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Metal-ion dependent reactivity of 2-(2′-thienyl)pyridine (Hthpy)

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Abstract

The reaction of 2-(2′-thienyl)pyridine (Hthpy) with palladium acetate results in a clean conversion to the μ-acetato-bridged dimeric cyclometallated complex [(thpy)Pd(μ-OAc)Pd(thpy)] in which a new Pd–C bond is formed at the 3′ position of the thienyl ring. In contrast, treatment with $Na[AuCl_4]$ under similar conditions only results in the formation of the complex $[(HL)AuCl_3]$ in which the ligand acts as a monodentate *N*-donor. At higher temperatures the reaction of $Na[AuCl_4]$ with Hthpy yields a complex mixture of products, including complexes of 2-(5′-chloro-2′-thienyl)pyridine and 5,5′-bis(2-pyridyl)-2,2′-bithienyl. Independent syntheses of these latter compounds have confirmed their identities. The reaction of 2-(2′-thienyl)pyridine with $[Ru(bpy)_2Cl_2]$ (bpy = 2,2′-bipyridine) in the presence of a chloride ion abstractor yields salts of the cation $[Ru(bpy)_2(Hthpy)]^{2+}$ which contains a bidentate *N,S*-bonded ligand.

Introduction

We have been interested in the development of a systematic synthetic methodology for the preparation of cyclometalated complexes incorporating a variety of chelation stabilised metal aryls for a number of years [1–14]. The ligand 6-(2″-thienyl)-2,2′-bipyridine (Htbpy) has proved to be of particular interest, and exhibits a very wide range of bonding modes which include monodentate *N*-donor, bidentate *N,N*-donor, terdentate *N,N,S*-donor and cyclometalated *N,N,C*-donor [3,6,13,14]. In the course of our studies we became aware that reactions involving d^8 gold(III) centres differed dramatically from those at analogous d^8 palladium(II) and platinum(II) centres [3,13]. In particular, we found that deceptively simple reactions with gold(III) resulted in metalation at C(5″) of the thienyl ring rather than at the expected C(3″) position [13]. The site of metalation may be determined by a careful analysis of the ^1H NMR spectra of the complexes, and in view of our

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experiences with Htbpy we have investigated direct cyclometalation reactions of the prototypical ligand 2-(2′-thienyl)pyridine.

In the past 25 years the coordination chemistry of 2-(2′-thienyl)pyridine has been the subject of sporadic interest. The direct reaction of Hthpy with $[MX_4]^{2-}$ (M = Pd or Pt; X = Cl, Br or I) initially yields the monodentate *N*-donor complexes $[M(Hthpy)_2X_2]$ (as *cis* and *trans* isomers in some cases), although the structural characterisation of $[Pd(Hthpy)_2Br_2]$ indicated weak diaxial Pd–S interactions [15,16]. Under more forcing conditions a variety of products has been obtained, including [M(Hthpy)(thpy)X] which contains monodentate *N*-bonded and bidentate cyclometalated *N,C*-bonded ligands [15,16]. Under slightly different conditions, the insoluble μ-chloro-bridged cyclometalated complexes $[(thpy)M(\mu\text{-}Cl)_2M(thpy)]$ are formed [17]. There are few other examples of the direct cyclometalation of Hthpy. A series of iridium complexes $[(thpy)_2IrXX']$ (X = halide, X′ = various) has been prepared [18], as have the compounds $[(thpy)(PBu_3)ClRh(\mu\text{-}Cl)_2Rh(thpy)(PBu_3)Cl]$ and $[(thpy)(CO)_2Rh(\mu\text{-}Cl)_2Rh(thpy)(CO)_2]$ [17].

Lithiation of 2-(2′-thienyl)pyridine may yield kinetic 3′-lithio or thermodynamic 5′-lithio products. The kinetic product has been extensively utilised in the preparation of unambiguously palladated and platinated homoleptic complexes [19]. The photochemical and photophysical properties of these cyclometalated complexes have been the subject of intensive investigation [19–29], as have those of some related rhodium and ruthenium complexes [29–33].

In this paper we describe the results of an investigation into the direct cyclometalation of 2-(2′-thienyl)pyridine.

Experimental

Infrared spectra were recorded on Perkin–Elmer 1710 Fourier Transform or 983 spectrophotometers, with the samples in compressed KBr discs. Proton NMR spectra were recorded on Bruker WM-250 or AM400 spectrometers. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Kratos MS-50 spectrometer, with 3-nitrobenzyl alcohol as matrix for the FAB spectra. Electrochemical measurements were performed as described previously [14]; potentials are quoted *vs* ferrocene/ferrocinium couple ($Fc/Fc^+ = 0.0$ V), and all potentials were referenced to internal ferrocene added at the end of each experiment. 2-(2′-Thienyl)pyridine was prepared in 73% yield by the coupling of the Grignard reagent from 2-bromothiophene with 2-bromopyridine in the presence of $[Ni(dppe)Cl_2]$ [34]; precious metal salts were used as supplied by Johnson Matthey.

Synthesis of [(thpy)Pd(μ-OAc)$_2$Pd(thpy)]

A solution of $[\{Pd(OAc)_2\}_3]$ (0.050 g, 0.0742 mmol) and Hthpy (0.033 g, 0.204 mmol) in CH_2Cl_2 (10 cm^3) was stirred at 40°C for 2.25 h, after which time TLC analysis indicated reaction was complete. The brown solution was diluted with further CH_2Cl_2 (20 cm^3) and the organic layer was washed with water (2 × 20 cm^3) and dried over $MgSO_4$, and the solvent was removed *in vacuo* to give a brown-yellow powder (0.065 g, 97%). Recrystallisation of this powder from CH_2Cl_2/hexane gave beautiful yellow needles. Found: C, 39.3; H, 2.7; N, 4.2. $C_{22}H_{18}N_2O_4Pd_2S_2$ calc.: C, 40.5; H, 2.7; N, 4.3%. IR: 3069w, 1603, 1572s, 1488s, 1417s, 1343w, 1282w,

1154w, 876m, 764m, 701m, 689m, 617m, 421w, 352w cm^{-1}; FAB-MS: *m/z* 652 ($Pd_2(thpy)_2(OAc)_2$), 593 ($Pd_2(thpy)_2(OAc)$), 533 ($Pd_2(thpy)_2$), 426 ($Pd(thpy)_2$) and 266 (Pd(thpy)).

