Available online at www.sciencedirect.com
ScienceDirect
Polyhedron 26 (2007) 708–718
POLYHEDRON
www.elsevier.com/locate/poly

Synthesis and solid-state structural characterisation of Pt(II,IV) bromide complexes containing bidentate organothiomethylpyridine heteroleptic ligands

Roderick C. Jones [a], Brian W. Skelton [b], Vicki-Anne Tolhurst [a,*], Allan H. White [b], Adele J. Wilson [a], Allan J. Canty [a,*]

[a] School of Chemistry, University of Tasmania, Private Bag 75, Hobart, TAS 7001, Australia
[b] Chemistry M313, University of Western Australia, Crawley, WA 6009, Australia

Received 24 July 2006; accepted 1 September 2006
Available online 5 September 2006

Abstract

A convenient synthetic method for the preparation of organothiomethylpyridine ligands 2-($RSCH_2$)C_5H_4N (R = Ph ($\mathbf{L}^1$), Me ($\mathbf{L}^2$)), 2-MeS–6-Me-C_5H_3N ($\mathbf{L}^3$), and 2-MeS–4-Me-C_5H_3N ($\mathbf{L}^4$) via the initial lithiation of substituted 2-picolines followed by the nucleophilic reaction with a diorganyldisulfide is described. The complexes [$PtBr_2$L] (L = $\mathbf{L}^1$–$\mathbf{L}^4$) have been prepared in good to high yields as yellow solids with low solubility in organic solvents. The solid state structures of the complexes have been determined, showing the spatial arrangement of the complexes to depend significantly upon varying substituents within the ligand. The complexes undergo oxidation by bromine to form the tetravalent complexes [$PtBr_4$(L)] (L = $\mathbf{L}^1$–$\mathbf{L}^4$). The solid state structures of [$PtBr_4$($\mathbf{L}^2$)] and [$PtBr_4$($\mathbf{L}_4$)] have been determined, and shown to be monomeric with the ligand chelating the platinum centre.

Keywords: Platinum; Mixed donor ligands; Pyridine; Thioether; X-ray crystal structures

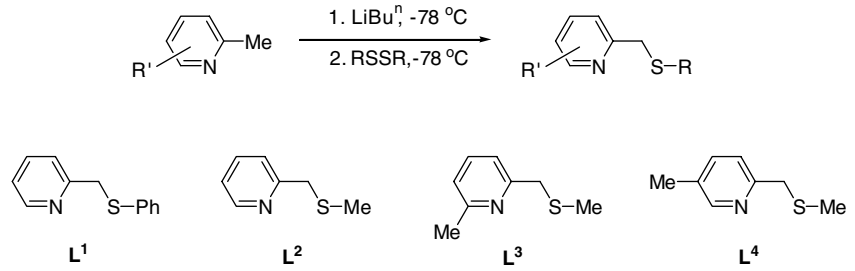
1. Introduction

The coordination chemistry of platinum(II) containing thio-, seleno- and telluroether ligands has been well established [1–3]. In contrast, reported platinum(IV) complexes containing N– and S– (or Se–) donor ligands are fewer [4–9]. Pyridylthioether ligands are a class of simple and fundamental heteroleptic ligands [10], and we have recently prepared a number of Pt(II) and Pd(II) chloride complexes, including Pd(II) complexes that facilitate Heck catalysis, containing the mixed donor ligands 2-($RECH_2$)C_5H_4N (RE = MeS, PhS, MeSe) and investigated their behaviour in solution using DFT calculations [11]. Comparison of the solid state structures of [MCl_2{2-($PhSCH_2$)C_5H_4N}] (M = Pd, Pt) and results from theoretical studies of solution processes indicate that the Pt–S bond is stronger than Pd–S, consistent with the softer Lewis acidity of platinum compared with palladium. Similar trends in bond distances in isomorphous structures of palladium and platinum complexes containing homoleptic and heteroleptic ligands have been observed and theoretical calculations have been performed [12–16].

There are several known methods for preparing thioether–pyridine heteroleptic ligand systems [17–25]. Reported methods of synthesis tend to be specific for the individual target molecule. However, an early report of the isolation of 2-($PhSCH_2$)-3-Me-C_5H_3N on reaction of 2,3-$Me_2C_5H_3N$ with $LiBu^n$ and PhSSPh [20] indicates the potential for development of a simple generic method. Herein, we describe the application of this method for the preparation of previously reported ligands $\mathbf{L}^1$–$\mathbf{L}^3$ [17,20,25] and the new ligand $\mathbf{L}^4$, that illustrates versatility

* Corresponding authors. Tel.: +61 3 6226 2162; fax: +61 3 6226 2858.
E-mail addresses: vicki-anne.gardiner@industry.gov.au (V.-A. Tolhurst), Allan.Canty@utas.edu.au (A.J. Canty).

0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.09.001



Scheme 1. Synthesis of substituted pyridyl thioether ligands, $\mathbf{L}^1$–$\mathbf{L}^4$.

in the range of substitution on the pyridyl ring and in the thioether group (Scheme 1). The synthesis and characterisation of Pt(II,IV) bromide complexes of ligands $\mathbf{L}^1$–$\mathbf{L}^4$ are described, allowing a systematic investigation into the effects of ligand, in particular the effect of adding a methyl group to the pyridyl ring in the 6-position, using single crystal X-ray diffraction studies.

2. Experimental

2.1. Materials and methods

All reactions were performed under argon gas using standard Schlenk techniques. Platinum(II) chloride was obtained as a loan from Johnson Matthey and was used without purification. All solvents were degassed prior to use. Infra-red spectra were recorded as KBr pressed discs on a Bruker IF55 Infra-red Spectrometer. Mass spectra of the complexes were recorded on a Kratos Analytical Concept ISQ mass spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Mercury Plus NMR spectrometer operating at 299.9 and 75.4 MHz in deuterated dimethylsulfoxide or deuterated chloroform and referenced to the residual resonances of the solvent (δ 2.33 and 7.25 ppm (^{1}H), respectively, 77.0 ppm (^{13}C{^{1}H} in $CDCl_3$)). Microanalyses (C, H, N, S) were determined by The Microanalysis Service, Central Science Laboratory, University of Tasmania.

2.2. Syntheses of ligands $\mathbf{L}^1$–$\mathbf{L}^4$

2.2.1. 2-(Phenylthiomethyl)pyridine ($\mathbf{L}^1$)

A solution of LiBu^n (6.00 mL of a 1.6 M hexane solution) was added dropwise to a stirred solution of 2-picoline (1.0 mL, 10.1 mmol) in Et_2O (25 mL) at −78 °C. The reaction was allowed to warm to ambient temperature, after which it was added dropwise to a stirred solution of diphenyl disulphide (2.36 g, 10.8 mmol) in THF (35 mL) at −78 °C. The solution was allowed to warm to room temperature and stirred for 12 h. Water was then added and the aqueous layer extracted with Et_2O (3 × 30 mL). The organic phase was dried (Na_2SO_4), and the solvent removed in a vacuum resulting in an oil. The product was purified by passing through a silica plug (5% Et_2O in petroleum spirit (b.p. 40–60 °C)) to give a yellow oil (0.96 g, 47%). *Anal.* Calc. for $C_{12}H_{11}NS$: C, 71.60; H, 5.51; N, 6.96; S, 15.93. Found: C, 71.86; H, 5.31; N, 6.85; S, 15.79%. ^{1}H NMR (299.9 MHz, $CDCl_3$, 25 °C) δ 8.54 (d, $^3J = 4.8$ Hz, 1H, H_6), 7.59 (“dt”, $^3J = 7.8$, 1.5 Hz, 1H, H_4), 7.32 (m, 2H, H_3,H_{2b}), 7.24 (t, $^3J = 7.2$ Hz, 1H, H_{2c}), 7.16 (m, 2H, H_5, H_{2d}), 4.27 (s, 2H, CH_2); ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, $CDCl_3$) δ 157.9 (C_2), 149.5 (C_6), 137.0 (C_4), 136.0 (C_{2a}), 129.9 (C_{2b}), 127.7 (C_{2c}), 126.6 (C_{2d}), 123.2 (C_3), 122.3 (C_5), 40.7 (CH_2). EI *m/z* 201 $[M]^+$, [$^{12}C_{12}$ $H_{11}$$^{14}N$$^{32}S_{201}$], 186 $[M - Me]^+$ [$^{12}C_{11}H_8$$^{14}N$$^{32}S_{186}$], 168 $[M - SH]^+$ [$^{12}C_{12}H_{10}$$^{14}N_{168}$], 92 $[M - SPh]^+$ [$^{12}C_6H_6$$^{14}N_{92}$].

