Co-ordination Chemistry of 2-Phenyl-6-(2-thienyl)pyridine and 2,6-Bis(2-thienyl)pyridine; New Ambidentate Ligands

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The new ligands 2-phenyl-6-(2-thienyl)pyridine (H_2pthpy) and 2,6-bis(2-thienyl)pyridine (H_2bthpy) exhibit a variety of reactivities with d^8 transition-metal complexes. Reaction of H_2bthpy with platinum(II) gives complexes in which the ligand adopts Hbthpy-*C,N* and bthpy-*CNC* bonding modes, whereas gold(III) converts the ligand into the dimer 5,5′-bis[6-(2-thienyl)-2-pyridyl]-2,2′-bithiophene. Palladium(II) gives mixtures of cyclometallated complexes and dimerised ligand. In contrast, H_2pthpy reacts with platinum(II) to give metallated complexes in which the site of metallation is the phenyl rather than the thienyl ring. The reaction of H_2pthpy with gold(III) results in clean conversion into the dimer 5,5′-bis(6-phenyl-2-pyridyl)-2,2′-bithiophene and a chlorinated derivative 2-(5-chloro-2-thienyl)-6-phenylpyridine. Once again mixtures of metallated product and ligand reaction products are obtained with palladium(II).

There has been considerable interest in the chemistry of cyclometallated compounds containing chelated ligands in which one of the donor sites is an anionic carbon centre.[1,2] The photochemical and photophysical properties of these compounds have been widely investigated in recent years, and examples incorporating a considerable variety of donor atoms are known. A common structural feature is a ligand in which the anionic carbon donor centre is generated by deprotonation of the C–H bond of an aromatic ring bonded to a heteroaryl ring; the latter may act as a heteroatom donor. The majority of examples of cyclometallated complexes which have been described are with d^8 or d^6 transition metals and incorporate a five-membered chelate ring, although specific examples with other ring sizes are known.

The ligand 2-(2-thienyl)pyridine (Hthpy) may act as a monodentate *N*-donor or the thiophene ring may be cyclometallated at C^3 to yield complexes with interesting photophysical and electronic properties.[3–5] We have independently been studying a series of 2-(2-thienyl)pyridine derivatives as part of a wider investigation into the preparation of cyclometallated complexes, and have shown that the ligand 6-(2-thienyl)-2,2′-bipyridine (Hthbipy) may co-ordinate to a metal ion in a number of different manners.[6] In the course of those studies we have become aware of a number of anomalous reactions involving metallation at C^5 and in this paper we describe the interaction of some analogues of Hthbipy with platinum(II), palladium(II) and gold(III) compounds.

Experimental

Infrared spectra were recorded on Perkin-Elmer 1710 or Philips PU9624 Fourier-transform spectrophotometers, with the samples in compressed KBr discs, ^1H and ^{31}P NMR spectra on Brüker WM-250 or AM400 spectrometers, fast atom bombardment (FAB) and electron-impact (EI) mass spectra on a Kratos MS-50 spectrometer, with 3-nitrobenzyl alcohol as matrix for the FAB spectra. The compounds $Na[AuCl_4]$, $K_2[PdCl_4]$, $K_2[PtCl_4]$, $[\{Pd(O_2CMe)_2\}_3]$ (Johnson Matthey), dimethylammonium chloride, $\{CH_2O\}_n$, bromoacetylbenzene and 2-acetylthiophene (Aldrich) were used as supplied.

Preparations.—N-[2-*Oxo*-(2-*thienyl*)*ethyl*]*pyridinium iodide.* 2-Acetylthiophene (5.0 cm^3, 0.046 mol) was added to a warm solution of I_2 (10.8 g, 0.046 mol) in pyridine (50 cm^3) and the mixture heated to reflux for 90 min. After this period the solution was cooled in ice, and the dark coloured product filtered off. Recrystallisation from methanol in the presence of activated charcoal gave gold-coloured crystals of *N*-[2-oxo-2-(2-thienyl)ethyl]pyridinium iodide (9.8 g, 65%) (Found: C, 39.6; H, 2.95; N, 4.3. Calc. for $C_{11}H_{10}INOS$: C, 39.9; H, 3.05; N, 4.25%). FAB mass spectrum: *m/z* 204 (*M* − 1). IR (KBr): 1662s, 1631m, 1483s, 1416m, 1408m, 1248m, 765m, 753m and 679m cm^{-1}.

N-(2-*Oxo*-2-*phenylethyl*)*pyridinium bromide.* Bromoacetylbenzene (4.90 g, 0.025 mol) and pyridine (2.0 cm^3, 0.025 mol) were dissolved in diethyl ether (90 cm^3) and the mixture stirred at room temperature for 24 h. After this period a white crystalline product had separated and was filtered off and washed with diethyl ether to give *N*-(2-oxo-2-phenylethyl)pyridinium bromide (4.1 g, 60%) (Found: C, 56.4; H, 4.2; N, 5.2. Calc. for $C_{13}H_{12}BrNO$: C, 56.2; H, 4.3; N, 5.1%). FAB mass spectrum: *m/z* 198 (*M* − Br). IR (KBr): 1696s, 1636m, 1487m, 1416m, 1237m, 1216s, 999m, 766m, 758s, 685m, 679m and 571m cm^{-1}.

Dimethyl[3-*Oxo*-3-(2-*thienyl*)*propyl*]*ammonium chloride.* Dried dimethylammonium chloride (5.2 g, 0.064 mol) and paraformaldehyde (4.4 g, 0.15 mol) were suspended in ethanol (30 cm^3) under an atmosphere of dinitrogen. 2-Acetylthiophene (7.1 cm^3, 0.065 mol) and three drops of concentrated hydrochloric acid were added, and the mixture heated to reflux for 6 h under an inert atmosphere. After this period the solution was cooled in ice, when a white crystalline product separated and was filtered off and washed with ice-cold ethanol to give dimethyl[3-oxo-3-(2-thienyl)propyl]ammonium chloride (9.1 g, 65%) (Found: C, 49.1; H, 6.5; N, 6.5. Calc. for $C_9H_{14}ClNOS$: C, 49.2; H, 6.4; N, 56.4%). FAB mass spectrum: *m/z* 184 (*M* − Cl). IR (KBr): 2662m, 2557m, 2446m, 1652s, 1469m, 1461m, 1415m, 1245m, 1226m, 936m and 764m cm^{-1}.