Synthesis of $[Ru(bpy)_2(Hthpy)][PF_6]_2$

A warmed slurry of $[Ru(bpy)_2Cl_2]$ (0.097 g, 0.2 mmol) and Hthpy (0.50 g, 3.1 mmol) in CH_2Cl_2 (10 cm^3) was added to a flask containing $Ag[BF_4]$ (0.085 g, 0.436 mmol) and the mixture heated to reflux for 30 min to give a yellow-brown slurry. The reaction mixture was cooled and filtered through Celite to remove silver chloride, and the clear yellow-brown filtrate treated with a solution of $[NH_4][PF_6]$ (0.13 g, 0.8 mmol) in MeOH (4 cm^3). The solution was concentrated *in vacuo*, treated with MeOH (5 cm^3) and cooled, after which the orange precipitate was filtered off. The solid was washed with methanol and dried to give $[Ru(bpy)_2(Hthpy)][PF_6]_2$ as an orange microcrystalline powder (0.14 g, 81%). Recrystallisation from methanol resulted in the deposition of a purple solid, but the filtrate gave small orange blocks of the compound. Found: C, 39.6; H, 2.6; N, 7.9. $C_{29}H_{23}F_{12}N_5P_2RuS$ calc.: C, 40.3; H, 2.7; N, 8.1%; IR: 1605w, 1466m, 1446m, 1423w, 1242w, 1161w, 870w, 839s, 763m, 729w, 704w, 558s, 422w cm^{-1}; FAB-MS: *m/z* 720 ($Ru(bpy)_2(Hthpy)(PF_6)$), 574 ($Ru(bpy)_2(Hthpy)$).

Synthesis of $[Au(Hthpy)Cl_3]$

A solution of Hthpy (0.048 g, 0.3 mmol) in MeCN (1.5 cm^3) was added to a stirred ice-cold solution of $Na[AuCl_4] \cdot 2H_2O$ (0.12 g, 0.3 mmol) in H_2O (2.5 cm^3). An orange precipitate was formed immediately. The mixture was stirred for 45 min, after which a further 1.5 cm^3 of H_2O was added during 90 min. The orange precipitate was filtered off and dried to yield $[Au(Hthpy)Cl_3]$ (0.115 g, 83%). Found: C, 23.2; H, 1.4; N, 2.9. $C_9H_7AuCl_3NS$ calc.: C, 23.5; H, 1.5; N, 3.0%; IR: 3099m, 3086m, 3042w, 1597m, 1562m, 1477s, 1435m, 1421w, 1274w, 1244m, 1222w, 1168w, 852m, 778s, 744w, 728s, 717m, 368s cm^{-1}.

Synthesis of 2-(5'-chloro-2'-thienyl)pyridine

A solution of Hthpy (0.20 g, 1.24 mmol) in dry thf (30 cm^3) was maintained under an atmosphere of dinitrogen and cooled to −78°C, then treated dropwise with a solution of n-butyllithium (1.3 *M* in hexane) until a brown colour appeared, followed by an additional portion of n-butyllithium (1.4 cm^3, 1.8 mmol). The brown solution was then stirred for 30 min at −78°C, after which chlorine was bubbled through for 3 min to yield a pale straw yellow mixture. The solution was then purged with dinitrogen to remove the excess of chlorine and allowed to warm to room temperature, after which saturated aqueous $[NH_4]Cl$ solution (0.1 cm^3) was added. All organic material was extracted into diethyl ether (3 × 25 cm^3) and the combined ether extracts were washed with water, dried ($MgSO_4$) and evaporated *in vacuo* to give a brown oil. This oil was purified by TLC (silica, 1/1 hexane/CH_2Cl_2) and the major component (R_f 0.7) was recrystallised from petroleum ether (60–80°C) to give cream-white needles of 2-(5'-chloro-2'-thienyl)pyridine (0.116 g, 48%). M.p. 69–70°C; Found: C, 54.8; H, 2.9; N, 7.0. C_9H_6ClNS calc.: C, 55.2; H, 3.1; N, 7.2%; IR: 3052w, 1639w, 1615w, 1588s, 1562m, 1470s, 1438m, 1428s, 1293m, 1213m, 1152m, 1013s, 992m, 803m, 772s, 712m, 619m, 486m, 451m, 402m, 281w cm^{-1}; EI-MS: *m/z* 195/197 (Clthpy), 160 (thpy).

Synthesis of 5,5'-bis(2-pyridyl)-2,2'-bithienyl

A solution of Hthpy (1.00 g, 6.20 mmol) in dry thf (25 cm^3) was maintained under an atmosphere of dinitrogen, cooled to −73°C, and treated dropwise with a solution of n-butyllithium (1.3 *M* in hexane, 5.0 cm^3) to give an orange-brown solution. After 30 min stirring at −73°C, this solution was treated with $CuCl_2$ (0.42 g, 3.1 mmol) and dioxygen was bubbled through the solution as it was allowed to warm to room temperature. The slurry was then maintained at 60°C for a further 2.5 h with the dioxygen bubbling through, then treated with hydrochloric acid (6 *M*, 10 cm^3). The thf was removed *in vacuo* to give a black tar. This was treated with water (10 cm^3) and the pH adjusted to 11 by the addition of sodium hydroxide pellets. The green slurry so obtained was extracted with CH_2Cl_2 (3 × 30 cm^3), and the combined extracts were washed with water and dried over $MgSO_4$. Removal of the solvent *in vacuo* gave a yellow-green solid (0.20 g). Repeated extraction of the green slurry eventually yielded 0.88 g of yellow-green product. This was recrystallised from $CHCl_3$ to give golden-yellow flakes of 5,5'-bis(2-pyridyl)-2,2'-bithienyl (0.171 g, 23%). M.p. 246–248°C; Found: C, 67.3; H, 4.0; N, 8.9. $C_{18}H_{12}N_2S_2$ calc.: C, 67.5; H, 3.8; N, 8.8%; IR: 3045w, 2999w, 1580s, 1562m, 1530m, 1462s, 1444m, 1428s, 1291m, 1151m, 994m, 806m, 773s, 741w, 710w, 450w, 402w, 279w cm^{-1}; FAB-MS: *m/z* 321 (pttp).