2.2.2. 2-(Methylthiomethyl)pyridine ($\mathbf{L}^2$)

The procedure used was as for $\mathbf{L}^1$, except that after drying of the Et_2O extract and removal of solvent, to give a pale yellow oil (85%). The product was used without further purification. *Anal.* Calc. for C_7H_9NS: C, 60.39; H, 6.52; N, 10.06; S, 23.03. Found: C, 60.35; H, 6.35; N, 10.18; S, 22.92%. ^{1}H NMR (299.9 MHz, $CDCl_3$, 25 °C) δ 8.51 (d, $^3J = 4.2$ Hz, 1H, H_6), 7.66 (“dt”, $^3J = 7.8$, 1.8 Hz, 1H, H_4), 7.35 (d, $^3J = 7.8$ Hz, 1H, H_3), 7.16 (ddd, $^3J = 4.2$, 1.5, 0.9 Hz, 1H, H_5) 3.79 (s, 2H, CH_2), 2.04 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, $CDCl_3$) δ 158.7 (C_2), 149.2 (C_6), 137.2 (C_4), 123.4 (C_3), 122.2 (C_5), 40.1 (CH_2), 15.4 (CH_3). EI *m/z* 139 $[M]^+$, [$^{12}C_7$-$H_9$$^{14}N$$^{32}S_{139}$].

2.2.3. 2-(Methylthiomethyl)-6-methylpyridine ($\mathbf{L}^3$)

The procedure used was as for $\mathbf{L}^2$ using 2,6 lutidine (68%). The product was used without further purification. *Anal.* Calc. for $C_8H_{11}NS$: C, 62.70; H, 7.24; N, 9.14; S, 20.92. Found: C, 62.56; H, 7.38; N, 8.98; S, 20.61%. ^{1}H NMR (299.9 MHz, $CDCl_3$, 25 °C) δ: 7.53 (“t”, $^3J = 7.8$ Hz, 1H, H_4), 7.15 (d,$^3J = 7.8$, 1H, H_3), 7.01 (d, $^3J = 7.8$ Hz, 1H, H_5), 3.76 (s, 2H, CH_2), 2.53 (s, 3H, C_6–CH_3), 2.04 (s, 3H, S–CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, $CDCl_3$) δ 158.0 (C_6), 157.9 (C_2), 137.3 (C_4), 121.8 (C_5), 120.2 (C_3), 40.2 (CH_2), 24.6 (C_6–CH_3), 15.4 (S–CH_3). LSIMS (*m/z*) 152 $(M - H)^+$ [$^{12}C_8H_{11}$$^{14}N$$^{32}S_{152}$].

2.2.4. 2-(Methylthiomethyl)-4-methyl pyridine ($\mathbf{L}^4$)

The procedure used was as for $\mathbf{L}^2$ using 2,4-lutidine (87%). The product was used without further purification. *Anal.* Calc. for $C_8H_{11}NS$: C, 62.70; H, 7.24; N, 9.14; S,

20.92. Found: C, 62.75; H, 7.24; N, 9.26; S, 20.68%. ^{1}H NMR (299.9 MHz, $CDCl_3$, 25 °C) δ 8.36 (d, $^3J = 5.1$ Hz, 1H, H_6), 7.18 (s, 1H, H_3), 6.98 (d, $^3J = 4.8$ Hz, 1H, H_5), 3.75 (s, 2H, CH_2), 2.33 (s, 3H, C_4–CH_3), 2.04 (s, 3H, S–CH_3); ^{13}C{^{1}H} NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 158.5 (C_2), 149.0 (C_6), 148.3 (C_4), 124.1 (C_3), 123.2 (C_5), 40.1 (CH_2), 21.3 (C_4–CH_3), 15.4 (S–CH_3). LSIMS (*m*/*z*) 152 $(M - H)^+$ [$^{12}C_8H_{11}{}^{14}N^{32}S_{152}$].

2.3. Syntheses of complexes [$PtBr_2L$] ($L = \mathbf{L}^1$ (**1**), $\mathbf{L}^2$ (**2**), $\mathbf{L}^3$ (**3**), $\mathbf{L}^4$ (**4**))

Sodium bromide (0.827 mmol) and $PtCl_2$ (0.376 mmol) were refluxed in MeCN (30 mL) for 24 h. The light brown solution was filtered and the appropriate ligand (0.381 mmol) was added. The mixture was allowed to stir at room temperature (16 h). The MeCN volume was reduced in a vacuum (ca. 1 mL) and Et_2O added to afford an off-white precipitate. The solid was collected and washed with Et_2O, yielding the desired compound.

[$PtBr_2(\mathbf{L}^1)$] (**1**) (69%). *Anal.* Calc. for $C_{12}H_{11}Br_2NPtS$: C, 25.91; H, 1.99; N, 2.52. Found: C, 25.50; H, 1.83; N, 2.26%. ^{1}H NMR (299.9 MHz, DMSO-d_6, 25 °C) δ: 9.69 (m, 1H, C_5H_4N), 8.15 (m, 1H, C_5H_4N), 7.84 (m, 1H, C_5H_4N), 7.75 (m, 2H, C_6H_5), 7.44 (m, 3H, C_6H_5), 5.23, 4.84 (m, 2H, CH_2). IR (KBr, cm^{-1}): 3114(w), 3085(w), 3056(w), 2968(w), 2942(s), 1892(m), 1605(m), 1476(s), 1446(s), 1394(m), 1312(w), 1268(w), 1160(w), 1111(w), 1063(w), 1021(w), 966(w), 895(w), 756(vs), 685(m), 483(m), 438(w). LSIMS (*m*/*z*): 476 ([$^{195}Pt^{80}BrC_{11}H_{12}NS$]$^+$ 476).

[$PtBr_2(\mathbf{L}^2)$] (**2**) (87%). *Anal.* Calc. for $C_7H_9Br_2NPtS$: C, 17.02; H, 1.84; N, 2.84; S, 6.49. Found: C, 17.20; H, 2.00; N, 2.85; S, 6.07%. ^{1}H NMR (299.9 MHz, DMSO-d_6, 25 °C) δ: 9.59 (m, 1H, C_5H_4N), 8.18 (m, 1H, C_5H_4N), 7.87 (m, 1H, C_5H_4N), 7.55 (m, 1H, C_5H_4N), 4.80, 4.50 (m, 2H, CH_2), 2.47 (s, $J_{Pt-H} = 18$ Hz, 3H, CH_3). IR (KBr, cm^{-1}): 3080(w), 2992(w), 1955(s), 2898(s), 1610(s), 1474(s), 1447(m), 1423(m), 1395(m), 1318(m), 1271(m), 1166(s), 1111(w), 1062(w), 993(m), 974(m), 898(w), 862(w) 827(w), 770(vs), 709(w), 473(w), 434(w). LSIMS (*m*/*z*): 414 ([$^{195}Pt^{80}BrC_7H_9NS$]$^+$ 414).

[$PtBr_2(\mathbf{L}^3)$] (**3**) (75%). *Anal.* Calc. for $C_8H_{11}Br_2NPtS$: C, 18.91; H, 2.18; N, 2.76. Found: C, 18.88; H, 2.24; N, 6.03%. ^{1}H NMR (299.9 MHz, DMSO-d_6, 25 °C) δ: 7.62 (m, 1H, C_5H_3N), 7.17 (m, 1H, C_5H_3N), 7.10 (m, 1H, C_5H_3N), 4.77 (s, br, 2H, CH_2), 2.49 (s, 3H, CH_3), 2.41 (s, 3H, CH_3). IR (KBr, cm^{-1}) 2994(w), 2958(m), 2907(s), 1606(m), 1568(w), 1465(s), 1412(m), 1315(m), 1263(w), 1170(m), 1140(w), 1110(w), 970(m), 877(w), 796(s). LSIMS (*m*/*z*): 531 ([$^{195}Pt^{80}Br_2C_8H_{11}NS$+Na]$^+$ 531).

[$PtBr_2(\mathbf{L}^4)$] (**4**) (81%). *Anal.* Calc. for $C_8H_{11}Br_2NPtS$: C, 18.91; H, 2.18; N, 2.76. Found: C, 18.94; H, 2.32; N, 2.73%. ^{1}H NMR (299.9 MHz, DMSO-d_6, 25 °C) δ: 9.39 (m, 1H, C_5H_3N), 7.72 (m, 1H, C_5H_3N), 7.38 (m, 1H, C_5H_3N), 4.75, 4.43 (m, 2H, CH_2), 2.43 (s, $J_{Pt-H} = 18.0$ Hz, 3H, CH_3), 2.32 (s, 3H, CH_3). IR (KBr, cm^{-1}): 2987(w), 2951(m), 2900(m), 1623(s), 1482(m), 1451(m), 1423(w), 1391(w), 1373(w), 1312(w), 1279(w), 1176(w), 1154(w), 1033(m), 977(m), 897(w), 823(m), 436(w). LSIMS (*m*/*z*): 531 ([$^{195}Pt^{80}Br_2C_8H_{11}NS$+Na]$^+$ 531).

