

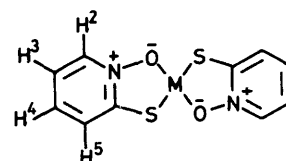
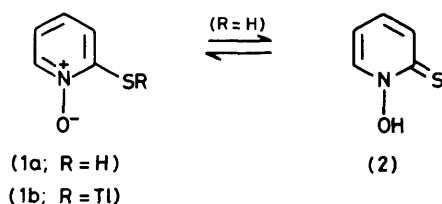
## Synthesis of 1-Oxidopyridinium-2-thiolato- and Pyridine-2-thiolato-complexes of Nickel, Palladium, and Platinum

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Quinoline *N*-oxide reacts with  $K[PtCl_3(CH_2=CH_2)]$  to give  $[PtCl_2(C_2H_4)(ONC_9H_7)]$  whereas 1-oxidopyridinium-2-thiol (1a) gives  $[Pt(SONC_5H_4)_2]$  (3a) and an insoluble oligomeric material containing at least four Pt atoms; complex (3a) and the oligomer can also be synthesised from  $K_2[PtCl_4]$ . The oligomeric material can be cleaved by  $PPh_3$  and  $PMe_2Ph$  to give  $[PtCl(SONC_5H_4)(PPh_3)]$  (5) and  $[PtCl(SONC_5H_4)(PMe_2Ph)_2]$  (6) respectively, and compound (3a) is converted by  $PPh_3$  into the monophosphine complex  $[Pt(SONC_5H_4)_2(PPh_3)]$  (7a). The complex (7a) and an analogue  $[Pd(SONC_5H_4)_2(PPh_3)]$  (7b) have been prepared from  $[MCl_2(PPh_3)_2]$  and the thallium salt of (1a), and related complexes  $[M(SC_5H_4N)_2(PPh_3)_2]$  [ $M = Pt$  (8a) or  $Pd$  (8b)] have been similarly synthesised from the thallium salt of 2-mercaptopyridine. Evidence for intramolecular scrambling in (7) and (8) has been adduced from variable temperature  $^1H$  n.m.r. spectra.

A variety of metallic complexes of pyridine *N*-oxides have been described<sup>1</sup> but particular attention has been focused on metal-containing compounds of the tautomeric ligand, 1-oxidopyridinium-2-thiol [(1a)  $\rightleftharpoons$  (2)] because of their useful



(3a; M = Pt)  
(3b; M = Mn)  
(3c; M = Ni)  
(3d; M = Cu)

biological activity (see for example, the use of  $Sn^{4+}$ ,<sup>2</sup>  $Al^{3+}$  and  $Zn^{2+}$ -containing compounds as antifungal<sup>2</sup> and antibacterial<sup>3,4</sup> agents). We recently described<sup>5</sup> the powerful ligating properties of 1-oxidopyridinium-2-thiol in its reaction with  $[WCl(CF_3C_2CF_3)_2(\eta-C_3H_5)]$  and now report further reactions of this, and the related pyridine-2-thiolato-ligand, in the Ni, Pd, and Pt series.