2,6-*Bis*(2-*thienyl*)*pyridine* (H_2bthpy). Dried ammonium acetate (12.0 g) and *N*-[2-oxo-(2-thienyl)ethyl]pyridinium iodide (1.95 g, 5.9 mmol) were dissolved in acetic acid (12 cm^3) and the mixture heated to 100 °C for 10 min, after which dimethyl[3-oxo-(2-thienyl)propyl]ammonium chloride (1.31 g, 6.0 mmol) was added and the suspension heated to 105 °C for 4 h under an inert atmosphere. After this period, the dark coloured solution was cooled and treated with aqueous methanol to precipitate 2,6-bis(2-thienyl)pyridine as a pale brown solid. Recrystallisation from methanol gave off-white crystals of 2,6-bis(2-thienyl)pyridine (1.0 g, 70%, m.p. 78–79 °C) (Found: C, 64.0; H, 3.7; N, 5.8. Calc. for $C_{13}H_9NS_2$: C, 64.2; H, 3.7; N, 5.8%). EI mass spectrum: *m/z* 243 (*M*). IR (KBr): 1557m, 1562s, 1457s, 1439m, 1270m, 1170m, 857m, 801s and 710s cm^{-1}.

2-*Phenyl*-6-(2-*thienyl*)*pyridine* (H_2pthpy). Dried ammonium acetate (12.0 g) and *N*-(2-oxo-2-phenylethyl)pyridinium bromide (1.65 g, 5.9 mmol) were dissolved in acetic acid (12 cm^3) and the mixture heated to 100 °C for 10 min, after which dimethyl[3-oxo-3-(2-thienyl)propyl]ammonium chloride (1.31 g, 6.0 mmol) was added and the suspension heated to 105 °C for 4 h under an inert atmosphere. After this period, the dark coloured solution was cooled and treated with aqueous methanol to precipitate 2-phenyl-6-(2-thienyl)pyridine as a cream solid. Recrystallisation from ethanol gave off-white needles of 2-phenyl-6-(2-thienyl)pyridine (0.92 g, 65%, m.p. 77–78 °C) (Found: C, 75.9; H, 4.7; N, 5.7. Calc. for $C_{15}H_{11}NS$: C, 75.9; H, 4.7; N, 5.9%). EI mass spectrum: *m/z* 237 (*M*). IR (KBr): 1566s, 1456m, 1497s, 1428m, 762s, 709m and 694m cm^{-1}.

Reactions of H_2bthpy.—*With* $K_2[PtCl_4]$. A solution of H_2bthpy (0.032 g, 0.13 mmol) in 2-methoxyethanol (4 cm^3) was added to a solution of $K_2[PtCl_4]$ (0.059 g, 0.14 mmol) in water (3 cm^3) and the solution heated to 110 °C for 4 h under an inert atmosphere, during which period a black solid precipitated. This solid was filtered off and extracted with CH_2Cl_2 to give a black residue and a yellow solution. The yellow solution was evaporated to dryness to give [Pt(Hbthpy)Cl] (0.025 g, 40%). Recrystallisation by the slow diffusion of hexane into a CH_2Cl_2 solution of the complex yielded small yellow-orange needles (Found: C, 31.9; H, 1.9; N, 3.05. Calc. for $C_{13}H_8ClNPtS_2\cdot0.25CH_2Cl_2$: 32.2; H, 1.75; N, 2.85%). FAB mass spectrum: *m/z* 473 {[Pt(Hbthpy)Cl]} and 437 {[Pt(Hbthpy)]}. IR (KBr): 1604s, 1560m, 1483s, 1453m, 1438m, 1280m, 1169m, 785m and 715s cm^{-1}. The black residue obtained after extraction with CH_2Cl_2 was suspended in CH_2Cl_2 (5 cm^3), $P(OMe)_3$ (10 µl) was added and the mixture heated to reflux for 4 h. After this period the reaction mixture was filtered through Celite, and the filtrate evaporated to dryness to give a mixture of H_2bthpy and [Pt(bthpy){$P(OMe)_3$}].

With $Na[AuCl_4]$. A solution of H_2bthpy (0.024 g, 0.10 mmol) in MeCN (4 cm^3) was added to a solution of $Na[AuCl_4]\cdot2H_2O$ (0.045 g, 0.11 mmol) in water (2 cm^3) and the solution heated to reflux for 26 h during which period a brown solid precipitated. This solid was filtered off and extracted with CH_2Cl_2 to give a black residue and a yellow solution. The yellow solution was chromatographed over silica using CH_2Cl_2–hexane (2:1) as eluent, and the major yellow band collected and recrystallised from CH_2Cl_2 to give small yellow crystals of 5,5′-bis[6-(2-thienyl)-2-pyridyl]-2,2′-bithiophene (tpbt) (0.010 g, 42%) (Found: C, 64.2; H, 3.4; N, 6.05. Calc. for $C_{26}H_{16}N_2S_4$: C, 64.45; H, 3.35; N, 5.75%). FAB mass spectrum: *m/z* 485 (tpbt). IR (KBr): 1584m, 1564ms, 1454s, 797ms, 709m and 697m cm^{-1}.

With $K_2[PdCl_4]$. A solution of H_2bthpy (0.026 g, 0.11 mmol) in MeCN (3 cm^3) was added to a solution of $K_2[PdCl_4]$ (0.034 g, 0.105 mmol) in water (3 cm^3) and the solution heated to reflux for 8 h under an inert atmosphere, during which period a black solid precipitated. This was filtered off and extracted with CH_2Cl_2 to give a black residue and a yellow solution. The yellow solution was combined with the filtrate and evaporated to dryness to give a yellow solid containing [Pd(Hbthpy)Cl], H_2bthpy and tpbt.

Reactions of H_2pthpy.—*With* $K_2[PtCl_4]$. A solution of H_2pthpy (0.033 g, 0.14 mmol) in 2-methoxyethanol (4 cm^3) was added to a solution of $K_2[PtCl_4]$ (0.063 g, 0.15 mmol) in water (3 cm^3) and the solution heated to 110 °C for 4 h under an inert atmosphere, during which period a black solid precipitated. This solid was filtered off and extracted with CH_2Cl_2 to give a black residue and a yellow solution. The yellow solution was combined with the filtrate and evaporated to dryness to give crude [Pt(Hpthpy)Cl] (0.010 g, 15%). FAB mass spectrum: *m/z* 431 {[Pt(Hpthpy)]}. IR (KBr): 1599m, 1576m, 1559m, 1480m, 1455s, 1445m, 805m, 762s and 704s cm^{-1}. The black residue obtained after extraction with CH_2Cl_2 was suspended in CH_2Cl_2 (5 cm^3), $P(OMe)_3$ (20 µl) added and the mixture heated to reflux for 1 h. After this period the reaction mixture was filtered through Celite, and the filtrate evaporated to dryness to give a pale brown mixture of H_2pthpy and [Pt(pthpy)-{$P(OMe)_3$}].