2.4. Synthesis of complexes [$PtBr_4L$] ($L = \mathbf{L}^1$ (**5**), $\mathbf{L}^2$ (**6**), $\mathbf{L}^3$ (**7**), $\mathbf{L}^4$ (**8**))

A solution of [$PtBr_2(\mathbf{L}^1)$] (50 mg, 0.101 mmol) in MeCN (3 mL) was added to a concentrated solution of Br_2 in CCl_4 (1 mL). The red solution was allowed to stir at room temperature for 25 min, Et_2O was added to the red solution to afford an orange precipitate which was then isolated and washed with Et_2O to give **5** (44 mg, 67%). *Anal.* Calc. for $C_{12}H_{11}Br_4NPtS$: C, 20.13; H, 1.55; N, 1.96; S, 4.48. Found: C. 20.21; H. 1.74; N. 2.01; S. 4.37%. ^{1}H NMR (299.9 MHz, DMSO-d_6, 25 °C) δ: 9.30–9.42 (m, 1H, C_5H_3N), 8.29–8.35 (m, 1H, C_5H_3N), 8.22–8.24 (m, 1H, C_5H_3N), 7.81–7.86 (m, 1H, C_5H_3N), 7.48–7.64 (m, 5H, C_6H_5), 5.64 (m, 2H, CH_2). IR (KBr, cm^{-1}): 3110(w), 3035(w), 1915(m), 2857(w), 1604(m), 1558(m), 1483(m), 1440(s), 1388(m), 1311(w), 1270(w), 1247(w), 1158(w), 1110(w), 1064(w), 1035(w), 896(w), 867(w), 821(w), 763(s), 750(vs), 677(m), 482(w), 419(w).

2.4.1. [$PtBr_4(\mathbf{L}^2)$] (**6**)

The procedure used was as for [$PtBr_4(\mathbf{L}^1)$] using $\mathbf{L}^2$ (70%). *Anal.* Calc. for $C_7H_9Br_4NPtS$: C, 12.86; H, 1.39; N, 2.14; S, 4.90. Found: C, 12.68; H, 1.40; N, 2.19; S, 4.20%. ^{1}H NMR (299.9 MHz, DMSO-d_6, 25 °C) δ: 9.40 (m, 1H, C_5H_4N), 8.23 (m, 1H, C_5H_4N), 7.99 (m, 1H, C_5H_4N), 7.81 (m, 1H, C_5H_4N), 5.21, 5.02 (AB spin system, 2H, CH_2), 2.69 (s, $J_{Pt-H} = 18.3$ Hz, 3H, CH_3). IR (KBr, cm^{-1}) 3109(w), 3068(w), 3028(w), 3004(w), 2956(s), 2897(s), 1652(m), 1602(s), 1558(m), 1474(s), 1398(s), 1385(s), 1316(w), 276(m), 1243(w), 1165(w), 1110(m), 1060(w), 1033(w), 959(m), 895(w), 866(w), 825(m), 775(vs), 754(m), 692 (w), 657(w), 483(w), 436(w).

2.4.2. [$PtBr_4(\mathbf{L}^3)$] (**7**)

The procedure used was as for [$PtBr_4(\mathbf{L}^1)$] using $\mathbf{L}^3$ (75%). *Anal.* Calc. for $C_8H_{11}Br_4NPtS$: C, 14.39; H, 1.66; N, 2.10; S, 4.80. Found: C, 14.20; H, 1.67; N, 2.16; S, 4.23%. ^{1}H NMR (299.9 MHz, DMSO-d_6, 25 °C) δ: 8.41 (m, 1H, C_5H_4N), 7.79 (m, 2H, C_5H_4N), 5.50 (s, broad, 2H, CH_2), 2.70 (s, $J_{Pt-H} = 18.1$ Hz, 3H, CH_3), 2.04 (s, 3H, CH_3). IR (KBr, cm^{-1}): 2957(s), 2910(m), 1616(s), 1481(w), 1394(m), 1311(w), 1269(s), 1032(m), 980(w), 956(m), 829(m), 563(w), 443(w).

2.4.3. [$PtBr_4(\mathbf{L}^4)$] (**8**)

The procedure used was as for [$PtBr_4(\mathbf{L}^1)$] using $\mathbf{L}^4$ (73%). *Anal.* Calc. for $C_8H_{11}Br_4NPtS$: C, 14.39; H, 1.66; N 2.10. Found: C, 14.87; H, 1.84; N, 2.17%. ^{1}H NMR (299.9 MHz, DMSO-d_6, 25 °C) δ: 9.20 (m, 1H, C_5H_4N), 7.84 (m, 1H, C_5H_4N), 7.63 (m, 1H, C_5H_4N), 5.12, 4.93 (AB spin system, 2H, CH_2), 2.69 (s, $J_{Pt-H} = 18.0$ Hz, 3H, CH_3), 2.51 (s, 3H, CH_3). IR (KBr, cm^{-1}): 2959(m),

2903(m), 1597(m), 1571(m), 1459(s), 1433(m), 1398(s), 1367(s), 1316(m), 1297(w), 1202(w), 1171(m), 1118(m), 1038(m), 970(s), 852(w), 779(s).

2.5. X-ray crystallographic studies

Suitable crystals for X-ray diffraction studies of $[PtBr_2L]$ ($L = \mathbf{L}^1$ (**1**), $\mathbf{L}^2$ (**2**), $\mathbf{L}^3$ (**3**), $\mathbf{L}^4$ (**4**)) and $[PtBr_4(\mathbf{L}^2)]$ were grown from $MeNO_2/Et_2O$ (vapour diffusion). Full spheres of CCD area-detector diffractometer data for all complexes were measured (Bruker AXS, ω-scans, monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å, T ca. 153 K), N_{total} reflections merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed" and used in the full matrix least squares refinements. $(x, y, z, U_{iso})_H$ were refined for **2a** only, constrained in the remainder. Neutral atom complex scattering factors were employed within the context of the XTAL 3.7 program system [26]. Pertinent results are given above and in the tables and figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

3. Results and discussion

3.1. Synthesis of ligands

Lithiation of the α-carbon of a substituted pyridine using $LiBu^n$ affords the carbanion which then undergoes a nucleophilic substitution reaction with an appropriate diorganyl disulfide to afford the desired heteroleptic substituted pyridyl thioether compounds, $\mathbf{L}^1$–$\mathbf{L}^4$, in 47–87% yield (Scheme 1). This is a relatively simple and efficient "one-pot" synthesis, suitable for both MeSSMe and PhSSPh. The ligands, including the new ligand $\mathbf{L}^4$, were characterised using ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, EI mass spectrometry, and elemental analysis.

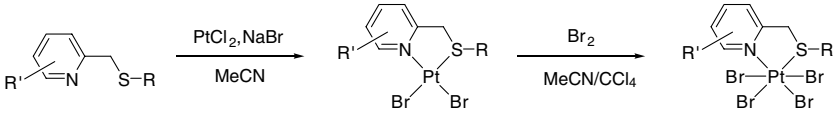
The room temperature ^1H NMR spectra of the methylthioether ligands, $\mathbf{L}^3$ and $\mathbf{L}^4$, are as expected and show no obvious trends upon substitution of the pyridyl ring compared with the spectrum of $\mathbf{L}^2$. The aromatic protons are observed as resonances between 6.98 and 8.36 ppm; methylene protons can be seen as a sharp singlet at 3.79 and 3.75 ppm for $\mathbf{L}^3$ and $\mathbf{L}^4$, respectively. The SMe moiety is observed as a singlet at 2.04 ppm for $\mathbf{L}^3$ and $\mathbf{L}^4$, respectively, while the second singlet, observed at 3.79 and 2.33 ppm, corresponds to the methyl substituent on the pyridyl ring at the 6- and 4-position, respectively.

The $^{13}C\{^1H\}$ NMR spectra of $\mathbf{L}^3$ and $\mathbf{L}^4$ exhibit resonances in the range of 158.5–120.2 ppm for the aromatic carbon atoms. The methylene carbons are observed at 40.2 and 40.1 ppm, while the resonance corresponding to the methyl substituent of the sulfur is observed at 15.4 ppm for both ligands. Another signal corresponding to the methyl substituent on the pyridyl ring occurs at 24.6 ppm and 21.3 ppm for $\mathbf{L}^3$ and $\mathbf{L}^4$, respectively.