Reaction of [Au(Hthpy)Cl_3] at 60°C in aqueous acetonitrile

A suspension of [Au(Hthpy)Cl_3] (0.080 g, 0.17 mmol) in 50% v/v aqueous acetonitrile (16 cm^3) was heated to 60°C for 23.5 h, then cooled. The brown precipitate was filtered off; 0.025 g. IR: 1603s, 1562m, 1489m, 1434m, 1394m, 1260m, 1161m, 806m, 772s cm^{-1}; FAB-MS: *m/z* 321 (pttp). The yellow filtrate was treated with water (18 cm^3) and cooled, when a mixture of yellow flakes and a yellow powder separated. The yellow material was filtered off; 0.029 g; *m/z* 321 and others; Found: C, 27.9; H, 1.6; N, 3.6. The ^1H NMR spectrum of a dmso solution of this gold complex indicates the presence of pttp but no Clthpy ligands. The aqueous filtrate was then evaporated to dryness *in vacuo* and the residue extracted with CH_2Cl_2 (3 × 20 cm^3). The organic extract was dried ($MgSO_4$) and concentrated *in vacuo* to yield a brown oil, which partially crystallised upon standing. The ^1H NMR spectrum of this material showed it to be a salt of $[H_2thpy]^+$.

Reaction of Na[$AuCl_4$] with Hthpy at 80°C in aqueous acetonitrile

A solution of Hthpy (0.065 g, 0.4 mmol) in MeCN (4 cm^3) was added to a solution of $Na[AuCl_4]\cdot 2H_2O$ (0.16 g, 0.4 mmol) in H_2O (3 cm^3) and the mixture was heated to 80°C for 48 h. The red slurry was filtered hot to give a red-brown solid and an orange filtrate (0.045 g). The ^1H NMR spectrum of the red-brown solid in dmso solution shows peaks assigned to free pttp (30%), Clthpy (5%) and other complexes. Upon cooling the filtrate, another red-brown solid separated (0.025 g). The ^1H NMR spectrum of this solid in dmso solution shows peaks assigned to free pttp (95%) and Clthpy (5%) only. Found: C, 26.6; H, 1.7; N, 3.8; IR: 357s cm^{-1}. The yellow filtrate was then treated with water (10 cm^3) and cooled, when yellow flakes separated and were filtered off (0.025 g). The ^1H NMR spectrum of a dmso solution of these yellow-gold complexes indicates the presence of pttp (23%) and Clthpy (77%) ligands. The aqueous filtrate was then evaporated

to dryness *in vacuo* and the residue extracted with CH_2Cl_2. The organic extract was dried ($MgSO_4$) and concentrated *in vacuo* to yield a brown oil, which partially crystallised upon standing (0.005 g). The ^1H NMR spectrum of this material showed it to consist of Clthpy (38%) and Hthpy (62%).

Reaction of Na[$AuCl_4$] with pttp

A solution of Hthpy (0.032 g, 0.1 mmol) and $Na[AuCl_4]\cdot 2H_2O$ (0.08 g, 0.2 mmol) in MeCN (10 cm^3) and H_2O (10 cm^3) was heated to 90°C for 44 h. The orange slurry was filtered hot to give an orange solid and an orange filtrate (0.035 g). Found: C, 33.6; H, 1.6; N, 4.3; FAB-MS: *m/z* 1137 ($(pttp)_2Au_2Cl_3$), 1102 ($(pttp)_2Au_2Cl_2$), 1069 ($(pttp)_2Au_2Cl$), 905 ($(pttp)_2AuCl_2$), 871 ($(pttp)_2AuCl$), 835 ($(pttp)_2Au$), 587 ($(pttp)AuCl_2$), 551 ((pttp)AuCl) and 517 ((pttp)Au). The ^1H NMR spectrum of the solid in dmso solution shows peaks assigned to free pttp (60%) and pttp complexes (40%). Upon cooling the filtrate, another orange solid separated (0.012 g). IR: 1601s, 1559m, 1517m, 1473s, 1436s, 1385m, 1325w, 1300w, 1247m, 1169m, 1038w, 874w, 772s, 708w, 620w, 403w, 358s cm^{-1}; Found: C, 28.1; H, 1.56; N, 3.7. $C_{36}H_{24}Au_3Cl_9N_4S_4$ calc.: C, 27.9; H, 1.6; N, 3.6%. The ^1H NMR spectrum of this solid in dmso solution shows only peaks assigned to free pttp.

Discussion

The ligand 2-(2′-thienyl)pyridine (Hthpy) is conveniently prepared in high yield (> 70%) by the nickel-mediated cross-coupling of the Grignard reagent derived from 2-bromothiophene with 2-bromopyridine [34]. The ^1H NMR spectrum (Fig. 1a) of Hthpy is solvent dependent, and relevant spectroscopic data in a number of solvents are presented in Table 1. The coupling constants within the thienyl ring are typical and of value in assignment ($^3J_{4'5'}$ 5.5, $^3J_{4'3'}$ 3.8, $^4J_{3'5'}$ 1.0 Hz).

The reaction of Hthpy with $[PdCl_4]^{2-}$ salts has been shown to yield the insoluble chloro-bridged dimers $[(thpy)Pd(\mu\text{-}Cl)_2Pd(thpy)]$ [17]; it has previously been shown that $[\{Pd(OAc)_2\}_3]$ is a superior source of palladium, which gives high yields of soluble μ-acetato-bridged cyclometalated dimers with 2-phenylpyridine [12,35]. Accordingly, we have investigated the reaction of Hthpy with $[\{Pd(OAc)_2\}_3]$. A golden-brown solution is obtained upon reacting Hthpy with $[\{Pd(OAc)_2\}_3]$ in CH_2Cl_2 at 40°C. The reaction was monitored by TLC, and all of the Hthpy had been consumed after 2.25 h. The reaction mixture was washed with water to remove acetic acid and then evaporated to dryness to give a brown-orange powder. Microanalysis indicated a formulation $\{(thpy)Pd(OAc)\}_n$ to be appropriate, and the FAB mass spectrum exhibited peaks at *m/z* 652, 593, 533, 426 assigned to ($Pd_2L_2(OAc)_2$), ($Pd_2L_2(OAc)$), (Pd_2L_2), (PdL_2) and (PdL) respectively (each showing the appropriate isotopomer distribution). The ^1H NMR spectrum of a CD_2Cl_2 solution of the product is shown in Fig. 2, and clearly consists of two subspectra. Multiple recrystallisation of the complex from CH_2Cl_2/hexane gave beautiful yellow needles which gave an identical NMR spectrum to the crude product.