### Results and Discussion

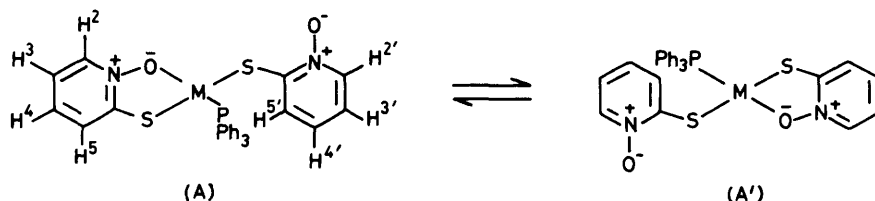
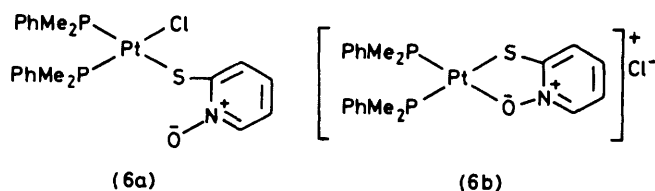
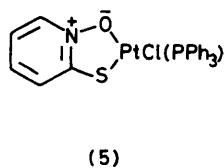
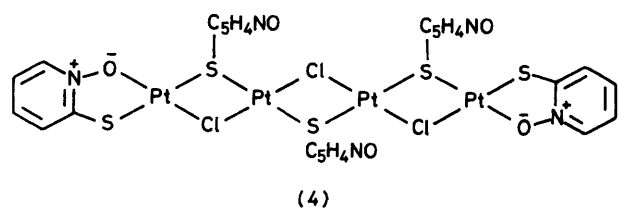
Pyridine *N*-oxide has been shown to react with Zeise's salt,  $K[PtCl_3(C_2H_4)]$ , to give the complex  $[PtCl_2(C_2H_4)L]$  ( $L = ONC_5H_5$ )<sup>6</sup> and we have now demonstrated that quinoline *N*-oxide behaves in similar fashion to give a related complex ( $L = ONC_9H_7$ ) in 54% yield. In contrast to this behaviour, the tautomeric 1-oxidopyridinium-2-thiol [(1a)  $\rightleftharpoons$  (2)]<sup>7</sup> reacts with Zeise's salt in acetone at room temperature to give an orange soluble compound in poor yield and a yellow insoluble material. Analytical data, including 'direct' measurement of oxygen content, for the soluble material provide an empirical formula of  $C_{10}H_8N_2O_2PtS_2$ . From spectral analyses we suggest structure (3a)<sup>†</sup> for this compound although we cannot exclude the alternative *cis* form. The N-O stretching frequency occurs as a single band at  $1095\text{ cm}^{-1}$  [cf.  $1083$  and  $1115\text{ cm}^{-1}$  in the free ligand<sup>8,9</sup> and single bands in the region  $1075$ — $1085\text{ cm}^{-1}$  in analogues (3b)—(3d)<sup>9</sup> of (3a)]. The  $^1H$  n.m.r.

parameters of (3a) are very close to those of the heteroaromatic component of the free ligand. ‡ In subsequent reactions of 1-oxidopyridinium-2-thiol with dipotassium tetrachloroplatinate it was shown that the complex (3a) was obtained using acetone as solvent, whereas the yellow insoluble material was again formed in water. Samples of the latter obtained from different sources (*i.e.* from Zeise's salt or  $K_2[PtCl_4]$ ) gave differing results for elemental analysis (C, 19.10—21.05; H, 1.35—1.70; Cl, 9.10—13.50%). Since this material is very insoluble, has a high melting point ( $>350^\circ\text{C}$ ), and has an i.r. spectrum which is almost identical to the complex (3a), we assume that it is oligomeric and contains bridging 1-oxidopyridinium-2-thiolato-ligands; from analytical data, it seems likely that the number of platinum atoms would be  $>4$  [cf. (4)]. The nature of bonding in the bridging ligand is unclear since we are unable to distinguish between a simple sulphur bridge and a situation where the  $SONC_5H_4$  acts as a bidentate bridging ligand (*cf.* unusual bidentate bridge-bonding in the quinoline-8-oxo-complex  $[PtMe_2(ONC_9H_6)_2]$ ).<sup>10</sup>

The oligomeric nature of (4) was demonstrated by allowing it to react with phosphine derivatives. It was converted by triphenylphosphine in low yield into a product believed to be (5), of undefined stereochemistry. The infrared spectrum of complex (5) was very similar to that of (3a) and the  $^1H$  n.m.r. low- ( $\delta$  8.31) and high-field ( $\delta$  6.87) resonances were also comparable (*cf.* 8.24, 6.85). The  $^{31}P$  and  $^{195}Pt$  n.m.r. spectra indicated the presence of one nuclear environment with a  $^{31}P$ — $^{195}Pt$  coupling constant (*ca.* 3870 Hz) in accord with a

<sup>†</sup> For recent studies of the chromatographic separation of 1-oxidopyridinium-2-thiol complexes of Group 8 metals, see K.-H. König, B. Steinbrach, G. Schneeweis, P. Chaudhuri, and H.-U. Ehancke, *Fresenius Z. Anal. Chem.*, 1979, **297**, 411.

<sup>‡</sup> For a detailed study of the  $^1H$  n.m.r. spectra of pyridine *N*-oxide derivatives, see R. A. Abramovitch and J. B. David, *J. Chem. Soc. B*, 1966, 1137.