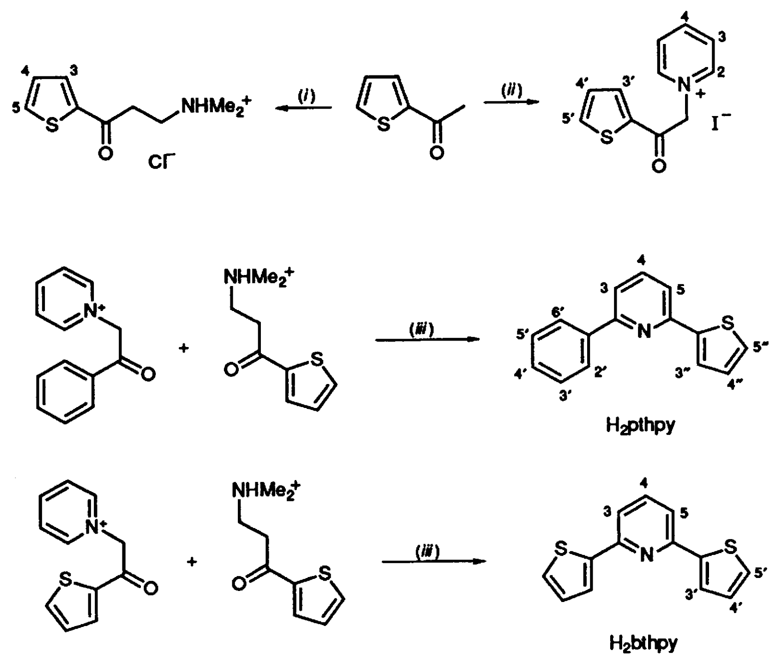
With $Na[AuCl_4]$. A solution of H_2pthpy (0.31 g, 1.3 mmol) in MeCN (7 cm^3) was added to a solution of $Na[AuCl_4]\cdot2H_2O$ (0.43 g, 1.1 mmol) in water (5 cm^3) and the solution heated to reflux for 48 h during which period a brown solid precipitated. This solid was filtered off from the hot solution and dried. Chromatography over silica [hexane–CH_2Cl_2 (1:1) eluent] gave 5,5′-bis(6-phenyl-2-pyridyl)-2,2′-bithiophene (ppbt) as a yellow solid (0.29 g, 81%) (Found: C, 73.8; H, 4.25; N, 5.7. Calc. for $C_{30}H_{20}N_2S_2\cdot0.25CH_2Cl_2$: C, 73.55; H, 4.2; N, 5.65%). EI mass spectrum: *m/z* 472 (ppbt). IR (KBr): 1586m, 1577m, 1564ms, 1457m, 805s, 760s and 696ms cm^{-1}. Upon cooling the filtrate after the removal of the brown solid, orange crystals separated. These were filtered off and dried *in vacuo* to give 2-(5-chloro-2-thienyl)-6-phenylpyridine (ctppy) (0.039 g, 14%) (Found: C, 64.95; H, 3.9; N, 5.1. Calc. for $C_{15}H_{10}ClNS\cdot0.25H_2O$: C, 65.2; H, 3.85; N, 5.05%). EI mass spectrum: *m/z* 271/273 (Clptpy). IR (KBr): 1589m, 1565m, 1460m, 1447ms, 1436ms, 796m, 759s and 691m cm^{-1}.

With $K_2[PdCl_4]$. A solution of H_2pthpy (0.055 g, 0.23 mmol) in MeCN (4 cm^3) was added to a solution of $K_2[PdCl_4]$ (0.072 g, 0.22 mmol) in water (3 cm^3) and the solution heated to reflux for 4 h under an inert atmosphere, during which period a black solid precipitated. This solid was filtered off and extracted with CH_2Cl_2 to give a black residue and an orange solution. Recrystallisation by slow diffusion of hexane into the orange solution yielded small yellow-orange needles of [Pt(Hpthpy)Cl] (0.025 g, 30%). FAB mass spectrum: *m/z* 342 {[Pd(Hpthpy)]}. IR (KBr): 1597m, 1573m, 1561ms, 1481m, 1438m, 1430ms, 1283m, 806m, 764s and 705ms cm^{-1}.

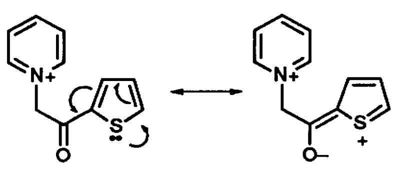
[Pd(Hpthpy-*C,N*)(acac-*O,O′*)]. A suspension of [Pd-(Hpthpy)Cl] (0.015 g, 0.02 mmol) in methanol (4 cm^3) was stirred for 16 h with an excess of Na[acac] (acac = acetylacetonate) at room temperature. The solvent was removed *in vacuo*, and the residue treated with water and methanol to give a yellow solid. This solid was recrystallised by the slow diffusion of Et_2O into a CH_2Cl_2 solution to give small yellow crystals of [Pd(Hpthpy-*C,N*)(acac-*O,O′*)] (0.009 g, 51%) {Found: C, 54.35; H, 3.9; N, 3.1. Calc. for $C_{20}H_{17}NO_2PdS$: C, 54.35; H, 3.9; N, 3.15%). FAB mass spectrum: *m/z* 342 {[Pd-(Hpthpy)]}. IR (KBr): 1584s, 1574s, 1553m, 1513s, 1472m, 1438m, 1396ms, 1266m, 807m, 758ms, 711m and 698m cm^{-1}.

Results and Discussion

The potentially tridentate ligand Hthbipy has been shown to exhibit a variety of *N,N*-, *N,N,S*-, *N,C*- and *N,N,C*-bonded modes in d^6 ruthenium(II) or rhodium(III) and d^8 palladium(II), platinum(II) or gold(III) complexes.[6] The formation of compounds metallated at C^5 with gold(III) prompted us to investigate the related ligands 2-phenyl-6-(2-thienyl)pyridine (H_2pthpy) and 2,6-bis(2-thienyl)pyridine (H_2bthpy). Initially, we investigated H_2pthpy as an analogue of Hthbipy in which a terminal pyridine ring had been replaced by a sterically similar non-co-ordinating group. Such a ligand was expected to allow us to determine whether the co-ordination of the terminal or the central pyridine ring of Hthbipy was important in the formation of precursors to metallated complexes. However, H_2pthpy could co-ordinate to a metal as a monodentate *N*- or *S*-donor, as a bidentate *N,S*-donor, as a chelating *N,C*-donor through either the thienyl or the phenyl ring, or as a monodentate *C*-donor through the 5 position of the thienyl ring. Similarly,



Scheme 1 (*i*) $[NMe_2H_2]Cl$, paraformaldehyde, EtOH, HCl; (*ii*) I_2, pyridine; (*iii*) $[NH_4][O_2CMe]$



Scheme 2

H_2bthpy could act as a monodentate *S*- or *N*-donor, a bidentate *N,S*-donor, a tridentate *S,N,S*-donor or as a metallated *N,C*-, *C,N,S* or *C,N,C*-donor.