The two subspectra are clearly very similar, and each contains six aromatic resonances, indicative of the formation of cyclometalated products. The major and minor species are present in a ratio 0.4/2.0. The ^1H NMR spectrum of the major component exhibits a single acetate methyl resonance (δ 2.20) whereas the minor

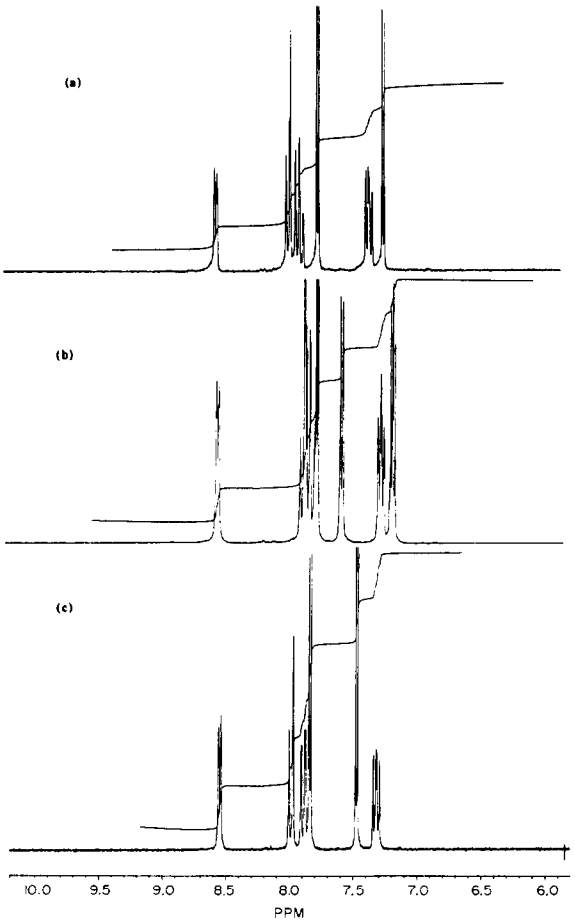
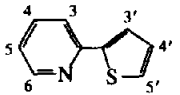


Fig. 1. 250 MHz ^{1}H NMR spectra of (a) Hthpy in CD_3COCD_3; (b) Clthpy in CD_3SOCD_3 and (c) pttp in CD_3SOCD_3.

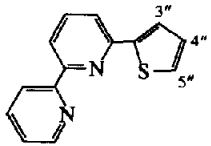
component shows two equal intensity resonances (δ 2.16, 2.24). This is consistent with the major product being the *anti* conformer (Fig. 3a) and the minor component the *syn* conformer (Fig. 3b) of the μ-acetato-bridged cyclometalated dimers, [(thpy)Pd(μ-OAc)$_2$Pd(thpy)]. This is also in accord with the X-ray structural determinations of [LPd(μ-OAc)$_2$PdL] (HL = 2-(4′-nitrophenyl)pyridine or 2,6-bis(4-chlorophenyl)pyridine, both of which adopt the *anti* conformation in the solid state [36]. The *anti* isomer exhibits six aromatic resonances, of which four may be assigned to the pyridine ring (δ 7.72, H(6), ddd, J_{56} 5.7, J_{46} 1.6, J_{36} 0.8 Hz; δ 6.48, H(5), ddd, J_{45} 7.6, J_{35} 1.3 Hz; δ 7.44, H(4), ddd, J_{34} 8.0 Hz; δ 6.84, H(3)). The cyclometalated thienyl ring gives rise to an AB multiplet with a coupling constant of 4.9 Hz. This coupling constant of ≈ 5 Hz is typical for $^3J_{45}$ and unambiguously allows the site of metalation to be established as C(3′) [13,17,18]. The NMR spectroscopic data for both the *syn* and *anti* isomers of [(thpy)Pd(μ-OAc)$_2$Pd(thpy)] is presented in Table 1. Further evidence for metalation at this site comes from the observation of a single aromatic C–H deformation mode in

Table 1

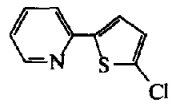
^{1}H NMR spectroscopic properties of the ligands and complexes (δ in ppm, J in Hz)



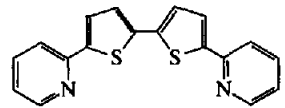
(Hthpy)



(Htbpy)



(Clthpy)



(pttp)

	H(6)	H(5)	H(4)	H(3)	H(3')	H(4')	H(5')	$J_{3'4'}$	$J_{4'5'}$	$J_{3'5'}$
Hthpy [a]	8.56	7.13	7.65	7.64	7.57	7.10	7.38	3.8	5.5	1.0
Hthpy [b]	8.52	7.24	7.79	7.85	7.74	7.14	7.54	3.8	5.5	1.0
Hthpy [c]	8.52	7.26	7.82	7.91	7.80	7.16	7.63	3.8	5.5	1.0
anti-[{(thpy)Pd(OAc)}$_2$] [d]	7.72	6.48	7.44	6.84	–	6.65	7.04	–	4.9	–
syn-[{(thpy)Pd(OAc)}$_2$] [d]	7.86	6.60	7.43	6.88	–	6.98	7.04	–	4.9	–
[Au(Hthpy)Cl$_3$] [a]	8.77	7.65	8.12	7.88	7.96	7.30	7.73	3.8	5.0	1.2
[Au(Hthpy)Cl$_3$] [b]	9.30	7.98	8.46	8.21	8.00	7.39	8.02	3.8	5.0	1.2
[Au(Hthpy)Cl$_3$] [c]	9.45	7.89	8.37	8.20	7.94	7.38	8.10	3.8	5.0	1.2
[Au(Hthpy)Cl$_3$] [d]	8.78	7.67	8.15	7.91	7.93	7.33	7.79	3.8	5.0	1.2
[Au(Hthpy)Cl$_3$] [e]	8.95	7.76	8.24	8.01	7.89	7.33	7.88	3.8	5.0	1.2
[Ru(bpy)$_2$(Hthpy)]$^{2+}$ [b]					7.94	7.58	7.70	3.7	5.1	0.9
pttp [c]	8.54	7.30	7.86	7.97	7.81	7.46	–	3.9	–	–
Clthpy [b]	8.50	7.28	7.83	7.86	7.60	7.07	–	4.0	–	–