3.2. Synthesis of $[PtBr_2L]$ and $[PtBr_4L]$ complexes

Treatment of $PtBr_2$ (formed in situ from $PtCl_2$ and NaBr) with a slight excess of **L** in MeCN afforded the complexes $[PtBr_2L]$ ($L = \mathbf{L}^1$ (**1**), $\mathbf{L}^2$ (**2**), $\mathbf{L}^3$ (**3**),$\mathbf{L}^4$ (**4**)) as pale yellow solids in 69–87% yield (Scheme 2). The compounds are stable to air and moisture and have limited solubility in organic solvents. LSI mass spectra of the complexes exhibit an ion, corresponding to $[M + Na]^+$, where the sodium atom entered the matrix from slight contamination of starting material. The mass spectrum of $[PtBr_2\mathbf{L}^1]$ exhibits an additional ion at m/z 553, corresponding to the ion $[M - Br+L]^+$. The $[PtBr_4L]$ complexes ($L = \mathbf{L}^1$ (**5**), $\mathbf{L}^2$ (**6**), $\mathbf{L}^3$ (**7**), $\mathbf{L}^4$ (**8**)) were prepared in good yield (67–75%) by treatment of $[PtBr_2L]$ in MeCN with a solution of Br_2/CCl_4 at room temperature for 30 min (Scheme 1). The complexes are air stable orange powders, with very limited solubility, thus making characterisation difficult.

The ^1H NMR spectra for all complexes exhibit a second-order spectrum with an AB spin system for the methylene protons between 5.64 and 4.43 ppm. Resonances corresponding to the pyridyl protons are observed as various multiplets between 9.69 and 7.10 ppm. The methyl protons in **2**–**4** are observed as singlets between 2.49 and 2.32 ppm which are further downfield than those of the analogous chloride complexes because of the increased *trans*-effect of the bromide ligand. Variable temperature ^1H NMR studies of $[PtBr_2\mathbf{L}^2]$ were used to investigate the effect of changing halide ligands on the *E*-inversion process. The coalescence temperature of the methylene protons in $[PtBr_2\mathbf{L}^2]$ (150 °C) is slightly lower than that for the analogous $[PtCl_2\mathbf{L}^2]$ complex (157 °C) [11], and has previously been observed for platinum halide complexes containing dithioether ligands, being explained in terms of the increased *trans*-influence of the heavier halide [27]. The ^1H NMR spectra of the Pt(IV) complexes **5**–**8** were similar



Scheme 2. Synthesis of $[PtBr_2L]$ (**1**–**4**) and $[PtBr_4L]$ (**5**–**8**) complexes.

to those of the Pt(II) complexes in that a second-order AB spin coupling pattern was observed for the methylene protons of the ligand. All other features of the spectra were as expected with aromatic protons observed in the typical region, and the methyl protons of complexes **6**, **3** and **4** being observed as singlets between 2.70 and 2.04 ppm.

*3.3. Structures of [$PtBr_2(L^1)$] (**1**), [$PtBr_2(L^2)$] (**2**), [$PtBr_2(L^3)$] (**3**), [$PtBr_2(L^4)$] (**4**), [$PtBr_4(L^2)$] (**6**), and [$PtBr_4(L^4)$] (8)*

All of the Pt(II) complexes (Figs. 1–8, and Tables 1 and 2) crystallise with the asymmetric unit comprised of a monomeric species with distorted square planar geometry for platinum. The Pt–S bond distances in all the [$PtBr_2L$] complexes (2.238(2)–2.250(3) Å) are comparable to those observed in [$PtBr_2(PhS(CH_2)_2SPh)$] (2.249(3), 2.248(3) Å) [28]. Similarly, the Pt–N bond distances (2.033(6)–2.058(4) Å) are comparable to those found in complexes such as [$PtBr_2(Me_2$-phen)] (Me_2-phen = 2,9-dimethyl-1,10-phenanthroline) (2.049(7), 2.058(9) Å) [29]. The Pt–Br bond distances in the complexes [$PtBr_2L$] range from 2.4220(9) to 2.4630(9) Å and are typical, with the shortest bond associated with the bromine atom *trans* to the pyridyl nitrogen and the longest associated with the bromine atom *trans* to the sulfur atom, the latter values also comparable with those of [$PtBr_2(PhS(CH_2)_2SPh)$] (2.430(1), 2.434(1)) [28].

The effect of changing the halide from Cl to Br in the coordination sphere about the platinum can be seen by comparing the structures of the analogous complexes [$PtCl_2(L^1)$] and [$PtBr_2(L^1)$] [11] (see also Table 2). Increases in Pt–S and Pt–N bond distances in [$PtBr_2(L^1)$] (2.2423(11) and 2.058(4) Å, respectively), compared to those of the complex [$PtCl_2(L^1)$] (2.235(1) and 2.034(3) Å, respectively), are consistent with the increased *trans*-influence of the bromide ligand. The strain of the two complexes appears comparable, with the puckering of the five-membered chelate

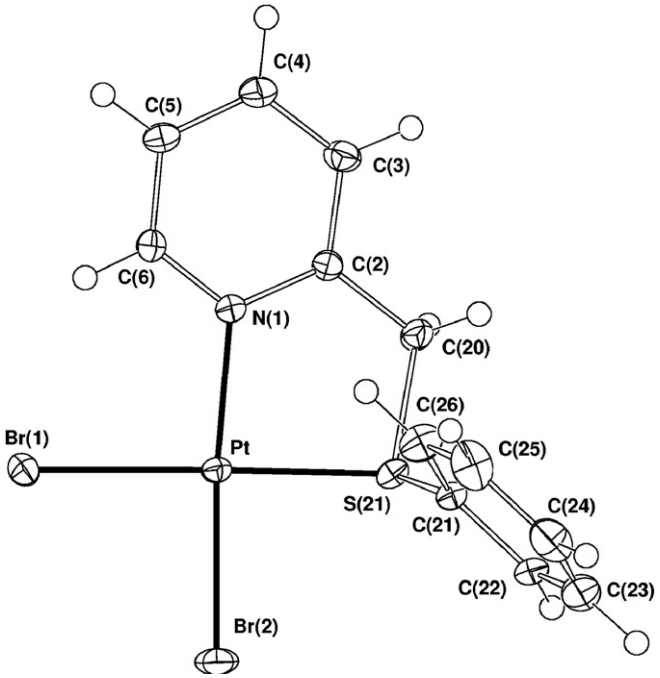


Fig. 1. Molecular projection of [$PtBr_2(L^1)$] (**1**).

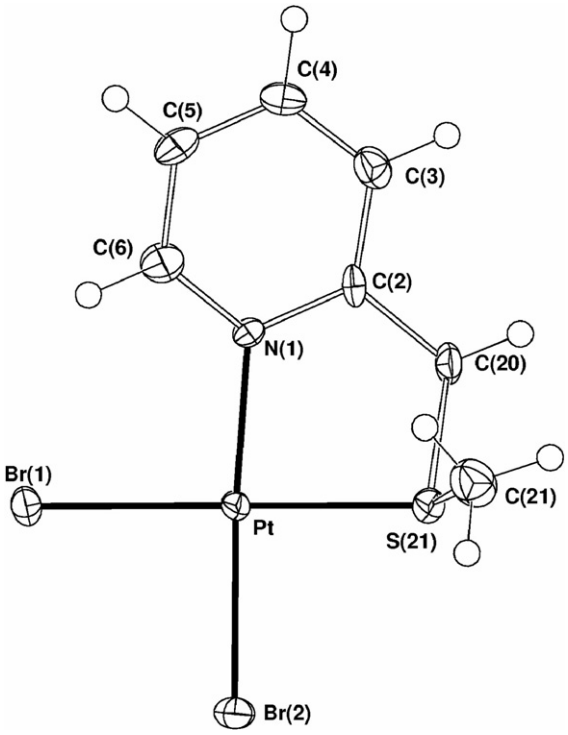


Fig. 2. Molecular projection of [$PtBr_2(L^2)$] (**2**).

