Cyclometallation Reactions of 6-(2-Thienyl)-2,2′-bipyridine with d^8 Transition Metal Ions†

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The potentially terdentate ligand 6-(2-thienyl)-2,2′-bipyridine (Hthbipy) reacts with $[MCl_4]^{2-}$ (M = Pd or Pt) under mild conditions to give cyclometallated complexes in which the thienyl ring is metallated at the 3 position. The metallated complexes [M(thbipy)Cl] (M = Pd or Pt) react with trimethyl phosphite to give phosphonate complexes $[M(thbipy)\{P(=O)(OMe)_2\}]$ and with Na[acac] (Hacac = acetylacetone) to give [M(thbipy)(acac)] with a *C*-bonded acac ligand. Under mild conditions, the non-metallated compound $[Pd(Hthbipy)Cl_2]$ can be isolated. In contrast, the reaction of Hthbipy with $Na[AuCl_4]$ at ambient temperature yields the non-metallated complex $[Au(Hthbipy)Cl_3]$, but upon heating this, or performing the reaction at higher temperatures, the metallated compound $[Au(thbipy)Cl_2]$ is obtained. X-Ray structural analysis of this complex reveals it to be dimeric where the ligand has metallated at the 5 position of the thienyl ring and adopts a bridging bidentate *N,C* mode [triclinic, space group $P\bar{1}$, a = 9.271(5), b = 14.214(10), c = 16.194(10) Å, α = 108.11(5), β = 96.55(5), γ = 111.46(5)°, Z = 2, R = 0.075, R' = 0.094].

Cyclometallated compounds contain chelated ligands in which one of the donor sites is an anionic carbon centre.[1,2] The photochemical and photophysical properties of such compounds have been extensively investigated in recent years, and examples incorporating a wide combination of donor atoms are known. A particularly common structural feature is a ligand in which the anionic carbon donor centre is generated by deprotonation of a C–H bond of an aromatic ring bonded to a heteroaryl ring; the latter acts as the 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 and it has recently been demonstrated that the thiophene ring may be cyclometallated at C^3 to yield complexes with interesting photophysical and electronic properties.[3,4] 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,[5] 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.[6,7] In this paper we describe the interaction of Hthbipy with platinum(II), palladium(II) and gold(III) compounds; we have briefly described some aspects of the interaction of gold(III) with Hthbipy previously.[6,7]

Experimental

Infrared spectra were recorded on Perkin-Elmer 1710 or Philips PU9624 Fourier-transform spectrophotometers, with the samples in compressed KBr discs, proton and ^{31}P NMR spectra on Brüker 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. The compounds $Na[AuCl_4]$, $K_2[PdCl_4]$, $K_2[PtCl_4]$ and $[\{Pd(O_2CMe)_2\}_3]$ (Johnson Matthey) were used as supplied; 6-(2-thienyl)-2,2′-bipyridine was prepared by the literature method.[7]

Preparations.—[Pd(thbipy)Cl]. A solution of Hthbipy (0.016 g, 0.066 mmol) in acetonitrile (1.5 cm^3) was added to a solution of $K_2[PdCl_4]$ (0.022 g, 0.066 mmol) in water (1 cm^3) and heated to 60° C for 2 h, during which period a yellow solid precipitated. This solid was filtered off and air-dried to give [Pd(thbipy)Cl] (0.026 g, 99%). Recrystallisation from dimethyl sulfoxide (dmso) yielded small orange needles (Found: C, 44.75; H, 2.4; Cl, 9.3; N, 7.2. Calc. for $C_{14}H_9ClN_2PdS$: C, 44.35; H, 2.4; Cl, 9.35; N, 7.4%). FAB mass spectrum: *m/z* 378 {[Pd(thbipy)Cl]} and 343 {[Pd(thbipy)]}. IR (KBr): 1594s, 1557m, 1493s, 1459m, 1434m, 872m, 766s, 644m and 370w cm^{-1}.

[Pt(thbipy)Cl]. A solution of $K_2[PtCl_4]$ (0.085 g, 0.205 mmol) in water (4 cm^3) was added to a solution of Hthbipy (0.050 g, 0.21 mmol) in acetonitrile (3 cm^3) and heated to 60 °C for 20 h, during which period a brown solid precipitated. This solid was filtered off, washed with water and MeCN, and air-dried to give [Pt(thbipy)Cl] (0.086 g, 97%) (Found: C, 35.7; H, 2.1; Cl, 4.75; N, 5.8. Calc. for $C_{14}H_9ClN_2PtS$: C, 35.9; H, 2.0; Cl, 7.6; N, 5.8%). FAB mass spectrum: *m/z* 468 {[Pt(thbipy)Cl]} and 432 {[Pt(thbipy)]}. IR (KBr): 1600s, 1554m, 1494s, 1459m, 1438m, 881m, 764s, 647m and 343w cm^{-1}.

$[Pd(thbipy)\{P(OMe)_2O\}]$. A solution of [Pd(thbipy)Cl] (0.019 g, 0.05 mmol) in CH_2Cl_2 (4 cm^3) was added to a solution of $P(OMe)_3$ (6.0 µl) in CH_2Cl_2 (3 cm^3) and stirred at 30 °C for 5 h. After this period the solvent was removed *in vacuo* to give a yellow-brown solid. This solid was recrystallised by the diffusion of diethyl ether vapour into a CH_2Cl_2 solution to give $[Pd(thbipy)\{P(OMe)_2O\}]$ as small yellow needles (0.021 g, 93%) (Found: C, 42.15; H, 3.2; N, 6.1. Calc. for $C_{16}H_{15}N_2O_3PPdS$: C, 42.45; H, 3.35; N, 6.2%. FAB mass spectrum: *m/z* 453 ($[Pd(thbipy)\{P(OMe)_2O\}]$) and 343 {[Pd(thbipy)]}. IR (KBr): 1592s, 1559m, 1492s, 1459m, 1436m, 1131s, 1091m, 1016vs, 869m, 778s, 739m, 721s and 571m cm^{-1}.

$[Pt(thbipy)\{P(OMe)_2O\}]$. A solution of [Pt(thbipy)Cl] (0.041 g, 0.088 mmol) in CH_2Cl_2 (4 cm^3) was added to a solution of $P(OMe)_3$ (5.0 µl) in CH_2Cl_2 (3 cm^3) and stirred at 30 °C for 5 h. After this period the solvent was removed *in vacuo* to give an orange solid. This solid was recrystallised by the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

diffusion of diethyl ether vapour into a CH_2Cl_2 solution to give [Pt(thbipy){P(OMe)$_2$O}] as small orange needles (0.038 g, 80%) (Found: C, 34.7; H, 2.8; N, 4.95. Calc. for $C_{16}H_{15}N_2O_3PPtS$: C, 34.7; H, 2.8; N, 5.0%). FAB mass spectrum: *m/z* 541 ([Pd(thbipy){P(OMe)$_2$O}]). IR (KBr): 1596s, 1559m, 1491s, 1459m, 1438m, 1380m, 1133s, 1021vs, 778s, 741m, 721s and 576 cm^{-1}.

[Pd(thbipy)(acac)]. A solution of Na[acac] in methanol [prepared by the addition of excess of acetylacetone (Hacac) to a freshly prepared sodium methoxide solution made from sodium (0.012 g, 0.5 mmol) and methanol (5 cm^3)] was added to a suspension of [Pd(thbipy)Cl] (0.053 g, 0.14 mmol) in methanol (4 cm^3) and stirred at 30 °C for 2 d. After this period the solvent was removed *in vacuo*, and the yellow-brown residue washed with water and a small amount of methanol. The yellow solid was filtered off and air-dried to give [Pd(thbipy)(acac)] (0.060 g, 97%) (Found: C, 51.65; H, 3.6; N, 6.2. Calc. for $C_{19}H_{16}N_2O_2PdS$: C, 51.55; H, 3.65; N, 6.35%). FAB mass spectrum: *m/z* 343 {[Pd(thbipy)]}. IR (KBr): 1667s, 1644m, 1618m, 1595s, 1493m, 1459m, 1400m and 769s cm^{-1}.