[a] $CDCl_3$. [b] CD_3COCD_3. [c] CD_3SOCD_3. [d] CD_2Cl_2. [e] CD_3CN.

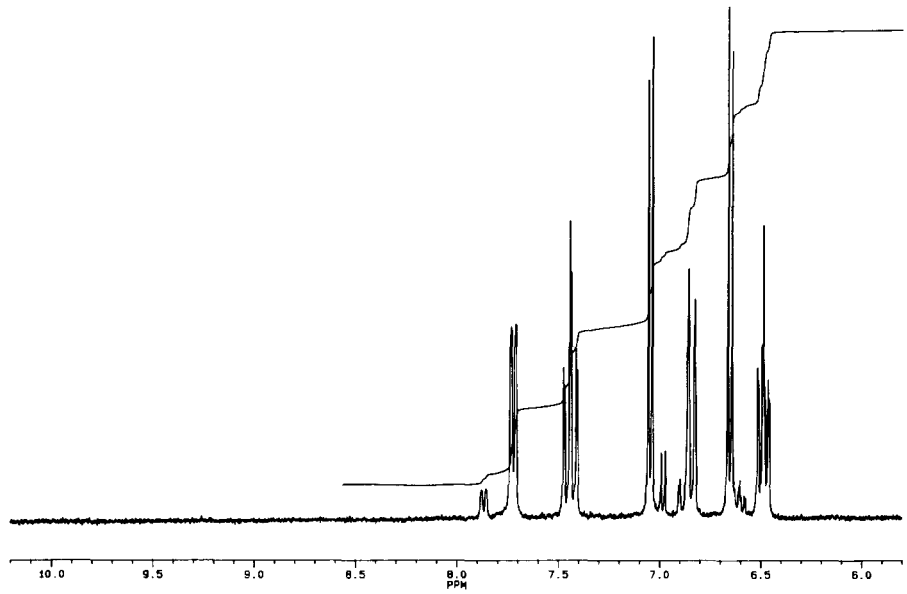
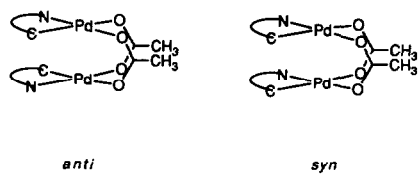


Fig. 2. 250 MHz ^{1}H NMR spectrum of mixture of *syn*- and *anti*-[(thpy)Pd(μ-OAc)$_2$Pd(thpy)] CD_2Cl_2.



anti *syn*

Fig. 3. Proposed isomers of [(thpy)Pd(μ-OAc)$_2$Pd(thpy)] (a) *anti* and (b) *syn*.

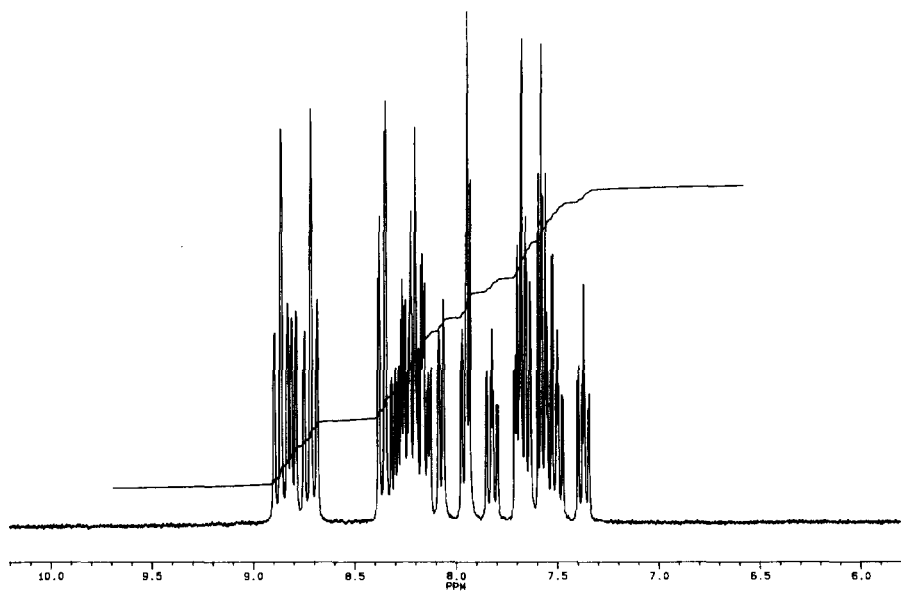


Fig. 4. 250 MHz ^{1}H NMR spectrum of [Ru(bpy)$_2$(Hthpy)][PF_6]$_2$ in CD_3COCD_3.

the IR spectrum at 876 cm^{-1}, typical of a 2,3-disubstituted thiophene [14,17,18].