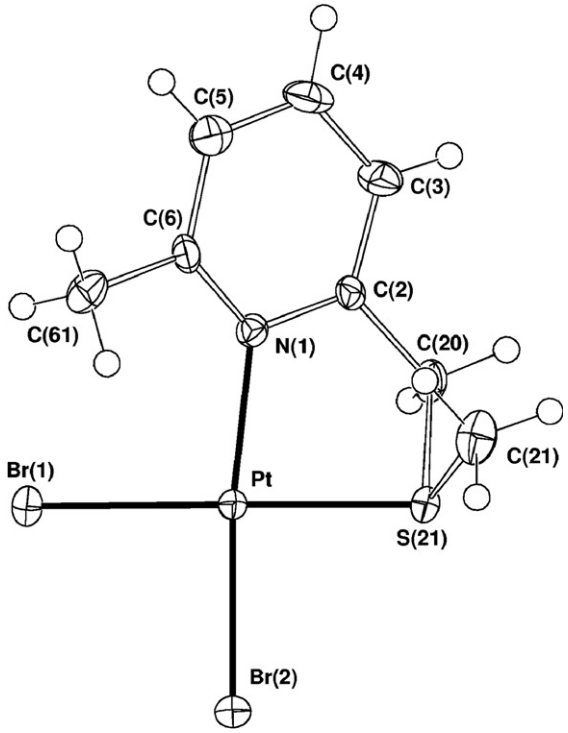


Fig. 3. Molecular projection of [$PtBr_2(L^3)$] (**3**).

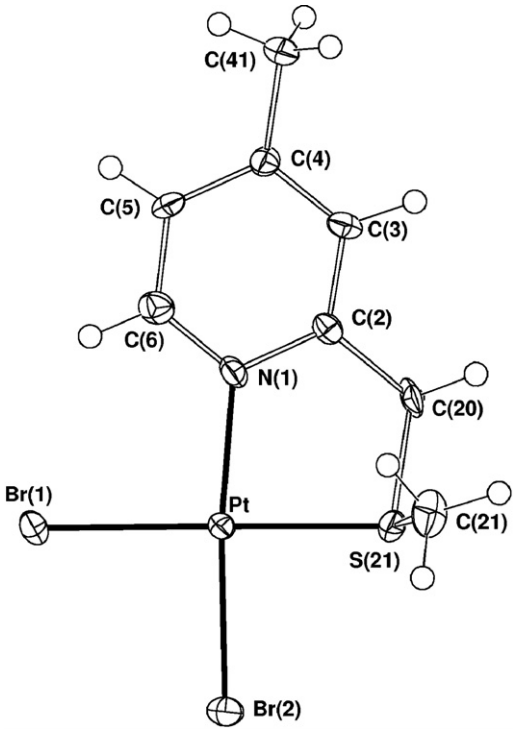


Fig. 4. Molecular projection of $[PtBr_2(L^4)]$ (**4**).

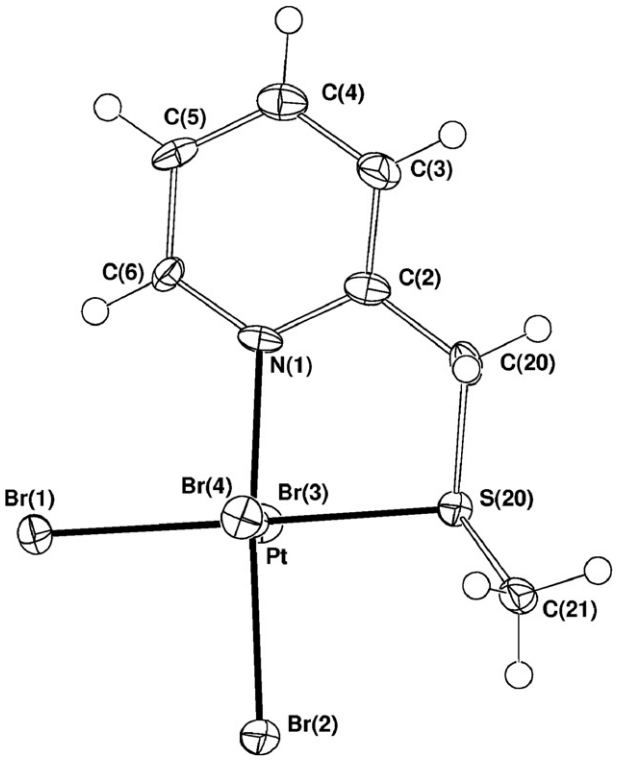


Fig. 6. Molecular projection of $[PtBr_4(L^2)]$ (**6**).

rings being similar, as are the associated atom deviations from the C_5N plane (the coordination plane in most cases is somewhat puckered). Changes in the Pt–S and Pt–N bond distances are negligible, despite the variation in *trans*-influence of the bromide atoms.

Variation of the thioether substituent from Ph to Me has little to no effect on bond lengths within the coordination environment of the platinum, but there are subtle effects on the bond angles and strain within the molecule. These are evident in the parameters of Table 2, where data for the present compounds is marshalled comparatively with other relevant data from the literature. The slightly more acute 'bite' angle of the methylthioether complex, **2** (Fig. 2), compared to the phenylthioether complex, **1**, is accompanied by an increase in the strain of the chelate ring, most evident in the differences in associated torsion angles (Table 2). The decrease in the bite angle in complex **2** (85.8(2)°) is offset by a relaxation of all other bond angles about the platinum except the Br(1)–Pt–Br(1) angle which is slightly more acute for the methylthioether complex (89.57(3)°; cf. 90.06(2)° for complexes **2** and **1**, respectively).

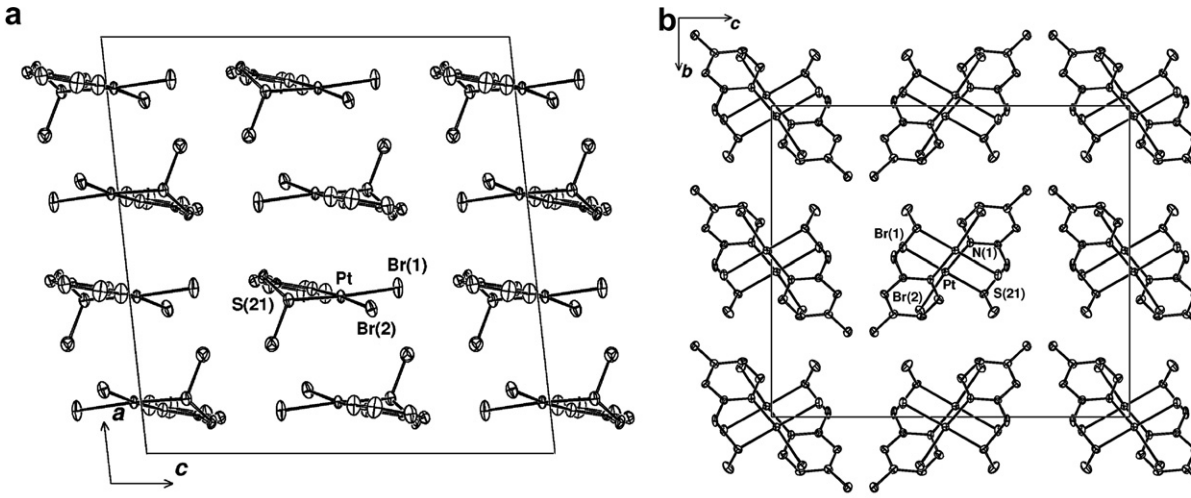


Fig. 5. (a,b). Unit cell contents of **2** and **4**, projected down *b* and *a*, respectively. (The closest Pt···Pt contacts in these structures are 4.2234(7), 3.7364(6) Å, respectively.)