(7a; M = Pt)  
 (7b; M = Pd)  
 (7c; M = Ni)

square planar  $\text{Pt}^{\text{II}}$  molecule.<sup>11</sup> In contrast to this behaviour, the oligomer (4) was transformed by dimethylphenylphosphine into a bis-phosphine complex  $[\text{PtCl}(\text{SONC}_5\text{H}_4)(\text{PMe}_2\text{Ph})_2]$  (6). It seems probable that the different stoichiometries of the products (5) and (6) isolated from the reactions of complex (4) with  $\text{PPh}_3$  and  $\text{PMe}_2\text{Ph}$  reflect the large excess of phosphine employed in the latter case. The  $^{31}\text{P}$  n.m.r. spectrum of (6) indicates two phosphorus magnetic environments with  $J(^{31}\text{P}-^{195}\text{Pt})$  values (3 002 and 3 415 Hz) in accord with a *cis* square planar  $\text{Pt}^{\text{II}}$  structure.<sup>11</sup> Accordingly two doublets are observed in the  $^{195}\text{Pt}$  n.m.r. spectrum. Two structures are possible on this basis (6a) and the ionic form (6b), which exhibits a  $\nu(\text{Pt}-\text{Cl})$  mode at  $320\text{ cm}^{-1}$  no such band is present in the i.r. spectrum of (6) which argues in favour of (6b). Related 1,1-dithiolato-complexes  $[\text{M}(\text{PR}^1)_2(\text{S}_2\text{PR}^2)_2]^+\text{X}^-$  (e.g.  $\text{R}^1 = \text{Ph}$ ,  $\text{R}^2 = \text{OEt}$ ) have been reported previously<sup>12</sup> and in one particular case the complex  $[\text{Pd}(\text{PET}_3)_2(\text{S}_2\text{PPh}_2)]$ - $[\text{S}_2\text{PPh}_2]$  was structurally characterised by X-ray diffraction methods. We favour such a structure for complex (6) but the small quantities of complex available precluded accurate conductivity measurements, to confirm the ionic nature of the species.

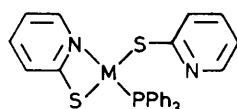
In an attempt to extend the range of available mixed phosphine-*N*-oxide complexes, compound (3a) was treated with triphenylphosphine in warm acetone. From analytical data, and from integral values in 360 MHz  $^1\text{H}$  n.m.r. spectra of the product, a stoichiometry of  $[\text{Pt}(\text{SONC}_5\text{H}_4)_2(\text{PPh}_3)]$

was apparent. The  $^{31}\text{P}$  and  $^{195}\text{Pt}$  n.m.r. spectra are unexceptional indicating one phosphorus [ $\delta$  6.30, t,  $J(^{31}\text{P}-^{195}\text{Pt})$  ca. 3 926 Hz] and one platinum [ $\delta$  -1 964, d,  $J(^{195}\text{Pt}-^{31}\text{P})$  ca. 3 295 Hz] environments. We assign structure (7a) to this complex and present evidence for the fluxional process (A)  $\rightleftharpoons$  (A') from high resolution  $^1\text{H}$  n.m.r. spectral data. Four pairs of heterocyclic ligand resonances are observed in the 360 MHz  $^1\text{H}$  n.m.r. spectrum of complex (7a) at 220 K. By analogy with literature data,\* the following tentative assignments can be made:  $\delta$  8.25 and 7.98 ( $\text{H}^2$  and  $\text{H}^{2'}$ ), 8.06 and 7.57 ( $\text{H}^5$  and  $\text{H}^{5'}$ ), 7.31 and 6.65 ( $\text{H}^3$  or  $4$  and  $\text{H}^{3'}$  or  $4'$ ), and 6.92 and 6.62 ( $\text{H}^3$  or  $4$  and  $\text{H}^{3'}$  or  $4'$ ). At higher temperatures the doublet  $\text{H}^2$  and  $\text{H}^{2'}$  resonances coalesce to a doublet and the  $\text{H}^5$  and  $\text{H}^{5'}$  doublets coalesce to a broad singlet; a similar effect is apparent in the triplet  $\text{H}^3$  or  $4$  and  $\text{H}^{3'}$  or  $4'$  resonances. These data provide evidence for a rapid intramolecular scrambling involving interconversion of unidentate and bidentate heterocyclic ligands *i.e.* (A)  $\rightleftharpoons$  (A'). The alternative explanation for this behaviour is the existence of a five-coordinate structure for (7a) containing two inequivalent bidentate pyridine-2-thiolato-ligands which undergoes a rapid intramolecular rearrangement without metal-oxygen bond cleavage. The latter interpretation seems less probable in view of the fact that related  $\text{Pd}^{\text{II}}$  and  $\text{Pt}^{\text{II}}$  dithiolato-complexes  $[\text{M}(\text{S}-\text{S})_2\text{L}]$  ( $\text{S}-\text{S} = \text{S}_2\text{PR}_2$ ,  $\text{S}_2\text{CNR}_2$ , or  $\text{S}_2\text{COR}$ ;  $\text{L} =$  tertiary phosphine,  $\text{R} =$  alkyl or aryl) consistently exhibit four-coordinate