The facile cyclometalation of the Hthpy ligand upon reaction with $[\{Pd(OAc)_2\}_3]$ suggested that cycloruthenation would be achieved with similar ease. The reaction of Hthpy with $[Ru(bpy)_2Cl_2]$ in CH_2Cl_2 in the presence of $Ag[BF_4]$ gives an orange-brown product, isolated as its hexafluorophosphate salt. The FAB mass spectrum of the orange product exhibited peaks at m/z 720 and 574 assigned to $(Ru(bpy)_2(Hthpy)(PF_6))$ and $(Ru(bpy)_2(Hthpy))$ respectively, but the microanalysis indicated the non-metalated formulation $[Ru(bpy)_2(Hthpy)][PF_6]_2$. This apparent formation of a non-metalated product is somewhat surprising, as the reaction conditions are exactly those under which 2-phenylpyridine (Hppy) reacts to give $[Ru(bpy)_2(ppy)]^+$ in high yield [4]. The ^1H NMR spectrum of the orange product is complex (Fig. 4), but analysis clearly indicates the presence of five chemically and magnetically distinct pyridyl rings, together with an AMX pattern assigned to a non-metalated thienyl ring. The resonances assigned to the thienyl ring (δ 7.70, H(5'), dd, $J_{3'5'}$ 0.7, $J_{4'5'}$ 5.1 Hz; δ 7.6, H(4), dd, $J_{3'4'}$ 3.4 Hz; δ 7.94, H(3'), dd) clearly establish the non-metalated nature of this complex. In the absence of further structural data, we propose that this complex contains a bidentate *N,S*-bonded Hthpy ligand. A number of other ruthenium(II) complexes containing *S*-bonded thiophenes with related ligands have been characterised [6,14,37–39]. The compound is electrochemically active, and the cyclic voltammogram (MeCN, $[N^nBu_4][BF_4]$ supporting electrolyte) exhibits a single fully reversible oxidation (+1.028 V *vs* Fc/Fc^+) and two fully reversible reductions (−1.782 and −1.983 V *vs* Fc/Fc^+). Recrystallisation of the compound from methanol gave orange blocks of the pure complex $[Ru(bpy)_2(Hthpy)][PF_6]_2$, but was accompanied by the formation of an insoluble purple material. In some cases, up to 50% of the material was converted to the purple product. The ^1H NMR spectrum of the purple residue indicated the presence of a cyclometalated product in which H(3') was missing, although attempts to isolate the purple compound in a pure form resulted in reversion to $[Ru(bpy)_2(Hthpy)][PF_6]_2$! We have previously found that heating non-metalated ruthenium(II) compounds in glacial acetic acid is a clean and effective means for the formation of cycloruthenates [14], and considered that the method might provide a means for the metalation of $[Ru(bpy)_2(Hthpy)][PF_6]_2$. Upon heating $[Ru(bpy)_2(Hthpy)][PF_6]_2$ in glacial acetic acid, small amounts of a purple material were formed, but all attempts to isolate this compound resulted in reversion to orange $[Ru(bpy)_2(Hthpy)][PF_6]_2$.

The reaction of Hthpy with $Na[AuCl_4] \cdot 2H_2O$ in aqueous acetonitrile is rapid and results in the immediate precipitation of the complex $[Au(Hthpy)Cl_3]$. The FAB mass spectrum of this complex showed neither a parent ion nor any recognisable fragments, but microanalysis was fully in accord with this formulation. The IR spectrum shows a strong absorption at 368 cm^{-1} which is typical for the ν(Au–Cl) stretching mode in $[LAuCl_3]$ complexes with monodentate *N*-donor ligands [3,13,40–42]. The complex is insoluble in water and alcohols, but is readily soluble without decomposition in $CHCl_3$, CH_2Cl_2, acetone and acetonitrile. The complex is also soluble in dmso, but the ^1H NMR spectrum of such solutions indicates that at least 90% of the complex has been destroyed and the dominant solution species is the free ligand Hthpy. The ^1H NMR spectrum of the complex is markedly solvent dependent, and data for solutions in a variety of solvents are presented in Table 1 (Fig. 5).

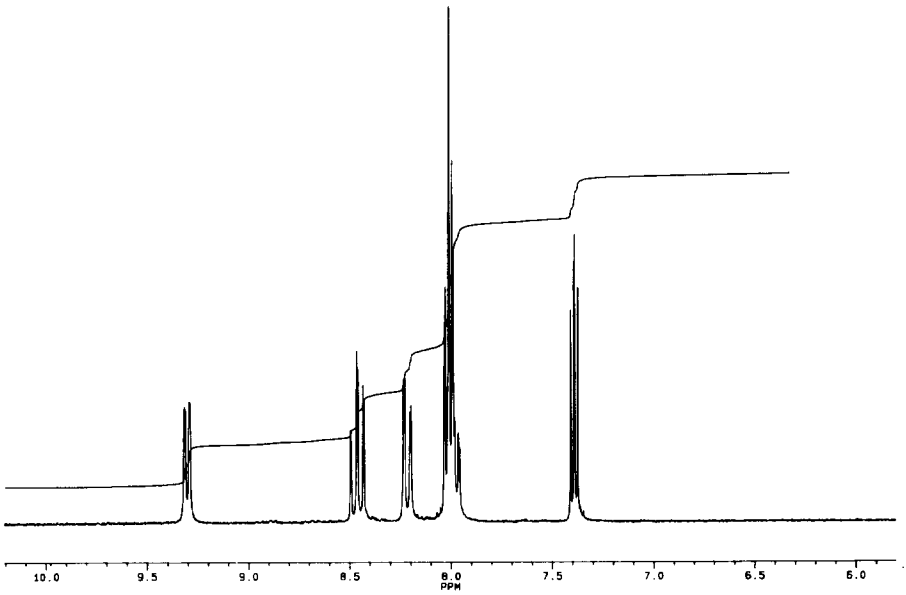


Fig. 5. 250 MHz ^{1}H NMR spectrum of $[AuCl_3(Hthpy)]$ in CD_3COCD_3.

This behaviour is reminiscent of that previously observed with Htbpy, which reacts with $Na[AuCl_4]$ to give the *N*-bonded complex $[Au(Htbpy)Cl_3]$ [3,13]. Upon warming a solution of $[Au(Htbpy)Cl_3]$ in aqueous acetonitrile a clean metalation reaction occurs at C(5′) to give quantitative conversion to $[Cl_2Au(tbpy\text{-}\kappa^1\text{-}N,\kappa^1\text{-}S)_2AuCl_2]$ (Fig. 6) [3,13]. However, in reactions of the related ligands 2,6-bis(2′-thienyl)pyridine and 2-phenyl-6-(2′-thienyl)pyridine with d^8 metal ions we have noted that a variety of products may be formed, including compounds chlorinated at the 5-position of the thiophene and dimers coupled through the 5-position of the thiophene [43]. In the light of these experiences, we unambiguously prepared the possible products 2-(5′-chloro-2′-thienyl)pyridine (Clthpy) and 5,5′-bis(2-pyridyl)-2,2′-bithienyl (pttp) before further investigating the reactions of Hthpy with gold(III).