[Pt(thbipy)(acac)]. A solution of Na[acac] in methanol [prepared by the addition of excess of Hacac to a freshly prepared sodium methoxide solution made from sodium (0.006 g, 0.25 mmol) and methanol (3 cm^3)] was added to a suspension of [Pt(thbipy)Cl] (0.017 g, 0.036 mmol) in methanol (4 cm^3) and the solution stirred at 30 °C for 2 d. After this period the solvent was removed *in vacuo*, and the brown residue washed with water and a small amount of methanol. This solid was recrystallised by the diffusion of diethyl ether vapour into a CH_2Cl_2 solution to give orange-brown needles of [Pt(thbipy)(acac)] (0.014 g, 73%) (Found: C, 42.25; H, 3.1; N, 5.2. Calc. for $C_{19}H_{16}N_2O_2PtS$: C, 42.85; H, 3.05; N, 5.25%). FAB mass spectrum: *m/z* 532 {[Pt(thbipy)(acac)]} and 432 {[Pt(thbipy)]}. IR (KBr): 1676s, 1655m, 1637m, 1594m, 1466m, 1383m and 767s cm^{-1}.

[Pt(thbipy)(MeCN)][PF$_6$]. A suspension of [Pt(thbipy)Cl] (0.018 g, 0.038 mmol) in acetonitrile (5 cm^3) and water (1 cm^3) was heated to reflux for 3 h. After this period the solution was filtered hot, and the filtrate treated with [NH$_4$][PF$_6$] (0.5 g) to give a brown precipitate. This brown product was filtered off, washed with water and dried *in vacuo* to give [Pt(thbipy)(MeCN)][PF$_6$] (0.015 g, 63%). FAB mass spectrum: *m/z* 473 {[Pt(thbipy)(MeCN)]}. IR (KBr): 1600m, 1553w, 1497m, 1466m, 1441m, 840vs, 809m and 773ms cm^{-1}.

[Pd(Hthbipy)Cl$_2$]. A solution of Hthbipy (0.071 g, 0.30 mmol) in acetonitrile (3 cm^3) was added to a stirred suspension of $K_2[PdCl_4]$ (0.098 g, 0.30 mmol) in water (2 cm^3) and stirred at 10 °C for 3 h, after which period an orange solid had precipitated. This was filtered off, washed with water and dried *in vacuo* to give [Pd(Hthbipy)Cl$_2$] (0.123 g, 98%) (Found: C, 40.0; H, 2.45; N, 6.95. Calc. for $C_{14}H_{10}Cl_2N_2PdS$: C, 40.45; H, 2.45; N, 6.75%). FAB mass spectrum: *m/z* 379 {[Pd(thbipy)Cl]} and 343 {[Pd(thbipy)]}. IR (KBr): 1599m, 1556m, 1490m, 1455s, 773s, 758m, 745m, 347m and 329m cm^{-1}.

Conversion of [Pd(Hthbipy)Cl$_2$] *into* [Pd(thbipy)Cl]. *Method* 1. A solution of [Pd(Hthbipy)Cl$_2$] in dmso was warmed to 40 °C. Upon cooling, orange crystals of [Pd(thbipy)Cl] identical in all respects to the material obtained earlier were obtained.

Method 2. A suspension of [Pd(Hthbipy)Cl$_2$] (0.018 g, 0.043 mmol) in water–MeCN (1:1, 4 cm^3) was warmed to 50 °C for 2 h. Upon cooling, orange-yellow crystals of [Pd(thbipy)Cl] identical in all respects to the material obtained earlier were obtained.

Method 3. A suspension of [Pd(Hthbipy)Cl$_2$] in CH_2Cl_2 was heated to reflux for 1.5 h. After filtration to remove unreacted [Pd(Hthbipy)Cl$_2$], treatment of the yellow filtrate with hexane gave orange-yellow crystals of [Pd(thbipy)Cl] identical in all respects to the material obtained earlier.

[Au(Hthbipy)Cl$_3$]. A solution of Hthbipy (0.145 g, 0.61 mmol) in acetonitrile (3 cm^3) was added to a solution of Na[AuCl$_4$] (0.22 g, 0.061 mmol) in water (5 cm^3) and the solution heated to 45 °C for 5 h, with the addition of water (3 cm^3) over this period. An orange solid was deposited over the 5 h, which was filtered off and air-dried to give [Au(Hthbipy)Cl$_3$] (0.288 g, 87%). Recrystallisation from dimethyl sulfoxide yielded small orange needles (Found: C, 30.9; H, 1.85; N, 5.3. Calc. for $C_{14}H_{10}AuCl_3N_2S$: C, 31.05; H, 1.85; N, 5.15%). IR (KBr): 1587m, 1565m, 1450s, 815m, 770s, 716m and 364m cm^{-1}.

[{Au(thbipy)Cl$_2$}$_2$]. *Method* 1. A solution of Hthbipy (0.024 g, 0.10 mmol) in acetonitrile (1.5 cm^3) was added to a stirred solution of Na[AuCl$_4$] (0.036 g, 0.10 mmol) in water (2 cm^3) and heated to 100 °C for 5 h. After this period, the orange-brown solid was filtered off and air-dried to give [{Au(thbipy)Cl$_2$}$_2$] (0.05 g, 95%) (Found: C, 33.15; H, 1.9; N, 5.4. Calc. for $C_{14}H_9AuCl_2N_2S$: C, 33.25; H, 1.8; N, 5.55%). IR (KBr): 1588m, 1561m, 1445s, 770s and 691m cm^{-1}.

Method 2. A suspension of [Au(Hthbipy)Cl$_3$] (0.10 g, 0.185 mmol) in 1:1 aqueous acetonitrile (8 cm^3) was heated to 100 °C for 6 h. After this period the orange-brown solid was filtered off and air-dried to give [{Au(thbipy)Cl$_2$}$_2$] (0.077 g, 83%).

Crystal Structure Determination of [{Au(thbipy)Cl$_2$}$_2$].—Poor quality single crystals of [{Au(thbipy)Cl$_2$}$_2$] were obtained by the slow diffusion of diethyl ether vapour into a solution of the compound in dimethylformamide.

Crystal data. $C_{28}H_{18}Au_2Cl_4N_4S_2$ + disordered solvent, irregular red blocks, crystal size 0.22 × 0.25 × 0.30 mm, $M = 1010.3$ + disordered solvent, triclinic, space group $P\bar{1}$, $a = 9.271(5)$, $b = 14.214(10)$, $c = 16.194(10)$ Å, $\alpha = 108.11(5)$, $\beta = 96.55(5)$, $\gamma = 111.46(5)^\circ$, $U = 1824(2)$ Å^3, $F(000) = 944$, $Z = 2$, D_m not measured, $D_c = 1.84$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.710\ 73$ Å), μ(Mo-Kα) = 8.464 mm^{-1}.

Data collection and processing. A suitable red single crystal of [{Au(thbipy)Cl$_2$}$_2$] was mounted on a glass fibre. All geometric and intensity data were taken using a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo-Kα radiation. 5170 Data were collected using a 96-step ω–2θ scan over the range $5 \leqslant 2\theta \leqslant 45^\circ$. Three standard reflections were measured every 97 scans, and showed no significant loss in intensity during the data collection. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction applied (transmission factors: minimum, maximum 0.455, 0.710). 4668 Independent reflections were collected and 2422 with $F \geqslant 4\sigma(F)$ were used in the refinement.