square planar geometries with one chelating and one terminal dithiolate ligand.<sup>12b,13</sup> Moreover  $^{77}\text{Se}$  n.m.r. studies of  $[\text{Pt}(\text{Se}_2\text{CNBu}'_2)_2(\text{PR}_3)]$  ( $\text{R} = \text{Et}$  or  $\text{Ph}$ ) provide evidence for a four-coordinate molecule in which the chelating and terminal  $\text{Se}_2\text{CNBu}'_2$  ligands undergo exchange *via* a five-coordinate intermediate.<sup>13</sup>

In an attempt to prepare the analogues (7b) and (7c) of complex (7a) an alternative synthesis was devised: thus  $[\text{PtCl}_2(\text{PPh}_3)_2]$  and the thallium salt (1b) gave the desired (7a) in moderate yield (52%) and this procedure was elaborated to provide the palladium analogue (7b) in 69% yield. It did not prove possible to synthesise the nickel compound (7c) by this route since  $[\text{NiBr}_2(\text{PPh}_3)_2]$  and  $\text{Tl}(\text{SC}_5\text{H}_4\text{NO})$  gave only the known complex (3c) in moderate yield (45%). The spectroscopic features of (7b) are very similar to those of (7a) except that four resonances due to the  $\text{SC}_5\text{H}_4\text{NO}$  ligands are observed in the  $^1\text{H}$  n.m.r. spectra down to 217 K where slight broadening is observed. This again suggests rapid exchange between the chelating and terminal  $\text{SC}_5\text{H}_4\text{NO}$  ligands but in this case with a significantly lower energy barrier for the process. This difference has been observed previously in intramolecular exchange processes involving platinum and palladium complexes<sup>14</sup> and is not unexpected in view of the greater lability generally associated with the latter metal.

\* See footnote on p. 783.



(9a; M = Pt)

(9b; M = Pd)

In an effort to prepare deoxy analogues of (7a) and (7b), the complexes  $[MCl_2(PPh_3)_2]$  (M = Pt or Pd) were separately treated with the thallium(I) salt, thallium pyridine-2-thiolate to give complexes of stoichiometry  $[M(SC_5H_4N)_2(PPh_3)_2]$  [M = Pt (8a), Pd (8b)]. Interestingly the  $^{31}P$  n.m.r. spectrum contains two phosphine resonances (integrated ratio 1 : 1) one of which has a chemical shift identical to that of the free phosphine and in the case of (8a) does not exhibit platinum satellites. Apparently complete phosphine dissociation occurs in solution to generate free  $PPh_3$  and (9a) and (9b), the deoxy analogues of (7a) and (7b). This is further supported by the presence of a doublet in the  $^{195}Pt$  n.m.r. spectrum of (8a),  $J(Pt-P) = 3872$  Hz. Variable temperature  $^1H$  n.m.r. spectra again suggest fluxional behaviour but in both cases the spectra were insufficiently resolved (even at 360 MHz) clearly to identify the separate resonances undergoing coalescence. Presumably a process related to that involving (7a) and (7b) is involved.

### Experimental

Unless otherwise stated i.r. spectra were recorded as  $CHCl_3$  solutions on a Perkin-Elmer 580 spectrophotometer. N.m.r. spectra were recorded in  $CDCl_3$  (unless stated otherwise) on JOEL MH 100, Bruker WP 200 SY, or Bruker WH 360 spectrometers;  $^1H$  (200 or 360 MHz),  $^{31}P$  (81 MHz), and  $^{195}Pt$  (43 MHz) chemical shifts are measured (293 K) relative to  $SiMe_4$ ,  $H_3PO_4$ , and  $K_2[PtCl_4]$  respectively. Melting points are uncorrected. Solvents were refluxed over sodium (tetrahydrofuran) or calcium hydride ( $CH_2Cl_2$ ,  $Et_2O$ , and hexane) and distilled under nitrogen prior to use. Acetone was dried over molecular sieves.

**Reaction of Zeise's Salt with Quinoline N-Oxide; Preparation of  $[PtCl_2(CH_2=CH_2)(ONC_9H_7)]$ .**—To a stirred solution of Zeise's salt (0.50 g, 1.36 mmol) in water (20  $cm^3$ ) was added quinoline N-oxide (0.59 g, 4.07 mmol) at room temperature. The yellow-green precipitate was filtered off and recrystallised from chloroform-ethanol to give the pure title compound (0.32 g, 54%), m.p. 158–160 °C (Found: C, 30.05; H, 2.55; Cl, 16.30.  $C_{11}H_{11}Cl_2NOPt$  requires C, 30.10; H, 2.50; Cl, 16.15%).