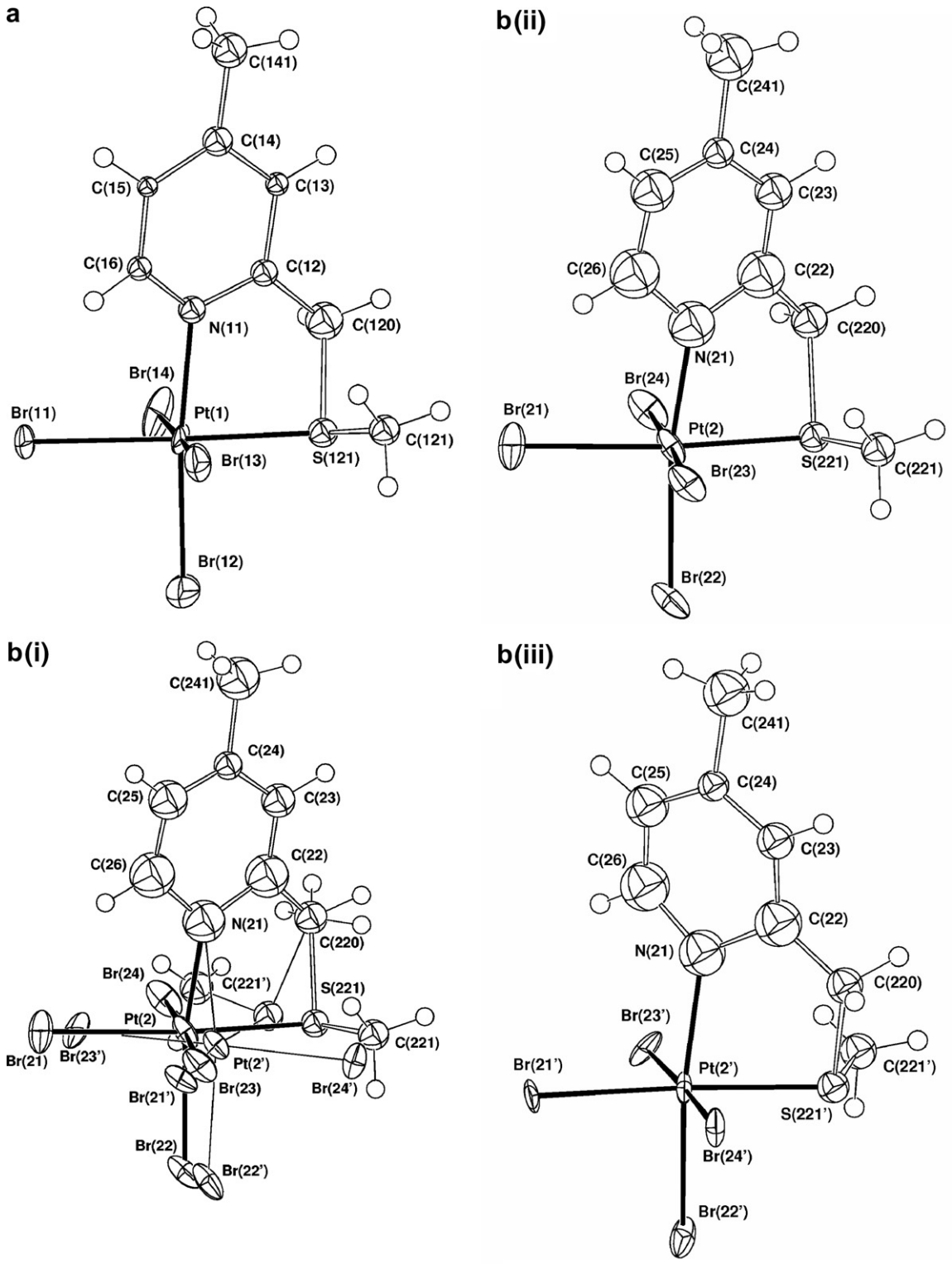


Fig. 7. Molecular projections of $[PtBr_4(\mathbf{L}^4)]$ (**8**). (a) Molecule 1. (b) Molecule 2: (i) the disordered composite and (ii, iii) the two deconvoluted components.

The addition of a methyl moiety at the 6-position of the pyridyl ring dramatically changes the overall shape of the molecule from that of the complex containing the unsubstituted ligand, the effects paralleling that previously observed in the counterpart *t*-butyl substituted palladium(II) chloride analogues (Table 2) [30]. This is most strongly evidenced in the changes in torsion angles in the chelate ring which in turn bring about a dramatic twist in the MX_2 array relative to the pyridine plane (Table 2). There is a lengthening of the Pt–N bond distance in **3** compared to that in **2** (2.055(7), 2.034(7) Å, respectively), associated with an increase in the Br(1)–Pt–N(1) bond angle

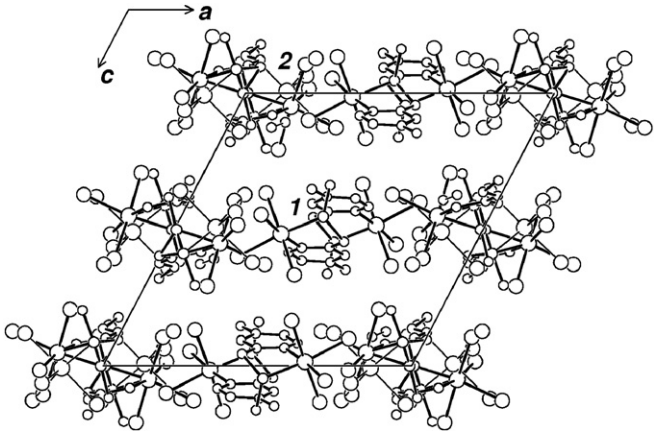


Fig. 8. Unit cell contents of $[PtBr_4(\mathbf{L}^4)]$ (**8**), projected down *b*.

(96.7(2), 94.5(2)°, respectively) because of steric interactions between the 6-methyl substituent of the pyridyl ring and the *cis* bromine atom. A concomitant of the lengthened Pt–N bond is a decrease in the bite angle of the ligand (83.7(2)° (**3**), 85.8(2)° (**2**)). When the substitution of the ligand occurs at the 4-position of the pyridyl ring, the overall shape of the complex (**4**, Fig. 4) resembles that of **2** where the ligand is unsubstituted, suggesting that the change in the structure of **3** is due mostly to the increased steric strain brought on by the addition of the methyl substituent at the 6-position rather than electronic differences in the complexes. Interesting stackings of the planar components of the molecules are observed (Fig. 5).

The Pt(IV) complex $[PtBr_4(\mathbf{L}^2)]$ (**6**) crystallises in the orthorhombic space group $Pna2_1$ with the asymmetric unit comprised of a monomeric species containing distorted octahedral geometry (Fig. 6). Bond distances and angles are listed in Table 3. The Pt–N bond distance of $[PtBr_4(\mathbf{L}^1)]$ (2.101(10) Å) is also shorter than that in $[PtBrMe_3$(2,6-bis(*p*-tolylthiomethyl)pyridine)] (2.311(6) Å) [4], and again can be attributed to the different *trans*-influence that the methyl group has on the nitrogen centre compared to the bromide atom. The five-membered chelate ring in $[PtBr_4(\mathbf{L}^2)]$ is significantly more puckered than observed in the structure of $[PtBr_2(\mathbf{L}^2)]$, with the sulfur atom out of the Pt–N(1)–C(2)–C(21) plane (χ^2 19) by 0.68(2) Å, which may be attributed to the increased steric hindrance between the lone pair of electrons on the sulfur atom with the bromine atoms due to the increased coordination number of the platinum. The large ring puckering is reflected in the larger than ideal Br(4)–Pt–S(21) bond angle (93.99(9)°) and the smaller than ideal Br(3)–Pt–S(21) bond angle (86.49(9)°). The ligand bite angle (N(1)–Pt–S(21)) at 83.6(3)° is significantly smaller than that seen in the $[PtBr_2(\mathbf{L}^2)]$ complex (85.8(2)°) but is consistent with the lengthening of the Pt–N and Pt–S bonds associated with the higher coordination number. The Pt–S bond distance in $[PtBr_4(\mathbf{L}^2)]$ (2.329(3) Å) is longer than in $[PtBr_2(\mathbf{L}^2)]$, consistent with an increase in the coordination number of the platinum. However, it is also shorter relative to the Pt–S bond distances of $[PtBrMe_3(Me_2N(CH_2)_2SC_6H_4$-Me-4)] (2.437(3) Å) [8] and $[PtBrMe_3$(2,6-bis(*p*-tolylthiomethyl)pyridine)] (2.419(4) Å)[4] which can be attributed to the difference in *trans* influence of the methyl compared to the bromide group.

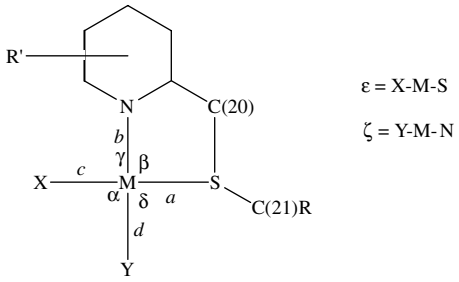
Crystals of $[PtBr_4(\mathbf{L}^4)]$ (**8**) were small and data of an unsatisfactory quality, with, further, a disordered model resulting in an inferior determination, replicated in a later study on an instrument of more recent manufacture and

Table 1
Crystallographic data of $[PtBr_2(\mathbf{L}^1)]$ (**1**), $[PtBr_2(\mathbf{L}^2)]$ (**2**), $[PtBr_2(\mathbf{L}^3)]$ (**3**), $[PtBr_2(\mathbf{L}^4)]$ (**4**), $[PtBr_4(\mathbf{L}^2)]$ (**6**), and $[PtBr_4(\mathbf{L}^4)]$ (**8**)