Structure analysis and refinement. The structure was solved by direct methods followed by iterative application of full-matrix least-squares refinement and Fourier difference syntheses. A disordered solvent molecule, for which no chemically reasonable model could be found, was present in the lattice; this was treated as seven partially occupied carbon sites. Atoms Au, Cl and S were refined anisotropically. The last cycle of refinement (249 parameters) gave $R' = 0.094$, $R = 0.075$ [$w^{-1} = \sigma^2(F) + 0.0040F^2$] with the largest peak in the final Fourier difference synthesis being 2.50 e Å^{-3}. Structure solutions employed SHELXTL-PLUS on a MicroVax II computer.[8]

Atomic coordinates and selected bond distances and angles for [{Au(thbipy)Cl$_2$}$_2$] are in Tables 1 and 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The potentially terdentate ligand Hthbipy has been shown to exhibit a variety of *N,N'*-, *N,N',S*- and *N,N',C*-bonded modes in d^6 ruthenium(II) and rhodium(III) complexes.[5] The reactions of Hthbipy with d^8 centres such as palladium(II), platinum(II) and gold(III) are expected to parallel this range of bonding modes. The reaction of Hthbipy with an aqueous acetonitrile solution of $K_2[PdCl_4]$ at 60 °C results in the deposition of a yellow solid. This yellow solid may be recrystallised as very

Table 1 Atomic coordinates (× 10^4) for $[\{Au(thbipy)Cl_2\}_2]$

Atom	*x*	*y*	*z*
Au(1)	403(2)	3 399(1)	62(1)
Au(2)	−1 872(2)	−665(1)	−3 497(1)
Cl(1)	478(12)	3 782(9)	−1 206(7)
Cl(2)	262(13)	3 210(9)	1 399(7)
Cl(3)	−3 238(15)	−2 405(9)	−3 629(8)
Cl(4)	−455(13)	1 016(9)	−3 517(7)
N(1)	2 739(36)	4 639(25)	686(21)
C(1)	3 077(42)	5 681(29)	769(23)
C(2)	4 404(48)	6 489(35)	1 126(27)
C(3)	5 780(47)	6 389(33)	1 426(26)
C(4)	5 584(46)	5 351(32)	1 372(26)
C(5)	4 073(43)	4 480(30)	971(25)
C(6)	3 777(35)	3 344(25)	911(21)
C(7)	4 541(38)	3 205(27)	1 610(22)
C(8)	4 297(42)	2 179(30)	1 503(25)
C(9)	3 226(39)	1 283(28)	722(22)
C(10)	2 534(39)	1 501(28)	61(23)
N(2)	2 828(30)	2 566(22)	128(18)
C(11)	1 437(39)	679(27)	−772(22)
C(12)	646(37)	−436(27)	−987(22)
C(13)	−364(39)	−1 027(28)	−1 893(22)
C(14)	−392(42)	−327(30)	−2 337(24)
S(1)	954(11)	1 011(8)	−1 669(7)
N(3)	−3 572(39)	−1 052(26)	−4 691(22)
C(15)	−2 796(48)	−1 060(31)	−5 409(26)
C(16)	−3 769(60)	−1 349(40)	−6 248(36)
C(17)	−5 259(65)	−1 634(41)	−6 368(38)
C(18)	−6 043(55)	−1 560(35)	−5 605(30)
C(19)	−4 977(49)	−1 207(33)	−4 805(28)
C(20)	−5 728(52)	−1 152(35)	−3 985(29)
C(21)	−7 244(56)	−1 842(39)	−4 109(33)
C(22)	−7 886(69)	−1 721(45)	−3 304(36)
C(23)	−6 824(49)	−928(34)	−2 504(29)
C(24)	−5 332(48)	−251(33)	−2 475(28)
N(4)	−4 750(31)	−370(22)	−3 216(19)
C(25)	−4 218(35)	598(25)	−1 639(21)
C(26)	−4 390(39)	877(27)	−808(22)
C(27)	−3 100(42)	1 769(29)	−175(25)
C(28)	−1 743(41)	2 221(29)	−561(24)
S(2)	−2 356(12)	1 490(9)	−1 665(7)
C(100)	11 014(155)	4 460(104)	6 542(88)
C(101)	7 594(157)	4 620(107)	5 980(91)
C(102)	11 503(490)	4 203(321)	6 212(280)
C(103)	9 188(135)	4 676(88)	6 283(73)
C(104)	8 010(118)	4 253(79)	6 441(66)
C(105)	9 951(194)	4 270(124)	6 002(106)
C(106)	11 920(516)	3 738(362)	5 741(308)

Table 2 Selected bond lengths (Å) and angles (°) for $[\{Au(thbipy)Cl_2\}_2]$

Au(1)–Cl(1)	2.285(14)	Au(1)–Cl(2)	2.275(12)
Au(1)–N(1)	2.101(25)	Au(1)–C(28)	1.959(29)
Au(2)–Cl(3)	2.255(13)	Au(2)–Cl(4)	2.279(12)
Au(2)–C(14)	2.002(39)	Au(2)–N(3)	2.130(35)
Cl(1)–Au(1)–Cl(2)	172.6(5)	Cl(1)–Au(1)–N(1)	89.9(10)
Cl(2)–Au(1)–N(1)	88.7(10)	Cl(1)–Au(1)–C(28)	88.6(13)
Cl(2)–Au(1)–C(28)	93.0(12)	N(1)–Au(1)–C(28)	177.7(16)
Cl(3)–Au(2)–Cl(4)	173.7(4)	Cl(3)–Au(2)–C(14)	91.1(12)
Cl(4)–Au(2)–C(14)	92.6(12)	Cl(3)–Au(2)–N(3)	87.1(10)
Cl(4)–Au(2)–N(3)	89.6(10)	C(14)–Au(2)–N(3)	176.3(16)
Au(1)–N(1)–C(1)	120.4(28)	Au(1)–N(1)–C(5)	125.4(26)

small orange crystals by the diffusion of diethyl ether vapour into a dmso solution. Microanalysis suggests the formulation [Pd(thbipy)Cl] to be appropriate, and the complex is formed in quantitative yield. A comparable reaction of Hthbipy with $K_2[PtCl_4]$ in boiling aqueous acetonitrile results in the formation of the analogous compound [Pt(thbipy)Cl] as a brown solid in 97% yield. The FAB mass spectra (3-nitrobenzyl alcohol matrix) of each of these complexes exhibit peaks assigned to $[M(thbipy)Cl]^+$ (M = Pd, *m/z* 378; M = Pt, *m/z* 468) and $[M(thbipy)]^+$ (M = Pd, *m/z* 343; M = Pt, *m/z* 432), all of which show the expected isotopomer distributions. The IR spectra of the two complexes are almost identical, suggesting that they possess similar structures. The spectrum of the free ligand Hthbipy exhibits a strong absorption at 853 cm^{-1} which is a characteristic aromatic C–H out-of-plane deformation of a 2-substituted thiophene.[9] For both the platinum and palladium complexes this band is absent and a new absorption (M = Pd, 872; M = Pt, 881 cm^{-1}) typical of the out-of-plane C–H deformation of a 2,3-disubstituted thiophene is seen.[9] The spectra also show single weak but sharp absorptions which are assigned to the M–Cl stretching modes (M = Pt, 343; M = Pd, 370 cm^{-1}).