The two new ligands were readily prepared by Krohnke syntheses (Scheme 1).[7] In each case the key step of the synthesis involves the assembly of the central pyridine ring from open-chain precursors. The thienyl rings of H_2bthpy and H_2pthpy are derived from 2-acetylthiophene whilst the phenyl ring of H_2pthpy originates in acetophenone. The Ortoleva-King reaction of 2-acetylthiophene with iodine in pyridine proceeds smoothly to give the golden-yellow ylide precursor, [2-oxo-2-(2-thienyl)ethyl]pyridinium iodide in 65% yield. This compound exhibits a characteristic carbonyl band in its infrared spectrum at 1662 cm^{-1}; this is to considerably lower energy than the corresponding mode for the related compound [2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (1690 cm^{-1}), and we suggest that this is due to conjugation with the thienyl group (Scheme 2). The FAB mass spectrum exhibited a base peak corresponding to the cation (*m*/*z* 204). The ^{1}H NMR spectrum is sharp and well resolved (δ 8.81, d, J = 5.8, H^2; 8.68, t, J = 7.9, H^4; 8.17, dd, J = 7.9, 5.8, H^3; 8.15, d, J = 4.0, H$^{3'}$; 8.07, d, J = 4.9, H$^{5'}$; 7.35, dd, J = 4.0, 4.9, H$^{4'}$) with the exception of marked broadening of the resonance associated with the acidic CH_2 group (δ 6.34 br s). In the preparation of H_2bthpy one thienyl ring originates in this salt, and the other is incorporated by using a Mannich salt as an enone equivalent. The Mannich salt dimethyl[3-oxo-3-(2-thienyl)propyl]ammonium chloride is readily prepared as a white solid in 65% yield by the reaction of 2-acetylthiophene with formaldehyde and dimethylammonium chloride in ethanol. This salt exhibits a characteristic carbonyl band in its infrared spectrum at 1652 cm^{-1}, and the FAB mass spectrum exhibited a base peak corresponding to the cation (*m*/*z* 184). The ^{1}H NMR spectrum is sharp and well resolved (δ 8.01, d, J = 3.9, H^3; 7.91, d, J = 5.0, H^5; 7.24, dd, J = 3.9, 5.0, H^4; 3.57, m, $COCH_2CH_2$; 2.95, s, Me_2N). The phenyl ring in H_2pthpy is incorporated using the ylide precursor *N*-(2-oxo-2-phenylethyl)pyridinium bromide, whilst the thienyl ring comes from the Mannich salt dimethyl[3-oxo-3-(2-thienyl)propyl]ammonium chloride.

The compound H_2bthpy is formed as an off-white solid in 70% yield by the reaction of dimethyl[3-oxo-3-(2-thienyl)propyl]ammonium chloride with *N*-[2-oxo-2-(2-thienyl)ethyl]pyridinium iodide in acetic acid in the presence of ammonium acetate. The EI mass spectrum of this new ligand exhibited a base peak corresponding to the parent ion (*m*/*z* 243). The ^{1}H NMR spectrum is sharp and well resolved and illustrates the high symmetry of the ligand [Table 1, Fig. 1(*a*)]. The other new ligand, H_2pthpy, is similarly prepared as an off-white solid in 65% yield by the reaction of *N*-(2-oxo-2-phenylethyl)pyridinium bromide with dimethyl[3-oxo-3-(2-thienyl)propyl]ammonium chloride in acetic acid in the presence of ammonium acetate. The EI mass spectrum of this new ligand exhibited a base peak corresponding to the parent ion (*m*/*z* 237). The ^{1}H NMR spectrum is also sharp and well resolved [Table 2, Fig. 1(*b*)].

The reaction of H_2bthpy with $K_2[PtCl_4]$ in boiling 2-methoxyethanol results in the precipitation of a black powder. Extraction of this powder with CH_2Cl_2 gives a yellow solution, from which an orange-yellow solid is obtained upon evaporation of the solvent and an insoluble black material. Microanalysis of the yellow compound indicates a formulation [Pt(Hbthpy)Cl], and the FAB mass spectrum exhibits a base peak at *m*/*z* 437, with the correct isotopomer distribution for [Pt(Hbthpy)]$^+$. The ^{1}H NMR spectrum of a CD_2Cl_2 solution of [Pt(Hbtpy)Cl] exhibits eight aromatic resonances, strongly supporting the suggestion that the ligand has metallated (Table 1). The spectrum was assigned on the basis of a correlation spectroscopy (COSY) experiment, and it is found that it consists of three separate sub-spectra corresponding to two AMX and one AM spin system, as expected for 2,6-disubstituted pyridine, 2-substituted thienyl and 2,x-disubstituted thienyl rings. The AM ring system (δ 7.24, 7.55) exhibits a coupling constant of 4.9 Hz, typical of $^3J(H^4H^5)$ in a thiophene, indicating that the ring has been cyclometallated at C^3. Both of the doublets of the AM pattern exhibit satellite patterns due to coupling to ^{195}Pt (δ 7.24, J 24; δ 7.55, J 12 Hz), allowing the assignment of these peaks to H^4 and H^5 of the thiophene respectively. These coupling constants are typical of those previously reported for [Pt(thpy-*NC*)$_2$] [^3J(PtH) 21.1 Hz].[4] Satellites are also noted on

Table 1 Proton NMR data for derivatives of H_2bthpy

	δ[a]								
Compound	$H^{5'}$	$H^{4'}$	$H^{3'}$	H^3	H^4	H^5	$H^{3''}$	$H^{4''}$	$H^{5''}$
H_2bthpy[b]	7.44 (5.1)	7.14 (3.7, 5.1)	7.65 (3.7)	7.53 (7.9)	7.72 (7.9)				
c	7.65 (5.1)	7.17 (3.8, 5.1)	7.82 (3.8)	7.75 (7.9)	7.84 (7.9)				
tpbt[b]	7.46 (5.1)	7.16 (3.7, 5.1)	7.68 (3.7)	7.55 (7.9)	7.73 (7.9, 7.9)	7.55 (7.9)	7.59 (3.9)	7.35 (3.9)	
[Pt(Hbthpy)Cl][b]	7.60 (5.3)[e]	7.31 (3.7, 5.3)[e]	7.48 (3.8)	7.46[d] (7.9)	7.87 (7.9, 7.9)[e]	7.29[d] (7.9)		7.24 (4.9) [24]	7.55 (4.9) [12]
[Pt(bthpy){P(OMe)$_3$}][b]	7.33 (4.6) [13]	7.13 (4.7) [7]		6.76 (7.9) [8]	7.37 (7.9)				
[Pd(Hbthpy)Cl][b]	7.56 (5.3)	7.31 (3.7, 5.3)	7.51 (3.7)	7.45[d] (7.9)	7.85 (7.9, 7.9)	7.28[d] (7.9)		7.33 (4.8)	7.38 (4.8)

[a] ^3J(HH)/Hz in parentheses, J(HPt)/Hz in square brackets. [b] In CD_2Cl_2 solution. [c] In CD_3SOCD_3 solution. [d] Ambiguity in assignment of $H^{3,5}$. [e] Satellites observed but not measurable.