**Preparation of the Thallium Salt of 1-Oxido-pyridinium-2-thiol, (1b).**—The title salt precipitated quantitatively when 1-oxido-pyridinium-2-thiol (1 mol equivalent) in the minimum amount of methanol or methanol-water was treated dropwise with thallium(I) acetate (1 mol equivalent) in methanol or methanol-water. The precipitate was washed ( $H_2O$  then MeOH) and dried to give the yellow salt (1b), m.p. 167–168 °C (Found: C, 18.40; H, 1.30; N, 4.35.  $C_5H_4NOSTl$  requires C, 18.20; H, 1.20; N, 4.25%). I.r.  $\nu_{max}$ . (KBr): 1580, 1530, 1450, 1405, 1260, 1180, 1125, 1075, 825, 750, and 695  $cm^{-1}$ .

**Reaction of 1-Oxidopyridinium-2-thiol with  $K_2[PtCl_4]$  in Acetone; Preparation of Bis(1-oxidopyridinium-2-thiolato)platinum(II) (3a).**—Dipotassium tetrachloroplatinate (0.55 g, 1.3 mmol) and 1-oxidopyridinium-2-thiol (0.305 g, 2.4 mmol)

were heated under reflux in acetone (25  $cm^3$ ) for 1 h. The product was filtered off and diethyl ether (20  $cm^3$ ) was added to the filtrate to precipitate orange (3a) (0.15 g, 27%), m.p. 248–250 °C (from  $CHCl_3$ ) (Found: C, 27.20; H, 1.75; N, 6.30; O (direct procedure), 6.40.  $C_{10}H_8N_2O_2PtS_2$  requires C, 26.85; H, 1.80; N, 6.25; O, 7.15%). I.r.  $\nu_{max}$ : 3010, 1610, 1550, 1465, 1425, 1260, 1180, 1145, 1095, 1040, 910, and 825  $cm^{-1}$ . N.m.r.:  $^1H$   $\delta$  8.24 (double multiplet,  $J$  ca. 8,  $H^2$ ), 7.54 (double multiplet,  $J$  ca. 8,  $H^5$ ), 7.24 (triple multiplet,  $J$  ca. 8,  $H^3$  or  $H^4$ ), 6.85 p.p.m. (t of d,  $J$  ca. 8 Hz,  $H^3$  or  $H^4$ );  $^{195}Pt$   $\delta$  -1039 p.p.m.

**Reaction of 1-Oxidopyridinium-2-thiol with  $K_2[PtCl_4]$  in Water; Preparation of the Oligomer (4).**—Dipotassium tetrachloroplatinate (0.76 g, 1.8 mmol), 1-oxidopyridinium-2-thiol (0.68 g, 5.4 mmol), and water (25  $cm^3$ ) were stirred at room temperature for 1 h. The precipitate was washed with acetone (20  $cm^3$ ) and then diethyl ether (20  $cm^3$ ). Evaporation of the filtrate gave orange bis(1-oxidopyridinium-2-thiolato)platinum(II) (3a) (0.15 g) which was spectroscopically (i.r. and n.m.r.) identical with the sample prepared previously. The insoluble material was washed successively with chloroform, acetone, and water to give a yellow-brown insoluble oligomeric material (4) (0.25 g), m.p. ca. 350 °C (decomp.). Samples from different preparative runs gave different analytical data (ranges given are data acquired from four samples unless otherwise stated) (Found: C, 19.10–21.05; H, 1.35–1.70; Cl, 9.10–13.50; N, 4.05–4.35; O (one sample, direct method) 5.65; S (one sample), 9.75.  $C_{25}H_{20}Cl_3N_5O_5Pt_4S_5$  requires C, 22.3; H, 1.50; Cl, 4.40; N, 5.20; O, 5.25; S, 11.90%). I.r.  $\nu_{max}$ . (Nujol mull): 1610, 1560, 1430, 1280, 1260, 1180, 1150, 1100, 1050, 835, 770, and 720  $cm^{-1}$ .