The ^1H NMR spectra of solutions of the complexes in CD_2Cl_2 are sharp and well resolved. In CD_3SOCD_3 solution some signals were broadened, but the greater dispersion of resonances in this solvent allowed facile assignment. There are considerable differences between the spectra in the two solvents, but it is possible to recover intact the [Pd(thbipy)Cl] complexes from CD_3SOCD_3 solutions, suggesting that the variations are due to solvent effects rather than displacement of the chloride by the CD_3SOCD_3. Similar solvent effects are observed in the ^1H NMR spectra of $[Pd(thbipy)Cl_2]$ and $[Pt(bipy)Cl_2]$, and data for these complexes are also included in Table 3. The co-ordination shifts $\Delta\delta$ [= δ(co-ordinated ligand) − δ(free ligand)] are remarkably similar in the two solvents (Table 4). Details of the ^1H NMR spectra of the complexes [M(thbipy)Cl] (M = Pd or Pt) and Hthbipy in a variety of solvents are presented in Table 3, and it is clear that those of the palladium and platinum complexes are very similar. The one-dimensional ^1H NMR spectrum and the COSY (correlation spectroscopy) spectrum of a CD_3SOCD_3 solution of [Pd(thbipy)Cl] is shown in Fig. 1. The most noticeable feature is the observation of only nine resonances in contrast to the 10 seen for Hthbipy. The lowest-field resonance at δ 8.62 may be unambiguously assigned to $H^{6'}$ of the terminal pyridine ring [$^3J(H^{5'}H^{6'})$ 5 Hz]; the COSY spectrum then allows the sequential assignment of $H^{5'}$, $H^{4'}$ and $H^{3'}$ of this ring. For the central pyridine ring the resonances for H^4 and one of either H^3 or H^5 are coincident; we have been unable to make an unambiguous assignment of the higher-field resonance to H^3 or H^5. No nuclear Overhauser effect (NOE) was observed between $H^{3'}$ of the terminal pyridine ring and any of the central ring protons. However, the co-ordination shifts support the assignment given in Table 3; the alternative assignments of H^3 and H^5 in the complexes gave widely varying and inconsistent values (the assignments of H^3 and H^5 for the *free* ligands is unambiguous). The most significant feature of the spectrum is the presence of only two doublet resonances for the protons on the thienyl ring. These two doublets exhibit a coupling constant of 4.7 Hz, which strongly suggests that they are to be assigned to $H^{4''}$ and $H^{5''}$ of the thiophene {in thiophenes $^3J(H^2H^3)$ [$\equiv {}^3J(H^4H^5)$] lies in the range 4.90–5.80 Hz, whereas $^3J(H^3H^4)$ is in the range 2.45–4.35 Hz}.[10] In the case of the platinum complexes some of the resonances exhibit satellites due to coupling with ^{195}Pt. These satellites are particularly noticeable on $H^{6'}$ {^3J(Pt–H) 15 Hz, *cf.* 19 Hz for $[Pt(thbipy)_2]$}, $H^{4''}$ {^3J(Pt–H) 19 Hz, *cf.* 21 Hz for $[Pt(thbipy)_2]$}, $H^{5''}$ [^4J(Pt–H) 5 Hz] and also on H^3 and H^5 [^4J(Pt–H) ≈ 12 Hz]. These data are all in accord with the formation of a cyclometallated complex, in which a terdentate ligand is bonded to the metal through $C^{3''}$ and the two nitrogen

Table 3 Proton NMR data for complexes of Hthbipy and some related compounds

	$\delta(^3J_{HH}/Hz)[J_{HPt}/Hz]$									
Compound	H$^{6'}$	H$^{5'}$	H$^{4'}$	H$^{3'}$	H^3	H^4	H^5	H$^{3''}$	H$^{4''}$	H$^{5''}$
Hthbipy^a	8.67	7.32	7.87	8.56	8.30	7.84	7.70	7.68	7.16	7.45
Hthbipy^b	8.70	7.48	8.01	8.45	8.26	7.97	7.97	7.89	7.20	7.69
[Pd(thbipy)Cl]^a	8.80 (5.1)	7.60 (5.3, 7.0)	8.05 (7.6, 7.6)	7.96 (7.8)	7.50 (8.1)	7.84 (8.0, 8.0)	7.31 (8.1)		7.24 (4.8)	7.45 (4.8)
[Pd(thbipy)Cl]^b	8.62 (5.0)	7.80 (5.0, 7.6)	8.28 (7.9, 7.9)	8.49 (7.9)	8.05	8.05	7.60		7.14 (4.7)	7.63 (4.7)
[Pt(thbipy)Cl]^a	9.03 (5.5) [14]	7.69 (5,5. 7.6)	8.11 (7.6, 7.7)	7.91 (7.7)	7.42 (8.2) [12]	7.75 (8.2, 8.1)	7.28 (8.1) [14]		7.14 (4.8) [20]	7.63 (4.8) [8]
[Pt(thbipy)Cl]^b	8.85 (5.2) [15]	7.91 (5.4, 7.0)	8.35 (7.8, 7.8)	8.47 (7.8)	7.98 (8.1)	7.98 (8.0, 8.0)	7.56 (8.1)		6.97 (4.7) [19]	7.83 (4.7) [5]
[Pd(bipy)Cl$_2$]^a	9.41	7.65	8.15	8.05						
[Pd(bipy)Cl$_2$]^b	9.12	7.81	8.36	8.59						
[Pt(bipy)Cl$_2$]^a	9.80	7.68	8.20	8.06						
[Pt(bipy)Cl$_2$]^b	9.41	7.84	8.42	8.58						
[Pd(thbipy){PO(OMe)$_2$}]^{a,c}	9.61	7.58	8.02	7.97	7.55^d	7.83	7.31^d		7.41 (4.9)	7.41 (4.9)
[Pt(thbipy){PO(OMe)$_2$}]^{a,e}	9.92 [23]	7.57	8.04	7.92	7.53^d	7.72	7.26^d		7.32 (4.9) [26]	7.43 (4.9) [14]
[Pd(thbipy)(acac)]^{a,f}	9.46	7.68	7.99	7.91	7.51	7.81	7.31		7.45	7.53
[Pt(thbipy)(acac)]^{a,g}	9.61 [14]	7.73	8.06	7.88	7.47	7.77	7.33		7.38 [22]	7.66 [11]
[Pt(thbipy)(MeCN)][PF$_6$]^{h,i}	8.56 [12]	7.71	8.22	8.03	7.51	7.79	7.24		6.84 [17]	7.63
[Pd(Hthbipy)Cl$_2$]^a	9.21 (5.6)	7.57 (5.6, 7.7)	8.12 (7.7, 7.7)	7.99 (7.7)	7.96^d (7.9)	8.09 (7.9)	7.72^d (7.9)	7.85 (3.7)	7.20 (3.7, 5.1)	7.68 (5.1)
[Au(Hthbipy)Cl$_3$]^a	9.07 (5.9)	7.78 (5.9, 7.6)	8.26 (7.6, 7.7)	8.12 (7.7)	7.95^d	7.98	7.73^d	8.04 (3.7)	7.21 (3.7, 5.0)	7.54 (5.0)
[Au(thbipy)Cl$_2$]^a	9.09 (5.7)	7.73 (5.7, 7.7)	8.18 (7.7, 7.8)	8.07 (7.8)	7.78^d (7.8)	7.90 (7.8)	7.65^d (7.8)		7.06 (3.9)	7.44 (3.9)
[Au(thbipy)Cl$_2$]^b	9.22 (5.5)	7.94	8.41	8.41	8.05^d	8.05	7.94^d		6.92 (4.0)	7.69 (4.0)

[a] In CD_2Cl_2 solution. [b] In CD_3SOCD_3 solution. [c] OCH_3, δ 3.62, ^3J(P–H) 12.2 Hz. [d] Ambiguity in the assignments of H^3 and H^5. [e] OCH_3, δ 3.60, ^3J(P–H) 11.8 Hz. [f] CH_3, δ 2.17; CH, δ 4.84. [g] CH_3, δ 2.19, ^4J(Pt–H) 14 Hz; CH, δ 5.52, ^2J(Pt–H) 120 Hz. [i] CH_3, δ 2.64, ^4J(Pt–H) 11 Hz.