Table 2 Proton NMR data for derivatives of H_2pthpy

	δ[a]										
Compound	$H^{5''}$	$H^{4''}$	$H^{3''}$	H^3	H^4	H^5	$H^{2'}$	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$
H_2pthpy[b]	7.44 (5.1)	7.15 (3.7, 5.1)	7.67 (3.7)	7.65[c] (7.8)	7.79 (7.8, 7.8)	7.63[c] (7.8)	8.12	7.47	7.50		
ppbt[b]		7.36 (3.8)	7.61 (3.8)	7.66[c] (7.8)	7.80 (7.8, 7.8)	7.65[c] (7.8)	8.15	7.48	7.52		
ctppy		6.92 (4.0)	7.37 (4.0)	7.61[c] (7.8)	7.74 (7.8, 7.8)	7.50[c] (7.8)	8.08	7.45	7.45		
[Pd(Hpthpy)Cl][b]	7.57 (5.0)	7.33 (3.8, 5.0)	7.51 (3.8)	7.61 (7.8)	7.95 (7.8, 7.8)	7.61 (7.8)		7.45[d]	7.09[d]	7.18[d]	7.75[d]
[Pd(Hpthpy)(acac)][b,e]	7.47 (5.1)	7.08 (3.8, 5.1)	7.64 (3.8)	7.68 (7.9)	7.86 (7.9, 7.9)	7.35 (7.9)		7.52[d]	7.14[d]	7.14[d]	7.52[d]
[Pt(Hpthpy)Cl][b]	7.62 (5.0)	7.34 (3.8, 5.0) [5]	7.49 (3.8)	7.58 (7.8)	7.99 (7.8, 7.8) [4]	7.58 (7.8)		7.46[d]	7.18[d]	7.18[d]	7.75[d]

[a] J(HH)/Hz in parentheses, J(HPt)/Hz in square brackets. [b] CD_2Cl_2 solution. [c] Ambiguity in assignment of $H^{3,5}$. [d] Ambiguity in the assignments of $H^{3',6'}$ and $H^{4',5'}$. [e] CH_3, δ 1.42 (s) and 1.99 (s); CH, δ 5.17 (s).

the resonances assigned to H^5 and H^4 of the non-metallated thienyl ring and the pyridyl ring protons. This is taken as evidence for the co-ordination of the ligand in an *C,N,S*-tridentate mode, and we propose a structure [Pt(Hbthpy-*C,N,S*)Cl] as indicated in Scheme 3. It it is not possible to eliminate dimeric structures such as [(Hbthpy-*N,C*)Pt(μ-Cl)$_2$-Pt(Hbthpy-*N,C*)] in which there is a weak interaction between the formally non-co-ordinated sulfur and the metal, as is seen in the complexes *trans*-[Pd(Hthpy-*N*)$_2$Br$_2$] and [Pt(thpy-*N,C*)-(Hthpy-*N*)I].[5] The yellow complex [Pt(Hbthpy-*C,N,S*)Cl] is isolated in 40% yield.

The black residue that was insoluble in CH_2Cl_2 gave no useful mass spectroscopic or microanalytical data, but was treated with an excess of P(OMe)$_3$ in CH_2Cl_2 to yield a yellow solution. The ^{1}H NMR spectrum of the yellow solid which could be isolated from this solution indicated that just two species were present. The first compound is the starting ligand H_2bthpy, and we believe that this has been displaced from a platinum H_2bthpy complex by the phosphite. The second species exhibits only four aromatic resonances in its ^{1}H NMR spectrum, forming two AM spin systems with coupling constants of 4.6 and 7.9 Hz. The system exhibiting the 7.9 Hz coupling represents the 2,6-disubstituted pyridine ring and is half the intensity of the one with the 4.6 Hz coupling, which suggests that we now have a compound with *two* thienyl rings metallated at C^3. The resonances assigned to H^4 and H^5 of the thienyl rings (δ 7.13 and 7.33) exhibit satellites due to coupling to ^{195}Pt of 7 and 13 Hz respectively. The FAB mass spectrum exhibits an intense ion at *m/z* 561 corresponding to [Pt(bthpy){P(OMe)$_3$}]$^+$. Although we have been unable to separate the free H_2bthpy from the yellow platinum complex by chromatographic or other methods, we propose that the complex [Pt(bthpy-*C,N,C*){P(OMe)$_3$}], containing a double metallated bthpy ligand, has been formed.

The reaction of Na[AuCl$_4$] with H_2bthpy in aqueous acetonitrile also results in the precipitation of a black-brown powder. Extraction of this with CH_2Cl_2 gives a yellow solution which may be purified by thin-layer chromatography to yield unreacted H_2bthpy and a new yellow compound. The ^{1}H NMR spectrum of the latter exhibits eight aromatic resonances which comprise two AMX and one AM spin system [Table 1, Fig. 2(*c*)]. This is indicative of a compound in which one of the thienyl rings exhibits a 2,x-disubstitution pattern. The coupling constant of the AM system is 3.9 Hz, which suggests that substitution has occurred at the 5 rather than the 3 position. The EI and FAB mass spectra exhibit peaks at *m/z* 484 and 242 assigned to [(Hbthpy)$_2$]$^+$ and [Hbthpy]$^+$ respectively, and no peaks corresponding to any gold(III) complexes. The elemental analysis of the compound closely corresponds to that expected for free H_2bthpy (from which it differs in its chromatographic and ^{1}H NMR spectroscopic properties). The above data are consistent with the gold(III) acting as an oxidising agent, and the H_2bthpy undergoing an oxidative dehydrogenation to give the new ligand 5,5′-bis[6-(2-thienyl)-2-pyridyl]-2,2′-bithiophene (tpbt, Scheme 3). Isolated yields of this compound were usually in the order of 50%, but the *conversion* of H_2bthpy into the dimer was essentially quantitative. We have isolated no gold complexes from reactions of H_2bthpy with Na[AuCl$_4$] under a