**Reaction of Zeise's Salt with 1-Oxidopyridinium-2-thiol.**—1-Oxidopyridinium-2-thiol (0.35 g, 2.76 mmol) was added to a stirred solution of Zeise's salt (0.50 g, 1.36 mmol) in acetone (20  $cm^3$ ) at room temperature. A yellow-brown precipitate was washed with hot chloroform to give a sample of the oligomeric material (4) (0.21 g) described above. The initial filtrate was evaporated to leave bis(1-oxidopyridinium-2-thiolato)platinum(II) (0.04 g), m.p. 248–250 °C (from  $CHCl_3$ ).

**Reaction of Oligomeric Material (4) with Triphenylphosphine; Preparation of Chloro(1-oxidopyridinium-2-thiolato)(triphenylphosphine)platinum(II) (5).**—The oligomer (4) (0.15 g) and triphenylphosphine (0.16 g) were heated under reflux in ethanol (30  $cm^3$ ) for 10 min. The solution was evaporated to low volume to precipitate a yellow product, recrystallisation of which from benzene-ethanol gave yellow microcrystalline (5) (0.05 g), m.p. 239–240 °C (Found: C, 44.65; H, 3.10; Cl, 6.20.  $C_{23}H_{19}ClNOPPtS$  requires C, 44.60; H, 3.05; Cl, 5.75%). I.r.  $\nu_{max}$ : 3020, 1610, 1552, 1485, 1465, 1440, 1255, 1180, 1145, and 1100  $cm^{-1}$ . N.m.r.:  $^1H$   $\delta$  8.31 (d,  $J$  7), 7.75 (m), 7.42 (m), 7.20 (m), 6.87 p.p.m. (t of d,  $J$  1.6 and 7 Hz);  $^{31}P$ - $\{^1H\}$   $\delta$  4.25 p.p.m. [ $J(^{31}P-^{195}Pt)$  3884 Hz];  $^{195}Pt$   $\delta$  -2253 p.p.m. [d,  $J(^{31}P-^{195}Pt)$  3866 Hz].

**Reaction of (4) with Dimethylphenylphosphine; Preparation of Chlorobis(dimethylphenylphosphine)(1-oxidopyridinium-2-thiolato)platinum(II) (6).**—The oligomer (4) (0.125 g) and dimethylphenylphosphine (0.5 g) in acetone (30  $cm^3$ ) were stirred at room temperature for 1 h. The solvent and excess dimethylphenylphosphine were evaporated to leave an impure white material, recrystallisation of which from acetone-diethyl ether gave white microcrystalline (6) (0.08 g), m.p. 127–129 °C (Found: C, 39.90; H, 4.10; Cl, 5.55; S, 5.10.  $C_{20}H_{26}ClNOP_2PtS$  requires C, 38.70; H, 4.20; Cl, 5.70; S, 5.15%). I.r.  $\nu_{max}$ : 3020, 2940, 1605, 1555, 1490, 1465,

1 440, 1 420, 1 310, 1 295, 1 255, 1 210, 1 185, 1 150, 1 115, 1 095, 950, 915—930, 850, and 830  $\text{cm}^{-1}$ . N.m.r.:  $^1\text{H}$   $\delta$  8.52 (d, 1 H, *J* 7), 7.78 (d, 1 H, *J* 8), 7.45 (m, 12 H, aryl H), 1.88 [d, 6 H, *J*(P—H) 11.3], 1.79 p.p.m. [d, 6 H, *J*(P—H) 11.2 Hz];  $^{31}\text{P}$ -{ $^1\text{H}$ }  $\delta$  6.78 [*J*( $^{31}\text{P}$ — $^{31}\text{P}$ ) 26, *J*( $^{31}\text{P}$ — $^{195}\text{Pt}$ ) 3 002], —24.83 p.p.m. [*J*( $^{31}\text{P}$ — $^{31}\text{P}$ ) 26, *J*( $^{31}\text{P}$ — $^{195}\text{Pt}$ ) 3 415 Hz].