Table 4 Proton NMR co-ordination shift (Δδ) data for complexes of Hthbipy [Δδ = δ(co-ordinated ligand) − δ(free ligand)]

	Δδ								
Compound	H$^{6'}$	H$^{5'}$	H$^{4'}$	H$^{3'}$	H^3	H^4	H^5	H$^{4''}$	H$^{5''}$
[Pd(thbipy)Cl]^a	+0.13	+0.28	+0.18	−0.60	−0.80 (−0.2^c)	0.00	−0.39 (−1.0^c)	+0.08	0.00
[Pd(thbipy)Cl]^b	−0.08	+0.32	+0.27	+0.04	−0.21 (+0.08^c)	0.08	−0.37 (−0.66^c)	−0.13	−0.02
[Pt(thbipy)Cl]^a	+0.36	+0.37	+0.24	−0.65	−0.88 (−0.28^c)	0.09	−0.42 (−1.02^c)	−0.02	+0.18
[Pt(thbipy)Cl]^b	+0.15	+0.43	+0.34	+0.02	−0.28 (−0.01^c)	0.01	−0.41 (−0.04^c)	−0.23	+0.14

[a] In CD_2Cl_2 solution. [b] In CD_3SOCD_3 solution. [c] Value based upon the alternative assignments of H^3 and H^5 in the complexes.

donors (Scheme 1). This is fully in accord with the known ability of 2-(2-thienyl)pyridine to form cyclometallated complexes which exhibit the analogous *C,N*-bonding mode.

The halide ligand in [M(thbipy)Cl] (M = Pd or Pt) is expected to be readily displaced by other ligands, and the reaction with trimethyl phosphite in CH_2Cl_2 at room temperature results in the formation of orange-yellow solutions, from which orange-yellow solids may be obtained. The ^1H NMR spectra of these complexes are reported in Table 3, and the aromatic region of the spectrum of the platinum complex is presented in Fig. 2. Each spectrum exhibits a complex aromatic region integrating to nine protons and a doublet at ≈δ 3.6 integrating to six protons, and showing a typical ^3J(P–H) coupling for a methyl group directly bonded to phosphorus of ≈12 Hz. The ^{31}P NMR spectra of each complex show a single resonance; in the case of the palladium complex this is observed at δ −62 [relative to external P(OMe)$_3$], whereas for the platinum compound it is found at δ −85.3, and exhibits satellites due to coupling to ^{195}Pt[^1J(Pt–P) 5650 Hz]. These data, together with partial elemental analysis, are all in accord with the formation of phosphonate complexes, [M(thbipy)-{P(=O)(OMe)$_2$}], in which the ligand has undergone an Arbusov-type reaction where halide has attacked one of the methyl groups of the ligand with loss of chloromethane. The complexes are formed in 80–90% yield. The infrared spectra of the complexes support the presence of this ligand, and show strong absorptions at 1021–1016 and 1131–1133 cm^{-1}, which are assigned to the P–O–C and the P=O stretching modes respectively.[11] The FAB mass spectra (3-nitrobenzyl alcohol matrix) of each of these complexes exhibit peaks assigned to [M(thbipy){P(=O)(OMe)$_2$}]$^+$ (M = Pd, *m/z* 453; M = Pt, *m/z* 541) which show the expected isotopomer distributions. The aromatic regions of the ^1H NMR spectra confirm that the cyclometallated ligand persists, with the resonances assigned to the cyclometallated thienyl ring appearing as two doublets with 4.9 Hz coupling constants. The platinum complex shows satellite peaks about the resonances assigned to H$^{6'}$[^3J(Pt–H) 23.2 Hz], H$^{4''}$[^3J(Pt–H) 26 Hz] and H$^{5''}$[^4J(Pt–H) 14 Hz] confirming the co-ordination of the terminal pyridine ring and the *terdentate* mode. The chemical shifts of the methyl groups

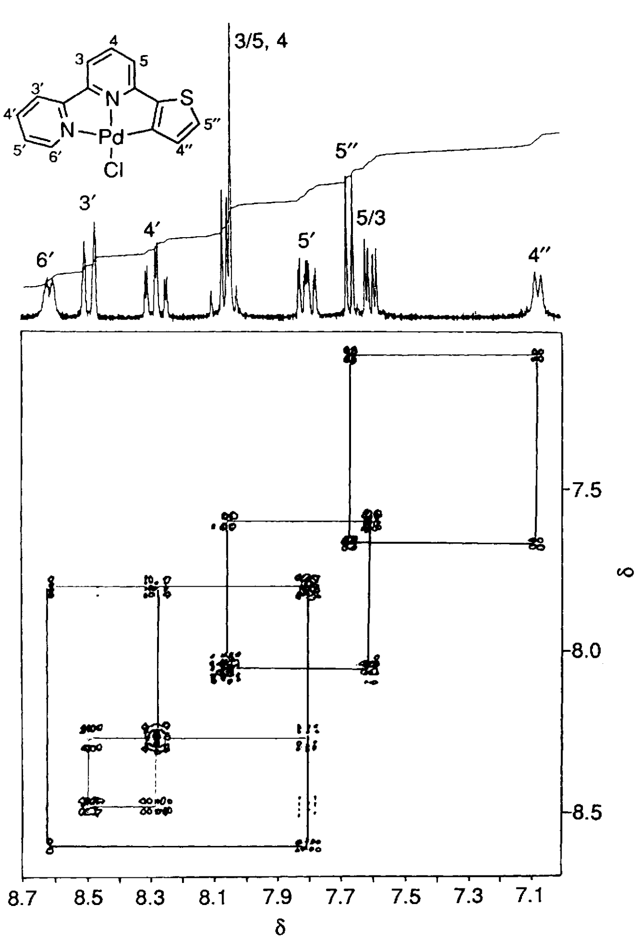


Fig. 1 Proton one-dimensional and COSY spectra of a CD_3SOCD_3 solution of [Pd(thbipy)Cl]

are typical of those for phosphonates co-ordinated to platinum (*trans*-[PtCl{PO(OMe)$_2$}(PBu$_3$)$_2$], δ 3.58, ^3J(H–P) 11.8 Hz).[12] We suggest that these complexes possess the structures indicated in Scheme 1.