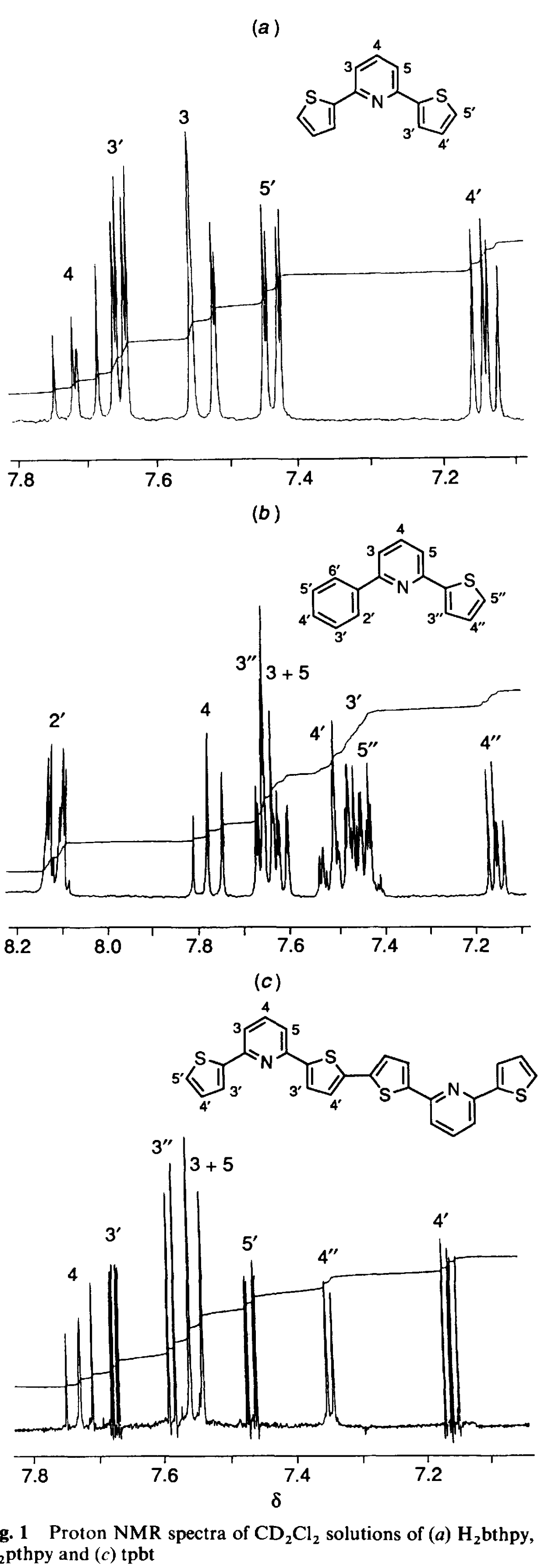


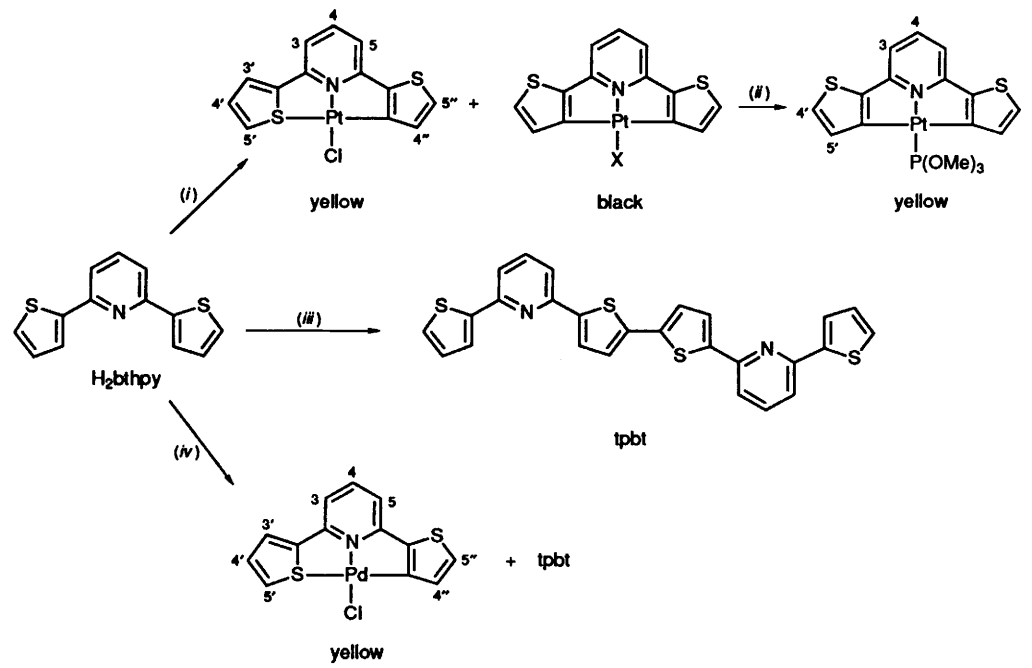
Fig. 1 Proton NMR spectra of CD_2Cl_2 solutions of (*a*) H_2bthpy, (*b*) H_2pthpy and (*c*) tpbt

wide variety of conditions. This behaviour upon treatment with gold(III) exactly parallels that we have previously described for Hthbipy, which gives mixtures of dimerised and 5-chlorinated products.[8] These reactions could proceed through the intermediacy of 5-aurated derivatives or simply by nucleophilic attack upon a thienyl ring co-ordinated to gold(III). We have no evidence in support of either of these possibilities.

In order further to probe the reactivity of the H_2bthpy ligand we investigated the reactions with palladium(II). The reaction of $K_2[PdCl_4]$ with H_2bthpy in boiling aqueous acetonitrile results in the precipitation of a black solid. Extraction with CH_2Cl_2 gives a yellow solution, from which a yellow solid is obtained upon evaporation. The ^{1}H NMR spectrum of the latter indicates that it is a mixture of unreacted H_2bthpy, the dimer tpbt and a new compound. The FAB mass spectrum of this mixture showed the expected peaks for the dimer (*m*/*z* 485), H_2bthpy (*m*/*z* 243), together with a very low-intensity peak at *m*/*z* 726 which is tentatively assigned to a trimer and a major peak at *m*/*z* 348 corresponding to [Pd(Hbthpy)]. The ^{1}H NMR spectrum of the third component in the mixture is consistent with its formulation as a cyclometallated complex [Pd(Hbthpy-*C*,*N*)Cl] (Table 1). In particular, the AM spin system with ^3J 4.8 Hz is consistent with metallation at C^3 of the thienyl ring. Attempts to isolate the palladium complex by chromatographic methods or crystallisation were unsuccessful, and resulted in decomposition to black insoluble products, H_2bthpy and tpbt. The reactions of H_2bthpy are summarised in Scheme 3.