**Preparation of Bis(1-oxidopyridinium-2-thiolato)(triphenylphosphine)platinum(II) (7a).**—(a) From (3a) and triphenylphosphine. Complex (3a) (0.14 g, 0.31 mmol) and triphenylphosphine (0.16 g, 0.62 mmol) were warmed in acetone (20  $\text{cm}^3$ ) until all the triphenylphosphine had dissolved. The solution was evaporated to low volume and the yellow precipitate was separated and recrystallised ( $\text{CHCl}_3$ —EtOH) to give pure (7a) (0.05 g, 23%), m.p. 245—247 °C (Found: C, 47.80; H, 3.40; S, 8.85.  $\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}_2\text{P}_2\text{PtS}_2$  requires C, 47.40; H, 3.25; S, 9.05%). I.r.  $\nu_{\text{max}}$ : 2 970, 1 605, 1 590, 1 551, 1 485, 1 452, 1 440, 1 420, 1 262, 1 250, 1 180, 1 140, 1 100, and 1 092  $\text{cm}^{-1}$ . N.m.r. (360 MHz, 220 K):  $^1\text{H}$   $\delta$  8.25 (d, 1 H,  $\text{H}^2$ ) 8.06 (d, 1 H,  $\text{H}^5$ ), 7.98 (d, 1 H,  $\text{H}^{2'}$ ), 7.63 (m, 6 H,  $\text{PPh}_3$ ), 7.57 (d, 1 H,  $\text{H}^5$ ), 7.35 (m, 9 H,  $\text{PPh}_3$ ), 7.31 (d, 1 H,  $\text{H}^3$  or  $\text{H}^4$ ), 6.92 (t, 1 H,  $\text{H}^3$  or  $^4$ ), 6.65 (t, 1 H,  $\text{H}^{3'}$  or  $^4$ ), 6.62 (t, 1 H,  $\text{H}^{3'}$  or  $^4$ ). N.m.r. (360 MHz, 298 K):  $^1\text{H}$   $\delta$  8.07 (d, 2 H,  $\text{H}^{2,2'}$ ), 7.82 (br, 2 H,  $\text{H}^{5,5'}$ ), 7.68 (m, 6 H,  $\text{PPh}_3$ ), 7.35 (m, 9 H,  $\text{PPh}_3$ ), 6.93 (br, 2 H,  $\text{H}^{3,3'}$  or  $^4,^4$ ), 6.73 p.p.m. (t, 2 H,  $\text{H}^{3,3'}$  or  $^4,^4$ ). N.m.r.:  $^{31}\text{P}$ -{ $^1\text{H}$ }  $\delta$  6.30 p.p.m. [*J*( $^{13}\text{P}$ — $^{195}\text{Pt}$ ) 3 926 Hz];  $^{195}\text{Pt}$   $\delta$  —1 964 p.p.m. [*J*( $^{195}\text{Pt}$ — $^{31}\text{P}$ ) 3 925 Hz].

(b) From dichlorobis(triphenylphosphine)platinum(II) and the thallium salt (1b). Dichlorobis(triphenylphosphine)platinum(II) (0.50 g, 0.63 mmol) and the thallium salt (1b) (0.42 g, 1.26 mmol) were heated under reflux in chloroform (30  $\text{cm}^3$ ) for 1.5 h. Addition of diethyl ether to the cooled solution gave a precipitate of yellow bis(1-oxidopyridinium-2-thiolato)(triphenylphosphine)platinum(II) (0.23 g, 52%), m.p. 233—236 °C (from  $\text{CHCl}_3$ —Et $_2\text{O}$ ). This material was spectroscopically (i.r.,  $^1\text{H}$  n.m.r.) identical with that described in (a) above.

**Preparation of Bis(1-oxidopyridinium-2-thiolato)(triphenylphosphine)palladium(II) (7b).**—Dichlorobis(triphenylphosphine)palladium(II) (0.3 g, 0.43 mmol) and the thallium salt (1b) (0.33 g, 1.0 mmol) were stirred in tetrahydrofuran (thf) (40  $\text{cm}^3$ ) at 20 °C for 6 h under nitrogen. Volatiles were evaporated under reduced pressure and the residue extracted with dichloromethane and filtered. Addition of hexane and cooling gave orange-red crystalline (7b) (0.18 g, 69%), m.p. 163—165 °C (darkens at 158 °C) (Found: C, 53.95; H, 4.15; N, 4.80.  $\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}_2\text{PdS}_2$  requires C, 54.15; H, 3.70; N, 4.50%). I.r.  $\nu_{\text{max}}$ : 3 000, 1 605, 1 590, 1 551, 1 485, 1 455, 1 440, 1 420, 1 268, 1 247, 1 187, 1 167, 1 140, 1 100, and 1 095  $\text{cm}^{-1}$ . N.m.r.  $^1\text{H}$   $\delta$  6.75 (t of d, 2 H, *J* 2 and 7), 6.90 (t of d, 2 H, *J* 2 and 7), 7.37 (m, 9 H,  $\text{PPh}_3$ ), 7.63 (dd, 2 H, *J* 2 and 7), 7.70 (m, 6 H,  $\text{PPh}_3$ ), 8.00 p.p.m. (d, 2 H, *J* 7 Hz);  $^{31}\text{P}$ -{ $^1\text{H}$ }  $\delta$  33.46 p.p.m.