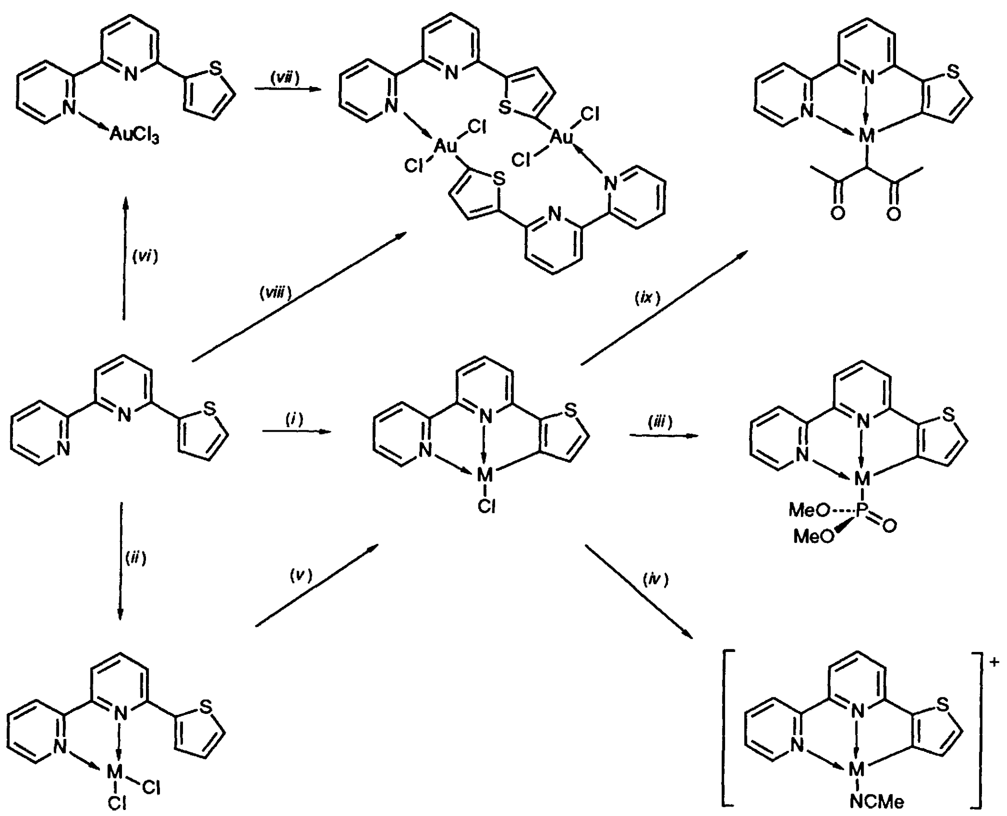
The complexes [M(thbipy)Cl] (M = Pd or Pt) also react smoothly with Na[acac] in methanol to yield yellow-brown solutions from which yellow or brown solids may be obtained. Elemental analysis indicates a formulation [M(thbipy)(acac)]; the FAB mass spectrum (3-nitrobenzyl alcohol matrix) of [Pd(thbipy)(acac)] only shows peaks assigned to [Pd(thbipy)]$^+$, but that of the platinum compound exhibits peaks assigned to [Pt(thbipy)(acac)]$^+$. In these complexes the acac ligand could be acting as a bidentate *O,O′*-donor, in which case the complexes must either be five-co-ordinate or contain a bidentate thbipy ligand, or contain a monodentate *C*-bonded acac with a terdentate thbipy ligand. The infrared spectra show two or three strong absorptions in the region 1615–1680 cm^{-1}, which are characteristic of the C=O stretching modes of monodentate *C*-bonded acac ligands.[13] Further evidence for this bonding mode comes from the absence of absorptions in the 1600–1500 cm^{-1} region which are characteristic of bidentate *O,O′*-bonded acac ligands. The ^{1}H NMR spectra of the complexes are reported in Table 3, and confirm both the presence of a cyclometallated thbipy ligand and single acac ligand per thbipy. The platinum complex shows satellite peaks about the resonances assigned to H$^{6′}$[^3J(Pt–H) 14 Hz], H$^{4″}$[^3J(Pt–H) 22 Hz] and H$^{5″}$[^4J(Pt–H) 11 Hz], once again confirming the co-ordination of the terminal pyridine ring and the *terdentate* mode for the ligand. The methyl groups of the acac are equivalent, and in the platinum complex both the methyl groups [^4J(Pt–H) 14 Hz] and the methine proton [^2J(Pt–H) 120 Hz] of the acac show satellites due to coupling to ^{195}Pt. The large coupling to the methine carbon is only compatible with a monodentate *C*-bonded mode.[13] Accordingly, these complexes may be confidently assigned the structures indicated in Scheme 1, which indicates the high stability of the terdentate *N,N′,C*-bonding mode for the thbipy$^-$ with the d^8 centres.

Upon heating a solution of [Pt(thbipy)Cl] in acetonitrile a brown solution is obtained, from which the complex [Pt(thbipy)(MeCN)][PF$_6$] may be isolated as a brown solid upon the addition of [NH$_4$][PF$_6$]. The ^{1}H NMR data for this compound are presented in Table 3; once again the presence of only nine resonances and the coupling of platinum to H$^{6′}$[^3J(Pt–H) 12 Hz] and H$^{4″}$[^3J(Pt–H) 17 Hz] confirm the presence of the terdentate *N,N′,C*-bonded cyclometallated ligand. The FAB mass spectrum of the complex exhibits a parent-ion peak at *m/z* 473 exhibiting the expected isotopic pattern. The palladium complex did not undergo an analogous reaction.

We were somewhat surprised at the facile formation of the cyclometallated complexes in these systems, particularly in view of our previous studies of 2-phenylpyridine reactions in which it was possible to isolate intermediate non-metallated compounds. Accordingly, we investigated the reaction of Hthbipy with K$_2$[PdCl$_4$] in aqueous acetonitrile at 10 °C in the hope of isolating intermediate non-metallated complexes. After stirring for 3 h at 10 °C an orange crystalline product had been precipitated. The FAB mass spectrum of this compound exhibits peaks at *m/z* 343 {[Pd(thbipy)]$^+$} and 379/381 {[Pd(thbipy)Cl]$^+$}. Elemental analysis suggested that this compound was the non-metallated intermediate species, [Pd(Hthbipy)Cl$_2$]. We suggest that this complex contains an *N,N′*-bonded non-metallated bidentate Hthbipy ligand which behaves simply as a substituted 2,2′-bipyridine. The infrared spectrum of the complex exhibits two M–Cl stretching modes at 347 and 329 cm^{-1} {*cf.* [Pd(bipy)Cl$_2$] 353 and 343 cm^{-1}}.[14] The ^{1}H NMR spectra of solutions of the complex in CD_3SOCD_3 or CD_2Cl_2 exhibit two separate sub-spectra, one of which is identical to that of [Pd(thbipy)Cl] in the same solvent. The second sub-spectrum is assumed to be that of [Pd(Hthbipy)Cl$_2$], and is reported as such in Table 3. The similarity between the chemical shifts of the terminal pyridine ring in [Pd(Hthbipy)Cl$_2$] (H$^{6′}$, δ 9.21; H$^{5′}$, δ 7.57; H$^{4′}$, δ 8.12; H$^{3′}$, δ 7.99) are very similar to those for [Pd(bipy)Cl$_2$] (H^6, δ 9.41; H^5, δ 7.65; H$^{4′}$, δ 8.15; H$^{3′}$, δ 8.05), providing further evidence for the presence of an *N,N′*-bonded bidentate Hthbipy ligand in this complex. Upon standing, solutions of [Pd(Hthbipy)Cl$_2$] are completely converted into [Pd(thbipy)Cl]. The non-metallated complex [Pd(Hthbipy)Cl$_2$] is converted quantitatively into [Pd(thbipy)Cl] upon warming to 40 °C in dmso, aqueous acetonitrile or CH$_2$Cl$_2$. No such non-metallated complex could be isolated from reactions with platinum(II) compounds under a wide variety of reaction conditions.

In view of the ready formation of cyclometallated d^8 palladium(II) and platinum(II) complexes we have also investigated the interactions of Hthbipy with gold(III). We have previously reported the reaction of Hthbipy with Na[AuCl$_4$] to yield the complex [Au(Hthbipy)Cl$_3$], which contains a bidentate *N,N′*-bonded ligand.[6a] In this same paper we also described the thermal conversion of [Au(Hthbipy)Cl$_3$] into [Au(thbipy)Cl$_2$], a compound to which we assigned a cyclometallated structure [Fig. 3(*a*)] analogous to those of the palladium(II) and platinum(II) complexes. We now describe our further studies on this complex and correct our earlier assignment of structure. In related studies we have demonstrated that Hthpy cyclometallates cleanly at the 3 position upon reaction with palladium(II) or platinum(II) centres, but only forms an *N*-bonded complex, [Au(Hthpy)Cl$_3$], upon reaction with Na[AuCl$_4$].[4] This compound undergoes further complex reactions under forcing conditions which include halogenation and C–C bond formation at the 5 position.[4]

The complex [Au(thbipy)Cl$_2$] is obtained in high yield (80–90%) as an orange microcrystalline solid by the direct reaction