Complex	$[PtBr_2(\mathbf{L}^1)]$ (**1**)	$[PtBr_2(\mathbf{L}^2)]$ (**2**)	$[PtBr_2(\mathbf{L}^3)]$ (**3**)	$[PtBr_2(\mathbf{L}^4)]$ (**4**)	$[PtBr_4(\mathbf{L}^2)]$ (**6**)[a]	$[PtBr_4(\mathbf{L}^4)]$ (**8**)
Formula	$C_{12}H_{11}NSPtBr_2$	$C_7H_9NBr_2PtS$	$C_8H_{11}NBr_2PtS$	$C_8H_{11}NBr_2PtS$	$C_7H_9NSPtBr_4$	$C_8H_{11}NSPtBr_4$
M	556.18	494.11	508.14	508.14	653.92	667.94
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$	*Pbca*	$Pna2_1$	$P2_1/c$
Unit cell dimensions						
a (Å)	9.334(1)	15.888(2)	8.3219(8)	8.687(1)	14.273(2)	15.018(6)
b (Å)	13.109(2)	8.947(1)	8.5534(8)	15.229(2)	9.179(2)	13.998(6)
c (Å)	11.307(1)	15.482(2)	16.421(2)	17.555(2)	9.800(2)	14.994(6)
β (°)	95.442(3)	96.279(3)	97.501(2)			117.530(7)
U (Å^3)	1377.3(5)	2187.5(8)	1158.8(3)	2322.3(8)	1283.9(6)	2795(3)
D_{calc} (g cm^{-3})	2.682	3.000	2.912	2.906	3.382	3.174
Z	4	8	4	8	4	8
μ (mm^{-1})	16.1	20.3	19.1	19.1	23.5	21.6
Specimen (mm)	0.10 × 0.10 × 0.09	0.08 × 0.06 × 0.04	0.16 × 0.07 × 0.03	0.17 × 0.06 × 0.04	0.35 × 0.12 × 0.04	0.18 × 0.06 × 0.02
$T_{min/max}$	0.53	0.44	0.47	0.42	0.34	0.39
$2\theta_{max}$ (°)	75	60	75	60	75	50
N_t	27022	21282	23212	41083	24621	20651
$N(R_{int})$	7220(0.057)	3148(0.087)	4090(0.061)	3338(0.048)	3465(0.094)	4903(0.17)
N_o	5467	2518	3244	2712	2877	3141
R	0.038	0.037	0.042	0.030	0.046	0.105
R_w	0.043	0.077	0.095	0.071	0.061	0.14
GOOF	1.09	1.30	1.18	1.19	1.11	0.92

[a] χ_{abs} 0.00(2).

Table 2
Selected bond angles and distances for $[PtBr_2\mathbf{L}^n]$ ($n = 1$(**1**), 2(**2**), 3(**3**), **4**(4)) and related $[MX_2L]$ species



M	Pd				Pt					
R	Me	^{t}Bu	^{t}Bu	Ph	Ph	Ph	Ph	Me	Me	Ph
R′	H	H	6-Me	H	H	H	H	6-Me	5-Me	H
X	Cl	Cl	Cl	Cl	Cl	Br	Br	Br	Br	Cl
Y	Me	Me	Me	Cl	Cl	Br	Br	Br	Br	COMe
Ref. (cpd)	(2 mols.) [31]	[30]	[30]	[11]	[11]	(**1**)[a]	(**2**)[a]	(**3**)[a]	(**4**)[a]	[32]
Distances (Å)										
a	2.257(5), 2.255(6)	2.259(1)	2.268(2)	2.2540(5)	2.235(1)	2.2423(11)	2.250(2)	2.248(2)	2.238(2)	2.257(2)
b	2.16(1), 2.17(1)	2.162(5)	2.229(4)	2.045(1)	2.034(3)	2.058(4)	2.034(7)	2.055(7)	2.033(6)	2.190(5)
c	2.315(6), 2.340(6)	2.347(1)	2.336(2)	2.3162(5)	2.316(1)	2.4504(5)	2.4512(9)	2.4630(9)	2.4597(8)	2.320(2)
d	2.01(1), 2.00(1)	2.035(7)	2.048(5)	2.2887(6)	2.296(1)	2.4307(6)	2.4243(10)	2.4220(9)	2.4322(9)	1.997(6)
Angles (°)										
α	91.6(6), 90.7(6)	89.3(2)	87.6(2)	90.90(2)	89.79(4)	90.06(2)	89.57(3)	89.77(3)	90.70(3)	89.6(2)
β	84.1(4), 83.8(4)	84.8(1)	82.8(1)	86.32(3)	86.6(1)	86.7(1)	85.8(2)	83.7(2)	85.5(2)	83.2(1)
γ	95.3(4), 95.7(4)	95.3(1)	99.4(1)	94.50(3)	94.2(1)	94.9(1)	94.5(2)	96.7(2)	95.1(2)	94.5(1)
δ	88.8(6), 89.6(6)	90.7(2)	89.9(2)	88.74(1)	89.70(4)	88.73(3)	90.37(6)	89.95(6)	88.81(5)	92.8(2)
ε	177.6(2), 176.2(2)	178.8(1)	168.4(1)	174.40(1)	175.15(3)	174.20(3)	175.87(6)	166.91(6)	179.10(5)	176.15(6)
ζ	172.3(7), 173.2(7)	174.9(2)	172.7(2)	172.95(3)	174.73(9)	173.7(1)	175.5(2)	173.5(2)	173.2(2)	175.2(2)
Torsion angles (°) (carbon atoms are denoted by number only) (presented in a common chirality)										
N–M–S–21	84.3(7), 83.1(7)	90.7(2)	76.7(2)	93.12(6)	92.5(2)	94.8(2)	80.0(4)	62.0(5)	82.6(4)	81.3(3)
2–20–S–21	−75(1), −74(1)	−87.0(4)	−72.3(4)	−91.3(1)	−91.1(3)	−93.3(3)	−75.4(6)	−62.3(7)	−75.5(6)	−74.5(5)
N–M–S–20	−19.2(6), −19.3(6)	−17.0(2)	−33.4(2)	−14.50(5)	−15.5(2)	−13.9(2)	−22.2(4)	−37.9(4)	−20.6(3)	−23.8(3)
M–S–20–2	32(1), 30(1)	25.5(4)	44.2(4)	20.1(1)	21.4(3)	19.4(3)	33.1(6)	47.5(6)	32.1(5)	37.0(5)
S–20–2–N	−31(2), −29(2)	−21.5(5)	−29.4(6)	−16.9(2)	−18.0(5)	−16.6(5)	−31.4(9)	−33.9(10)	−31.1(8)	−33.9(7)
20–2–N–M	13(2), 10(2)	4.1(5)	−4.7(6)	2.7(2)	3.1(5)	3.2(5)	10.3(9)	−3.1(10)	11.6(9)	10.9(8)
2–N–M–S	7.1(9), 9(1)	10.2(3)	27.1(4)	9.12(9)	9.6(3)	8.3(3)	10.4(6)	29.3(6)	8.6(5)	11.4(5)
Atom deviations from the C_5N plane (δÅ) (C(21) as datum)										
δM	0.25(2), 0.13(2)	0.059(9)	−0.089(9)	0.001(2)	−0.005(6)	−0.007(6)	0.20(1)	0.08(1)	0.27(1)	0.27(1)
δX	−0.08(3), −0.16(3)	−0.34(1)	−1.58(1)	−0.621(3)	−0.627(8)	−0.644(9)	−0.54(2)	−1.64(2)	−0.21(1)	−0.36(1)
δY	0.65(4), 0.35(4)	0.07(2)	−0.06(2)	0.243(3)	0.181(10)	0.22(1)	0.57(3)	0.39(2)	0.77(2)	0.63(2)
δC(20)	−0.10(3), −0.10(3)	−0.05(1)	0.123(9)	−0.029(2)	−0.028(7)	−0.033(8)	−0.08(2)	0.18(1)	−0.12(1)	−0.12(1)
δS	0.66(3), 0.55(3)	0.49(1)	0.984(9)	0.394(2)	0.415(7)	0.365(8)	0.72(2)	1.25(1)	0.67(1)	0.76(1)
δC(21)	2.40(3), 2.33(3)	2.34(1)	2.79(1)	2.151(3)	2.177(8)	2.127(9)	2.44(2)	2.76(1)	2.43(1)	2.47(1)

[a] This work.