It has previously been reported that 5-chlorothiophenes may be prepared from the parent thiophene by lithiation followed by chlorination with Cl_3CCN [44]. In our hands this procedure was unsuccessful with 2-(2′-thienyl)pyridine, but replac-

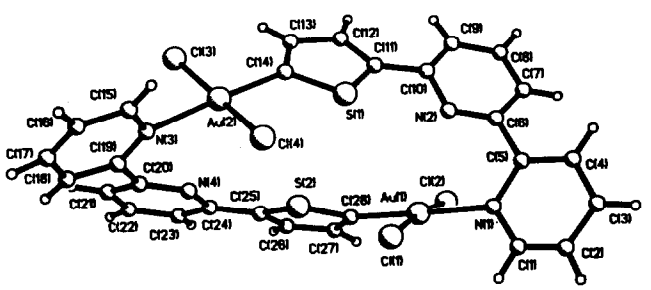


Fig. 6. Molecular structure of $[Cl_2Au(tbpy\text{-}\kappa^1\text{-}N,\kappa^1\text{-}S)_2AuCl_2]$ [13].

ing the Cl_3CCN by chlorine as the chlorinating agent gave respectable yields of 2-(5′-chloro-2′-thienyl)pyridine as a cream solid. Relevant ^1H NMR spectroscopic data for this new compound are presented in Table 1 (Fig. 1b). The dimer 5,5′-bis(2-pyridyl)-2,2′-bithienyl has been briefly described by Kauffman, but full details of the preparation have not been published. We have modified the preparation somewhat to obtain a pure material which melts some 20°C higher than that previously described. Treatment of Hthpy with n-butyllithium at low temperature generates the 5′-lithio derivative. Oxidative coupling of this was achieved by bubbling oxygen through the solution in the presence of anhydrous copper(II) chloride. The yellow product is very insoluble, but does dissolve in warm hydrochloric acid and in dmso. The ^1H NMR spectrum of a dmso solution shows the expected six resonances confirming the symmetrical nature of the coupling product (Table 1, Fig. 1c).

In contrast to the clean metalation behaviour of gold(III) complexes of Htbpy, reactions of Hthpy with gold(III) under forcing conditions or of [Au(Hthpy)Cl_3] lead to complex mixtures of products. Many of these products are insoluble gold complexes which we have only been able to characterise by solvolysis in dmso and ^1H NMR analysis to identify the ligands present. Upon warming a solution of [Au(Hthpy)Cl_3] in aqueous acetonitrile to 60°C a brown solid was deposited. This was collected by filtration to give a brown powder and a clear yellow solution. The FAB mass spectrum of this brown solid showed no peaks which could be assigned to the free ligand Hthpy or obvious gold complexes, but the major peak was observed at m/z 321. No peaks due to chlorinated ligand (Clthpy) were observed. The mass spectrum suggests that the Hthpy may have undergone a dimerisation reaction to pttp. The IR spectrum of this product exhibits no absorptions due to Au–Cl stretching modes. The brown material is insoluble in all solvents except dmso and we have not been able to further purify it; the ^1H NMR spectrum of a dmso solution shows that a complex mixture of products is present, but that about 25% of pttp was present. We suggest that this material consists of gold complexes of the dimer, but we have been unable to further characterise the mixture.

The pale yellow filtrate was treated with an excess of water and cooled, when it deposited a flaky yellow material. The mass spectrum exhibits peaks due to pttp (m/z 320, 321) but none which may be assigned to Clthpy or Hthpy. The ^1H NMR spectrum of this material in CD_3CN solution showed it to consist of 10–15% of the starting [Au(Hthpy)Cl_3] and 50% of two equally abundant 5′-substituted derivatives of Hthpy. Significantly, no peaks due to free pttp were present. In contrast, the ^1H NMR spectrum of a dmso solution shows 12% free Hthpy, 50% free pttp, and 40% of a species exhibiting two 5′-substituted Hthpy patterns. The reaction of gold(III) complexes with dmso frequently results in ligand loss and the observation of free pttp in the dmso solution is not unexpected, and suggests that the golden yellow material contains gold(III) complexes of pttp. The two 5′-substituted patterns may be due to asymmetrically coordinated pttp. Attempts to further purify the yellow flaky solid were unsuccessful, but preparative TLC allowed isolation of pttp identical in all respects to authentic material.

Evaporation of the filtrate from which the yellow flaky solid had been obtained yielded a mixture of hydrochloride and tetrachloroaurate salts of $[H_2thpy]^+$ characterised by ^1H NMR and FAB mass spectroscopy. It is noteworthy that there is no Clthpy or pttp in this fraction. This reaction is clearly complex, but we may

make some observations. The insoluble brown material is a gold complex of pttp which possibly also contains some Hthpy complexes. The water insoluble yellow material is a relatively pure gold complex of pttp. The remaining Hthpy is found as protonated salts. The thermal reactions of the isolated complex [Au(Hthpy)Cl_3] give predominantly pttp and no ligand chlorination products. These reactions are in contrast to those of [Au(Htbpy)Cl_3] which yield metalated products in quantitative yield.

In order to further probe the interactions of Hthpy with gold(III) we have also investigated the direct reaction at 80°C in aqueous acetonitrile. When the reaction is performed at 80°C a red-brown solid (A) is precipitated from solution. After removal of this red-brown solid (A) by filtration, cooling of the orange filtrate results in the precipitation of a second brown powder (B). Addition of water to the filtrate then results in the precipitation of a yellow flaky solid (C).