Scheme 1 (*i*) $[MCl_4]^{2-}$, MeCN, H_2O, 60 °C (M = Pd or Pt); (*ii*) $[MCl_4]^{2-}$, MeCN, H_2O, 30 °C (M = Pd); (*iii*) $P(OMe)_3$ (M = Pd or Pt); (*iv*) MeCN (M = Pd or Pt); (*v*) warming; (*vi*) $Na[AuCl_4]$, MeCN, H_2O, 45 °C; (*vii*) MeCN, H_2O, 100 °C; (*viii*) MeCN, H_2O, 90 °C; (*ix*) Na[acac], MeOH

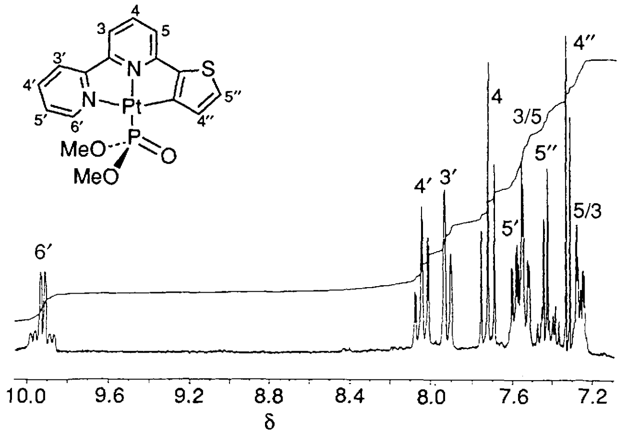


Fig. 2 Proton NMR spectrum of a CD_2Cl_2 solution of $[Pt(thbipy)\{P(=O)(OMe)_2\}]$

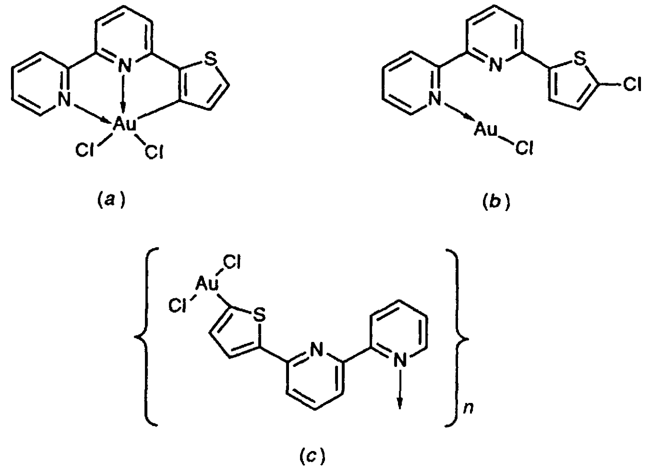


Fig. 3 Possible structures for the complex $[Au(thbipy)Cl_2]$: (*a*) cyclometallated, (*b*) a gold(I) complex of 6-(5-chloro-2-thienyl)-2,2′-bipyridine and (*c*) metallated at C^5

of Hthbipy with $Na[AuCl_4]$ in boiling aqueous acetonitrile or by heating $[Au(Hthbipy)Cl_3]$ in boiling aqueous acetonitrile. The latter compound is the product of the low-temperature reaction of $Na[AuCl_4]$ with Hthbipy. Elemental analysis is fully in accord with the formulation $[Au(thbipy)Cl_2]$, but the only peaks which could be assigned in the FAB or EI mass spectra were at *m*/*z* 272/274 ($[thbipy + Cl]^+$) and 238 ($[Hthbipy]^+$); no Au–Cl stretching modes could be detected in the infrared spectrum. The complex is insoluble in water and alcohols, sparingly soluble in chlorinated solvents and readily soluble in dmf or dmso.

The ^1H NMR and COSY spectra of a CD_3SOCD_3 solution of $[Au(thbipy)Cl_2]$ are shown in Fig. 4; it is evident that only nine proton environments are present, and that the thiophene ring gives rise to an AM doublet of doublets. It was this feature which initially led us to propose the cyclometallated formulation. However, there are a number of features in this spectrum which are not fully consistent with the proposed cyclometallated structure. The AM pattern assigned to the two protons of the metallated thiophene ring exhibit a coupling constant of 4.0 Hz. This is indicative of a coupling between $H^{3''}$ and $H^{4''}$ rather than $H^{4''}$ and $H^{5''}$ as expected for a cyclometallated complex. This is suggestive of a compound which has been substituted at $C^{5''}$ rather than $C^{3''}$. The ^1H NMR spectra of solutions of the complex are solvent dependent, and CD_2Cl_2 solutions exhibit rather different spectra (see Table 3). A number of interesting features emerge from a comparison of the ^1H NMR spectra of $[Au(Hthbipy)Cl_3]$ and $[Au(thbipy)Cl_2]$; if we consider the terminal pyridine ring of the ligand, the similarities in chemical shifts ($H^{6'}$, $\Delta\delta$ −0.02; $H^{5'}$, $\Delta\delta$ 0.05; $H^{4'}$ $\Delta\delta$ 0.08; $H^{3'}$, $\Delta\delta$ 0.05; $\Delta\delta = \delta[Au(Hthbipy)Cl_3] - \delta[Au-$

(thbipy)Cl_2]) are quite remarkable, indicating that in both cases this ring is co-ordinated to the gold(III) centre. However, these correlations are not found for the central pyridine ring, and chemical shift arguments suggest that the central rings are in rather different environments in the two complexes.

On the basis of these observations a number of possible structures may be suggested; the originally proposed structure [Fig. 3(*a*)] could be correct, and the coupling constant between $H^{5''}$ and $H^{4''}$ is abnormally low in the compound. In view of the 'normal' coupling constants in the palladium(II), platinum(II) and ruthenium(II) cyclometallates this did not appear to be likely. Alternative formulations which maintain the stoichiometry include a gold(I) complex of the derivatised ligand 6-(5-chloro-2-thienyl)-2,2′-bipyridine [Fig. 3(*b*)] or a complex which has been metallated at $C^{5''}$. In order to maintain the four-co-ordination about the gold it is necessary for a 5″-metallated complex to be oligomeric or polymeric [Fig. 3(*c*)].

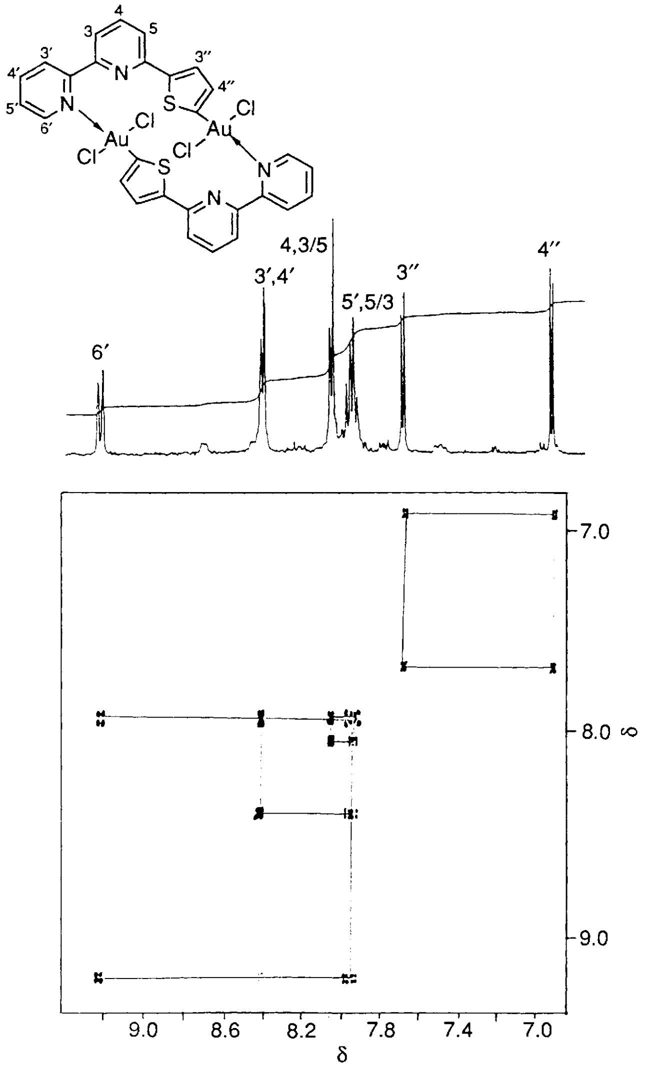


Fig. 4 Proton one-dimensional and COSY spectra of a CD_3SOCD_3 solution of [{Au(thbipy)Cl_2}$_2$]

