienyl)-3-oxopropyl}-*N,N*-dimethylammonium chloride were prepared by modifications of the general methods [11].

Synthesis of HL

A solution of ammonium acetate (8.50 g) and 2-(2-pyridyl)-2-oxoethylpyridinium iodide (1.30 g, 4.0 mmol) in acetic acid (8 cm^3) was heated at 100°C for 10 min after which *N*-{3-(2-thienyl)-3-oxopropyl}-*N,N*-dimethylammonium chloride (0.88 g, 4.00 mmol) was added and the mixture was kept at 105°C for 4 h under dinitrogen. The dark solution was then cooled and treated with water and methanol to yield HL as a pale brown solid (0.72 g, 75%). Recrystallisation from methanol

gave pale yellow needles (m.p. 75–78 °C, lit. [11] 78 °C) (Found: C, 69.4; H, 4.2; N, 11.2. $C_{14}H_{10}N_2S \cdot 1/4H_2O$ calc.: C, 69.3; H, 4.3; N, 11.4%; m/z 238).

Synthesis of [Au(HL)Cl₃]

A solution of **HL** (0.145 g, 0.61 mmol) in MeCN (3 cm³) was added to a stirred aqueous solution of Na[AuCl₄] (0.222 g, 0.61 mmol, 5 cm³) maintained at 45 °C. A further 3 cm³ of water was added in portions during 5 h, after which [Au(HL)Cl₃] was isolated as an orange microcrystalline solid (0.288 g, 87%) (Found: C, 30.9; H, 1.9; N, 5.3. $C_{14}H_{10}N_2SAuCl_3$ calc.: C, 31.0; H, 1.9; N, 5.2%. IR: 1587m, 1565m, 1450s, 815m, 770s, 716m, 364m cm⁻¹).

Synthesis of [Au(L)Cl₂]

Method A. A solution of **HL** (0.024 g, 0.1 mmol) in MeCN (1.5 cm³) was added to a stirred aqueous solution of Na[AuCl₄] (0.036 g, 0.1 mmol, 2 cm³) maintained at 100 °C. After 5 h [Au(L)Cl₂] was isolated as an orange-brown microcrystalline solid (0.048 g, 95%) (Found: C, 33.2; H, 1.9; N, 5.4. $C_{14}H_9N_2SAuCl_2$ calc.: C, 33.3; H, 1.8; N, 5.55%; IR: 1588m, 1561m, 1445s, 770s, 691m cm⁻¹).

Method B. A solution of [Au(HL)Cl₃] (0.10 g, 0.185 mmol) in a mixture of water (4 cm³) and MeCN (3 cm³) was heated under reflux for 6 h, after which the solid had darkened to orange brown. The product (0.77 g, 83%) was shown to be identical to that obtained by method A.

Acknowledgements

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