**Preparation of Bis(pyridine-2-thiolato)bis(triphenylphosphine)platinum(II) (8a).**—Dichlorobis(triphenylphosphine)platinum(II) (0.4 g, 0.5 mmol) and thallium pyridine-2-thiolate (0.35 g, 1.1 mmol) were stirred under nitrogen in thf (40  $\text{cm}^3$ ) for 15 h. Volatiles were evaporated under reduced pressure and the residue was extracted with dichloromethane and filtered. Addition of diethyl ether and cooling gave yellow (8a) (0.28 g, 66%), m.p. ca. 235 °C (Found: C, 59.15; H, 4.20; N, 3.00; S, 7.20.  $\text{C}_{46}\text{H}_{38}\text{N}_2\text{P}_2\text{PtS}_2$  requires C, 58.80; H, 4.05; N, 3.00; S, 6.80%). I.r.  $\nu_{\text{max}}$ : 3 025, 2 980, 1 585, 1 575, 1 482, 1 450, 1 447, 1 430, 1 410, 1 260, 1 120, and 1 100  $\text{cm}^{-1}$ . N.m.r. ( $\text{CD}_2\text{Cl}_2$ ):  $^1\text{H}$   $\delta$  6.73(br), 7.33(br), 7.64(br), 8.10 p.p.m. (br);

$^{31}\text{P}$ -{ $^1\text{H}$ }  $\delta$  7.96 [*J*( $^{31}\text{P}$ — $^{195}\text{Pt}$ ) 3 882 Hz], —4.28 p.p.m. (free  $\text{PPh}_3$ );  $^{195}\text{Pt}$   $\delta$  —2 413 p.p.m. [*J*( $^{195}\text{Pt}$ — $^{31}\text{P}$ ) 3 872 Hz].

**Preparation of Bis(pyridine-2-thiolato)bis(triphenylphosphine)palladium(II) (8b).**—Dichlorobis(triphenylphosphine)palladium(II) (0.3 g, 0.43 mmol) and thallium pyridine-2-thiolate (0.3 g, 0.95 mmol) were stirred under nitrogen in thf (40  $\text{cm}^3$ ) for 15 h. Volatiles were evaporated and the residue was extracted with dichloromethane and filtered. Addition of hexane and cooling gave orange (8b) (0.28 g, 76%), m.p. 185—186 °C (Found: C, 63.70; H, 4.45; N, 3.45; P, 7.20; S, 8.85.  $\text{C}_{46}\text{H}_{38}\text{N}_2\text{P}_2\text{PdS}_2$  requires C, 64.90; H, 4.45; N, 3.30; P, 7.30; S, 7.50%). I.r.  $\nu_{\text{max}}$ : 1 585, 1 575, 1 480, 1 450, 1 438, 1 430, 1 410, 1 320, 1 125, and 1 100  $\text{cm}^{-1}$ . N.m.r.:  $^1\text{H}$  aromatic multiplets at  $\delta$  7.77, 7.62, 7.25, and 6.56 p.p.m. (t of d);  $^{31}\text{P}$ -{ $^1\text{H}$ }  $\delta$  33.4 and —4.38 p.p.m. (free  $\text{PPh}_3$ ).

**Preparation of Bis(1-oxidopyridinium-2-thiolato)nickel(II) (3c).**—Dibromobis(triphenylphosphine)nickel(II) (0.2 g 0.27 mmol) and thallium pyridine-2-thiolate (0.2 g 0.6 mmol) were stirred under nitrogen in thf (40  $\text{cm}^3$ ) for 2 h. Volatiles were evaporated and the residue was extracted with dichloromethane and filtered. Addition of diethyl ether and cooling gave brown (3c) (38 mg, 45%), m.p. 258—260 °C (decomp.) [lit.,<sup>10</sup> 260 °C (decomp.)] (Found: C, 38.90; H, 2.70; N, 9.20.  $\text{C}_{10}\text{H}_8\text{N}_2\text{NiO}_2\text{S}_2$  requires C, 38.60; H, 2.25; N, 9.00%). I.r.  $\nu_{\text{max}}$ : 3 020, 1 605, 1 565, 1 465, 1 430, 1 250, 1 190, and 1 150  $\text{cm}^{-1}$ . N.m.r.:  $^1\text{H}$   $\delta$  8.01 (d of m, *J* 7), 7.36 (d of m, *J* 7), 7.11 (t of d, *J* 7 and 1), 6.79 p.p.m. (*J* 7 and 1 Hz).

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