We have performed a number of experiments to investigate these various possibilities. Reaction of [Au(thbipy)Cl_2] with hydrazine under aqueous conditions results in reduction and the deposition of gold metal as a mirror on the flask. Extraction of the aqueous suspension with dichloromethane yields a brown solid. The EI mass spectrum and the ^{1}NMR spectrum of this reveals it to be predominantly Hthbipy. This suggests that the formulation in Fig. 3(*b*) is unlikely to be correct, since hydrazine is not expected to reduce 6-(5-chloro-2-thienyl)-2,2′-bipyridine to Hthbipy under these mild conditions. This result is not conclusive, however, since the FAB mass spectrum of [Au(thbipy)Cl_2] exhibits a small but reproducible peak at *m*/*z* 272/274 assigned to 6-(5-chloro-2-thienyl)-2,2′-bipyridine!

The ^{1}H NMR spectra of solutions of [Au(thbipy)Cl_2] in CD_3SOCD_3 (but not in CD_2Cl_2) change with time. This appears to be associated with the formation of an, as yet, unidentified solvento species. However, two features of the spectrum of this solvento species are of note; first the AM system of the thiophene is retained and little shifted, and, secondly, the resonance due to $H^{6'}$ shifts upfield to δ 8.70, which is exactly the position observed for the free ligand. These two observations suggest that it is possible to displace the terminal ring from the metal at the same time as retaining an Au–C bond. In order to resolve these problems we have determined the crystal and molecular structure of the compound [Au(thbipy)Cl_2].

Very poor quality crystals of [Au(thbipy)Cl_2] were obtained by the diffusion of diethyl ether vapour into a solution of the complex in dimethylformamide. The crystal and molecular structure is presented in Fig. 5; the compound is dimeric, of stoichiometry [{Au(thbipy)Cl_2}$_2$], with two crystallographically non-equivalent gold centres. Each gold centre is four-co-ordinate in an approximately square-planar $CNCl_2$ environment. At each gold centre, the two bonded chlorine ligands are mutually *trans* with Cl–Au–Cl angles of 172.6(5) and 173.7(4)°. The gold–chlorine distances [2.255(13)–2.285(14) Å] are all in the typical range for gold(III)–chlorine bonds; an analysis of the 236 Au–Cl distances for four-co-ordinate gold(III) complexes in the Cambridge Crystallographic Data Base yielded bond distances in the range 2.235–2.666 Å, with a mean value of 2.281(42) Å.[15] The remaining co-ordination sites of the gold are occupied by mutually *trans* nitrogen and carbon donors from two different thbipy ligands. The carbon donor is provided by a thienyl ring metallated at the 5″ position, and the gold–carbon

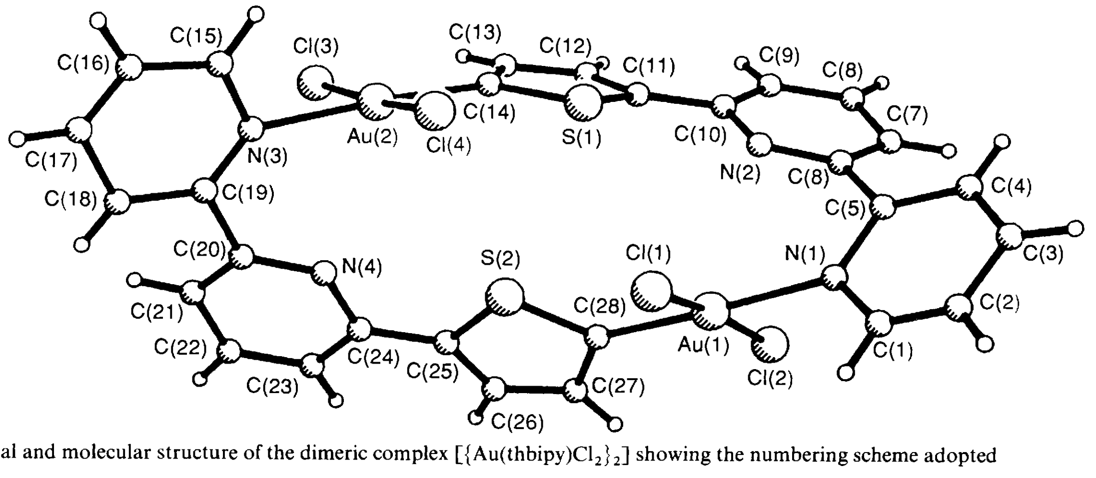


Fig. 5 Crystal and molecular structure of the dimeric complex [{Au(thbipy)Cl_2}$_2$] showing the numbering scheme adopted

bond distances Au(1)–C(28) 1.96(3) Å and Au(2)–C(14) 2.00(4) Å are unremarkable and typical of gold(III) organometallic compounds; an analysis of the 96 Au–C distances for four-co-ordinate gold(III)–aryl complexes in the Cambridge Crystallographic Data Base yielded bond distances in the range 1.871–2.733 Å, with a mean value of 2.07(12) Å.[15] The two gold centres are approximately square planar, with the greatest deviation of any atom from each of the square planes being 0.1 Å. The co-ordination sphere about each gold is completed by the nitrogen of the terminal pyridine ring of a second ligand. Each ligand acts as a bridging *C,N*-donor to two gold centres; the ligands are metallated but not *cyclo*metallated. The central pyridine ring of each ligand is non-co-ordinated. The dimeric structure is achieved by twisting about the internuclear C–C bonds between the pyridyl (33.4, 41.5°) and the pyridyl and thienyl rings (14.8, 4.4°).

The auration of the ligand at the 5 position of the thienyl ring is somewhat unexpected in view of the palladation and platination results discussed above, and of our previous results for ruthenation and rhodation,[5] although fully in accord with our recent studies with Hthpy which undergoes clean cyclopalladation and cycloplatination reactions at the 3′ position of the thienyl ring, but which gives products derived from reaction at the 5′ position upon reaction with gold(III).[4] The origins of these differences are not easily discerned. Simple arguments based upon size do not appear to be solely responsible as the covalent radii for gold, palladium and platinum are similar (1.5 Å), as are ionic radii for the four-co-ordinate metal ions [gold(III), 0.68; palladium(II), 0.64; platinum(II), 0.60 Å]. Similarly, charge effects cannot be solely responsible since we have previously shown that Hthbipy cyclometallates at the 3 position of the thienyl ring with rhodium(III). The observed reactivity patterns appear to reflect a subtle balance of charge and steric effects.

We are currently further investigating the metal-ion dependency of metallation reactions involving isoelectronic metal centres.

Acknowledgements

We thank the SERC for support, Johnson Matthey for the loan of precious metals and the Royal Society and the Isaac Newton Trust for grants towards the cost of spectrometers. We also thank Troy A. Leese for recording the ^{1}H NMR spectra.

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Received 20*th January* 1992; *Paper* 2/00307D