In the light of this variety of behaviour, we investigated the behaviour of H_2pthpy with a variety of d^8 metal ions. The reaction with $K_2[PtCl_4]$ in aqueous 2-methoxyethanol results in the precipitation of a black powder. Extraction of this powder with CH_2Cl_2 gives a yellow solution, from which a yellow solid is obtained. The FAB mass spectrum of the latter exhibits a peak at *m*/*z* 431, with the correct isotopomer distribution for $[Pt(Hpthpy)]^+$. The ^{1}H NMR spectrum of a CD_2Cl_2 solution of [Pt(Hpthpy)Cl] exhibits ten aromatic resonances, supporting the metallated formulation (Table 2). The spectrum was assigned on the basis of a COSY experiment, which revealed three separate sub-spectra corresponding to two AMX and one four-proton spin system. This is only consistent with a structure in which the 2-substituted thienyl ring is intact, and metallation has occurred at the phenyl ring. The IR spectrum is as expected for a 1,2-disubstituted benzene derivative, specifically the strong absorption at 694 cm^{-1} observed for H_2pthpy (out-of-plane skeletal mode for monosubstituted benzene) is absent for the complex. In contrast, the C–H out-of-plane bending observed at 762 cm^{-1} for H_2pthpy is only slightly shifted to 764 cm^{-1} for the complex. After recrystallisation the metallated complex was isolated in 15% yield. Metallation at the phenyl ring is fully in accord with the previously reported behaviour of platinum(II) with 2-phenylpyridine, and suggests that the ring strain associated with the formation of the five-membered chelate ring is less if the *C*-donor is in a six- rather than a five-membered aromatic ring. The only other characterised compound obtained from the reaction was unreacted H_2pthpy. However, the black insoluble residue left after extraction with CH_2Cl_2 reacts with $P(OMe)_3$ to give a mixture of yellow compounds. There is some ^{1}H NMR evidence for the presence of doubly metallated complexes in this mixture, but no pure compounds were isolated. We propose a structure [Pt(Hpthpy-*C*,*N*,*S*)Cl] on the basis of a small coupling between the platinum and $H^{4''}$ of the thienyl ring, although it is not possible to eliminate dimeric structures such as [(Hpthpy-*N*,*C*)Pt(μ-Cl)$_2$Pt(Hpthpy-*N*,*C*)] in which there is a weak interaction between the sulfur and the metal as seen in some complexes of Hthpy.[5]

The reaction of H_2pthpy with $Na[AuCl_4]$ in boiling aqueous acetonitrile results in the precipitation of a brown solid and the formation of a pale yellow solution. The brown solid was filtered off and the yellow solution cooled, to give orange needles of a second product. Extraction of the brown solid with dichloromethane gives a yellow solution from which a yellow solid is obtained. The ^{1}H NMR spectrum of a solution of this yellow solid (Table 2) is very similar to that of a solution of H_2pthpy, but the AMX pattern of the 2-thienyl ring is replaced by an AM system with a coupling constant of 3.8 Hz. This is consistent



Scheme 3 (*i*) $K_2[PtCl_4]$, $MeOCH_2CH_2OH$, water; (*ii*) $P(OMe)_3$, CH_2Cl_2; (*iii*) $Na[AuCl_4]$, MeCN, water; (*iv*) $K_2[PdCl_4]$

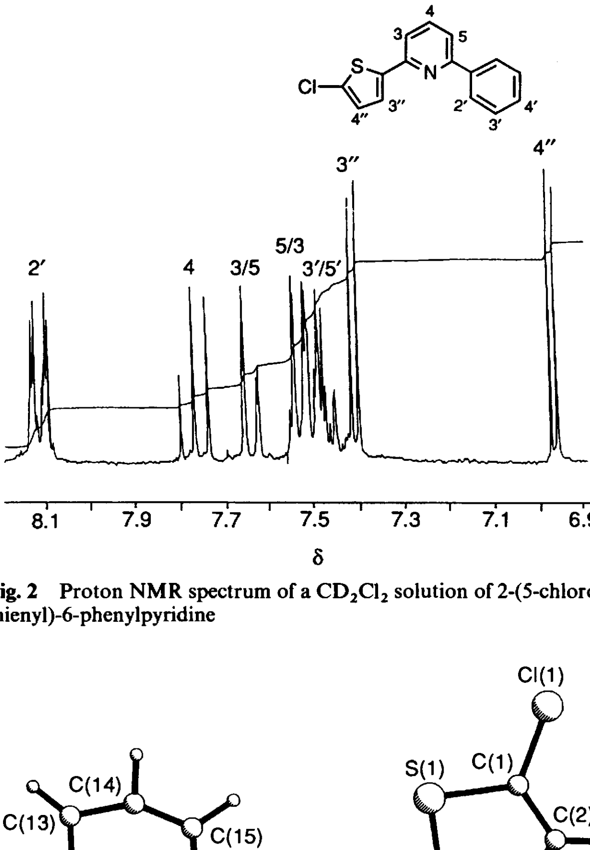


Fig. 2 Proton NMR spectrum of a CD_2Cl_2 solution of 2-(5-chloro-2-thienyl)-6-phenylpyridine

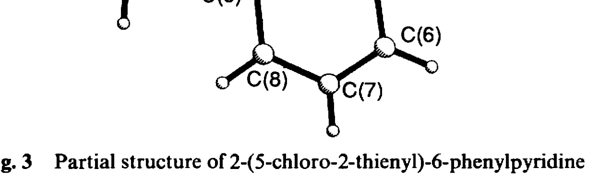
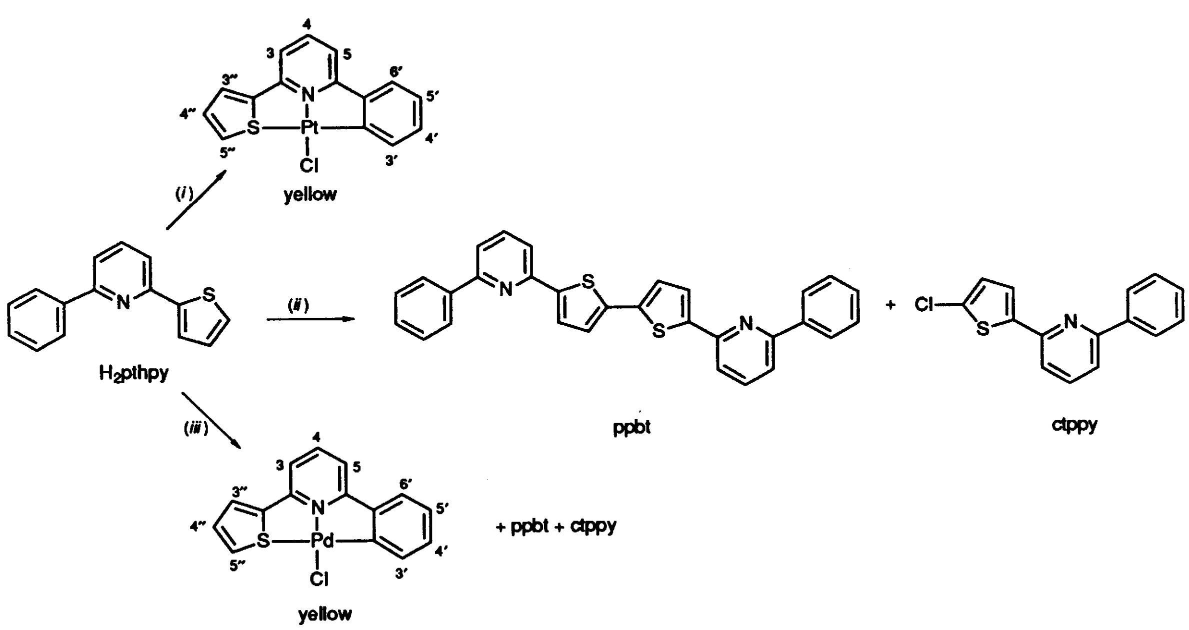


Fig. 3 Partial structure of 2-(5-chloro-2-thienyl)-6-phenylpyridine

with the formation of a 5-substituted derivative of H_2pthpy. The EI mass spectrum of this yellow compound exhibits a parent ion at *m*/*z* 472, corresponding to the dimer, 5,5′-bis(6-phenyl-2-pyridyl)-2,2′-bithiophene (ppbt). This compound is strictly analogous to the dimer tpbt which was obtained from H_2bthpy.