Solid A is soluble in dmso, and the ^{1}H NMR spectrum of the solution shows a very complex mixture of products, including 30% free pttp and 5% free Clthpy. Solid A is a mixture of various insoluble gold(III) complexes. The second brown solid (B) is a relatively pure compound. The ^{1}H NMR spectrum of a dmso solution exhibits peaks which are predominantly those of free pttp (> 95%) with a small amount (< 5%) of Clthpy. The IR spectrum exhibits a strong absorption at 357 cm^{-1}, suggesting an *N*-coordinated $AuCl_3$ unit. Microanalysis is suggestive of a formulation such as {$(pttp)_2(AuCl_3)_3$}, and a structure such as shown in Fig. 5 is possible. The ^{1}H NMR spectrum of the yellow flaky material (C) shows it to consist only of free pttp (23 mol-%) and free Clthpy (77 mol-%). Finally, extraction of the remaining aqueous solution with CH_2Cl_2 gave an oil which was shown by ^{1}H NMR spectroscopy to consist of 38 mol-% Clthpy and 62 mol-% Hthpy.

In an attempt to further elucidate the nature of the gold pttp complexes, we have investigated the direct reactions of pttp with Na[$AuCl_4$]. In these studies, as in those described above, we were hindered by the insoluble nature of all the complexes formed, and also by the insolubility of the pttp ligand. The reaction of pttp with Na[$AuCl_4$] in warm aqueous acetonitrile gives an orange solid which is precipitated from the hot solution. This orange solid exhibited no ν(Au–Cl) modes at 350–370 cm^{-1} in the IR spectrum, and the ^{1}H NMR spectrum in dmso showed the presence of 60% free pttp and 40% coordinated pttp in three different environments. The FAB mass spectrum of the solid exhibited peaks assigned to ($(pttp)_2Au_2Cl_3$), ($(pttp)_2Au_2Cl_2$), ($(pttp)_2Au_2Cl$), ($(pttp)_2AuCl_2$), ($(pttp)_2AuCl$), ($(pttp)_2Au$), ($(pttp)AuCl_2$), ((pttp)AuCl) and ((pttp)Au). Microanalysis indicates the overall stoichiometry of the solid to be 1/1 pttp/$AuCl_3$. We have been unsuccessful in further characterising this material which is insoluble in all solvents except dmso, in which it decomposes.

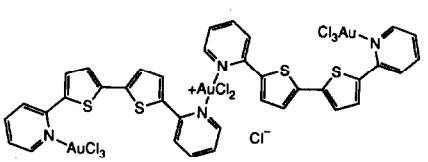
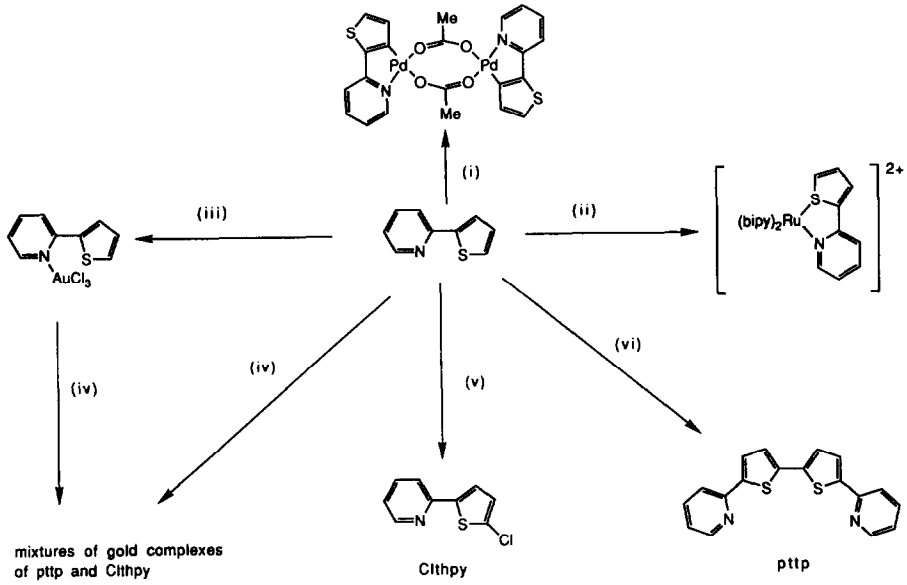


Fig. 7. Proposed structure for 2/3 pttp/$AuCl_3$ complex.



Scheme 1. (i) $[\{Pd(OAc)_2\}_3]$, CH_2Cl_2; (ii) $[Ru(bpy)_2Cl_2]$, $Ag[BF_4]$, CH_2Cl_2; (iii) $Na[AuCl_4]$, MeCN, H_2O, 40°C; (iv) MeCN, H_2O, heat; (v) ^nBuLi in thf then Cl_2; (vi) ^nBuLi in thf then $CuCl_2/O_2$.

Upon cooling the solution from which the orange solid had been precipitated, a second orange solid was precipitated. The IR spectrum of this compound suggests that it is the same as the material (B) obtained from the direct reaction of Hthpy with $Na[AuCl_4]$ in hot solution. The ^1H NMR spectrum of a solution in dmso shows only peaks due to free pttp. Microanalysis confirms the 2/3 pttp/$AuCl_3$ ratio and supports a formulation such as indicated in Fig. 7.

In conclusion, the reactions of Hthpy appear to be rather more complex than might originally have been expected. Reaction with $[\{Pd(OAc)_2\}_3]$ results in near-quantitative cyclometalation at the 3′-position of the thienyl ring to give $[(thpy)Pd(\mu\text{-}OAc)_2Pd(thpy)]$. In contrast, the reaction with $[Ru(bpy)_2Cl_2]/Ag^+$ yields the complex $[Ru(bpy)_2(Hthpy)][PF_6]_2$ containing an *N,S*-bonded Hthpy ligand. Attempts to convert $[Ru(bpy)_2(Hthpy)][PF_6]_2$ to a cycloruthenated derivative were not successful. The reaction of Hthpy with $Na[AuCl_4]$ in the cold gives $[Au(Hthpy)Cl_3]$, containing an *N*-bonded ligand, in quantitative yield. However, reaction in warm solution, or warming solutions of $[Au(Hthpy)Cl_3]$, yields a mixture of products including Clthpy, pttp and their gold complexes. We have no evidence for the formation of any cycloaurated derivatives of Hthpy. These interconversions are summarised in Scheme 1.

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