The ^1H NMR spectrum (Table 2, Fig. 2) of the orange needles which were obtained from cooling the reaction mixture closely resembles that of tpbt with eight aromatic resonances and an AM pattern for the thienyl ring (^3J 4.0 Hz). The EI mass spectrum exhibits peaks at *m*/*z* 271/273 assigned to the 5″-chlorinated derivative 2-(5-chloro-2-thienyl)-6-phenylpyridine (ctppy), and elemental analysis is fully in accord with this formulation. The crystals of this chlorinated product were very thin and of low quality, but a preliminary structural solution confirms the formulation (Fig. 3). The molecule is approximately planar, with a cisoid arrangement of the thiophene S and pyridine N atoms about the interannular C–C bond. The reactions of H_2pthpy with gold(III) are clean, and yields of the dimer and the chloro-compound were 81 and 14% respectively. The chloro-compound does not appear to be an intermediate in the formation of the dimer, and may be recovered unchanged from reaction with gold(III) under the conditions of the original experiment. The reactions are not catalytic, and the formation of the dimer requires 1 mol of gold(III) for every 2 mol of H_2pthpy consumed. This is consistent with the gold acting as an oxidising agent for the dimerisation process, with the concomitant formation of gold(I) compounds, although we have been unable to isolate *any* gold-containing products from the reaction. It is notable that significant amounts of gold metal are not precipitated during the reaction.

Finally, the reactions of H_2pthpy with palladium(II) were investigated. Upon heating $K_2[PdCl_4]$ with H_2pthpy in aqueous acetonitrile solution, a black powder is precipitated. Extraction with CH_2Cl_2 gives a yellow solution from which an orange microcrystalline solid is readily obtained. The ^1H NMR spectrum reveals it to consist of a mixture of three compounds. Two of these are the previously described dimer ppbt and the chloro compound ctppy. The third component, which is the major species present, exhibits a total of ten aromatic resonances, and the COSY spectrum (Fig. 4) indicates that the resonance $H^{2'}$ of the phenyl ring is absent. The chemical shifts are remarkably similar to those of the previously described



Scheme 4 (*i*) $K_2[PtCl_4]$, $MeOCH_2CH_2OH$, water; (*ii*) $Na[AuCl_4]$, MeCN, water; (*iii*) $K_2[PdCl_4]$

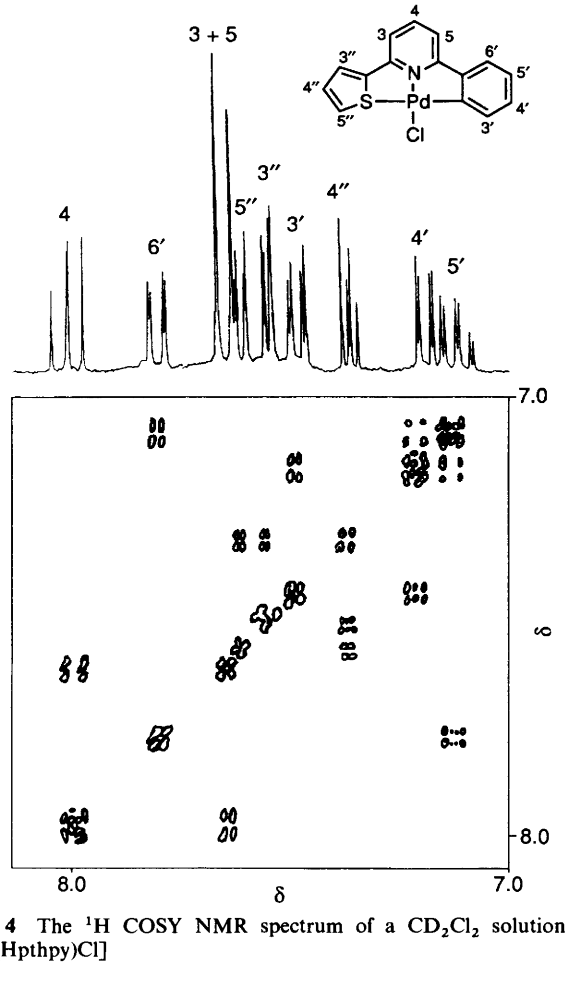


Fig. 4 The ^{1}H COSY NMR spectrum of a CD_2Cl_2 solution of [Pd(Hpthpy)Cl]

cyclometallated platinum(II) complex, and we suggest that this species is [Pd(Hpthpy-*C*,*N*,*S*)Cl]. The FAB mass spectrum exhibits a peak at *m*/*z* 342 [Pd(Hpthpy)], and the IR spectrum lacks a band close to 690 cm^{-1}. Once again, metallation has occurred upon the phenyl rather than the thienyl ring.

The reaction of crude [Pd(Hpthpy-*C*,*N*,*S*)Cl] with Na[acac] gives a yellow complex. The ^{1}H NMR spectrum exhibits ten non-equivalent aromatic resonances in addition to resonances at δ 1.42, 1.99 and 5.17. The presence of ten resonances confirms the persistence of the cyclometallated mode, and the two methyl environments for the acac ligand indicate that it is acting as a bidentate-*O*,*O*′ donor. The complex may thus be assigned the structure [Pd(Hpthpy-*C*,*N*)(acac-*O*,*O*′)]. The IR spectrum exhibits strong bands at 1584 and 1574 (C=O stretching modes) and 1513 cm^{-1} (C–C stretching mode) which are characteristic of a chelating acac ligand.[9] The reactions of H_2pthpy are summarised in Scheme 4.

In conclusion, the two new ligands exhibit the same versatility of co-ordination mode and reactivity patterns that we have previously shown for Hthpy and Hthbipy. With palladium(II) and platinum(II) both form cyclometallated complexes. In the case of H_2bthpy, metallation occurs at C^3 of the thienyl ring, whereas with H_2pthpy it is the *phenyl* ring that is metallated. Both ligands give doubly metallated palladium(II) and platinum(II) complexes. With gold(III) no metallated complexes are formed, but products resulting from reactivity of the ligands at C^5 of the thienyl rings are obtained.

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