Table 3
Selected bond distances and angles for $[PtBr_4L]$ ($L = L^2$(**6**), L^4(**8**))

	$[PtBr_4(L^2)]$ (**6**)	$[PtBr_4(L^4)]$ (**8**)	
		Molecule 1	Molecule 2 (2 cpts.)
Bond distances (Å)			
Pt–Br(1)	2.490(2)	2.469(5)	2.49(1), 2.45(2)
Pt–Br(2)	2.445(1)	2.431(5)	2.46(1), 2.43(2)
Pt–Br(3)	2.468(1)	2.467(4)	2.47(1), 2.47(1)
Pt–Br(4)	2.473(1)	2.448(4)	2.45(1), 2.47(1)
Pt–N(1)	2.10(1)	2.08(3)	2.03(4), 2.13(4)
Pt–S(21)	2.329(3)	2.301(11)	2.28(2), 2.34(3)
Bond angles (°)			
Br(1)–Pt–Br(2)	88.93(5)	91.1(2)	91.7(4), 90.3(7)
Br(1)–Pt–Br(3)	88.66(5)	89.4(1)	89.2(4), 90.0(5)
Br(1)–Pt–Br(4)	90.84(5)	88.6(2)	88.1(3), 87.4(4)
Br(1)–Pt–N(1)	95.7(5)	94.8(9)	97(1), 100(1)
Br(1)–Pt–S(21)	177.25(8)	173.5(2)	172.3(5), 171.9(6)
Br(2)–Pt–Br(3)	91.45(8)	91.1(1)	90.4(4), 88.8(5)
Br(2)–Pt–Br(4)	89.49(5)	89.4(2)	89.4(4), 91.1(4)
Br(2)–Pt–N(1)	175.3(7)	174.1(9)	169.7(9), 164(1)
Br(2)–Pt–S(21)	91.71(9)	89.3(3)	90.7(5), 89.1(8)
Br(3)–Pt–Br(4)	178.93(6)	177.9(2)	177.3(3), 177.4(6)
Br(3)–Pt–N(1)	88.9(3)	88.7(6)	83(1), 79(1)
Br(3)–Pt–S(21)	93.99(9)	97.0(2)	98.1(5), 98.1(6)
Br(4)–Pt–N(1)	90.2(3)	91.0(6)	97(1), 101.2(9)
Br(4)–Pt–S(21)	86.49(9)	85.0(2)	84.6(5), 84.5(6)
N(1)–Pt–S(21)	83.6(3)	84.9(9)	82(1), 82(1)
Torsion angles (°)			
S(21)–Pt–N(1)–C(2)	−12.2(8)	13(2)	26(3), −38(3)
Pt–N(1)–C(2)–C(20)	−9.4(1)	11(4)	−2(4), 23(4)
N(1)–C(2)–C(20)–S(21)	32.8(15)	−35(4)	−32(4), 12(5)
C(2)–C(20)–S(21)–Pt	−35.3(1)	37(3)	45(3), −35(7)
C(20)–S(21)–Pt–N(1)	23.7(5)	−26(1)	−33(2), 32(1)
C(21)–S(21)–Pt–N(1)	128.6(6)	79(1)	78(3), −72(5)
Out-of-plane deviations (Å)			
$\delta Pt(C_5N)$	0.14(2)	0.10(4)	0.05(6), −0.75(6)

at a lower temperature. Two independent molecules, devoid of crystallographic symmetry comprise the asymmetric unit of the structure. One is ordered, refining unproblematically, albeit with isotropic displacement parameter forms for S, C, N. The other comprises a pair of disordered superimposed components (Fig. 7), the disorder resolvable in all atoms except MeC_5H_3NC, occupancies refining to 0.605(9) and complement. The disorder is a consequence of co-crystallisation at site 2 of molecules differing in the orientation of the S–Me group. Although the geometries are imprecise, with the chelate rings of similar conformations in molecules 1 and the two components of molecule 2 (one component of the latter being of opposite chirality) (Table 2), it is interesting to find that the chelate ring conformation is somewhat different to that found in $[PtBr_4(L^2)]$ (**6**), best appreciated by observation of the pendant S–Me disposition. Disorder is not resolved in the aromatic ring of molecule 2, although its displacement parameters are high, perhaps because of the constraint of parallel packing of the aromatic planes in the lattice (Fig. 8), their being some tendency for the molecules to be disposed in sheets.

4. Conclusions

A relatively simple generic synthetic method has been developed for the preparation of substituted pyridyl thioether ligands, one of the most fundamental heteroleptic ligand systems. The solid-state structures of a number of $PtBr_2L$ complexes containing pyridyl thioether ligands were elucidated. The deviation from ideal square planar geometry is influenced by the substitution of a methyl group at the 6-position of the pyridyl ring. The electronic effects of the methyl group have minimal effect on the structure. Variation of the thioether substituent from Ph to Me has little to no effect on bond lengths within the coordination environment of the platinum, but there are subtle effects on the bond angles and strain, with the square planar geometry becoming less tetrahedrally distorted and the distance between the sulfur atom and the chelate ring becoming greater in the thiomethyl complex $[PtBr_2(L^2)]$. It is hoped that such investigations into the effect of ligand variation on the structure of the compounds will help to understand what characteristics influence their catalytic activity.

Acknowledgements

We thank the Australian Research Council for funding this project (V.-A.T. is an ARC APD Fellow). We also thank Johnson-Matthey for the generous loan of $PtCl_2$.

Appendix A. Supplementary material

CCDC Nos. 258137, 258138, 258139, 258140, 258141 and 615111 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.09.001.

References

[1] S.G. Murray, F.R. Hartley, Chem. Rev. 81 (1981) 365.
[2] E.G. Hope, W. Levason, Coord. Chem. Rev. 122 (1993) 109.
[3] W. Levason, S.D. Orchard, G. Reid, Coord. Chem. Rev. 225 (2002) 159.
[4] E.W. Abel, P.J. Heard, K.G. Orrell, M.B. Hursthouse, M.A. Mazid, J. Chem. Soc., Dalton Trans. (1993) 3795.
[5] B. Pitteri, G. Marangoni, L. Cattalini, T. Bobbo, J. Chem. Soc., Dalton Trans. (1995) 3953.
[6] S. Chattopadhyay, C. Sinha, P. Basu, A. Chakravorty, Organometallics 10 (1991) 1135.
[7] P.J. Heard, D.A. Tocher, J. Organomet. Chem. 549 (1997) 295.
[8] V.K. Jain, S. Chaudhury, R. Bohra, Polyhedron 12 (1993) 2377.
[9] A. Knödler, W. Kaim, V.K. Jain, S. Záliš, J. Organomet. Chem. 655 (2002) 218.
[10] L. Canovese, G. Chessa, F. Visentin, P. Uguagliati, Coord. Chem. Rev. 248 (2004) 945.
[11] R.C. Jones, R.L. Madden, B.W. Skelton, V.–A. Tolhurst, A.H. White, A.J. Wilson, A. Williams, B.F. Yates, Eur. J. Inorg. Chem. (2005) 1048.
[12] J.M. Wisner, T.J. Bartczak, J.A. Ibers, J.J. Low, W.A. Goddard III, J. Am. Chem. Soc. 108 (1986) 347.
[13] J.M. Wisner, T.J. Bartczak, J.A. Ibers, Organometallics 5 (1986) 2044, and references therein.
[14] W. Kläui, M. Glaum, T. Wagner, M.A. Bennett, J. Organomet. Chem. 472 (1994) 355.
[15] R.E. Marsh, W.P. Schaefer, D.K. Lyon, J.A. Labinger, J.E. Bercaw, Acta Crystallogr., Sect. C 48 (1992) 1603.
[16] A.J. Canty, A. Dedieu, H. Jin, A. Milet, B.W. Skelton, S. Trofimenko, A.H. White, Inorg. Chim. Acta 287 (1999) 27.
[17] K. Kahmann, H. Sigel, H. Erlenmeyer, Helv. Chim. Acta 47 (1964) 1754.
[18] L. Bauer, L.A. Gardella, J. Org. Chem. 28 (1963) 1323.
[19] E.W. Ainscough, E.N. Baker, A.M. Brodie, N.G. Larsen, K.L. Brown, J. Chem. Soc., Dalton Trans. (1981) 1746.
[20] E. Ghera, Y. Ben-David, H. Rapoport, J. Org. Chem. 48 (1983) 774.
[21] B.M. Trost, R. Braslau, J. Org. Chem. 53 (1988) 532.
[22] L. Canovese, F. Visentin, P. Uguagliati, G. Chessa, A. Pesce, J. Organomet. Chem. 566 (1998) 61.
[23] L. Canovese, F. Visentin, P. Uguagliati, G. Chessa, V. Lucchini, G. Bandoli, Inorg. Chim. Acta 275 (1998) 385.
[24] H.L. Holland, C.D. Turner, P.R. Andreana, D. Nguyen, Can. J. Chem. 77 (1999) 463.
[25] L. Canovese, G. Chessa, C. Santo, F. Visentin, P. Uguagliati, Inorg. Chim. Acta 346 (2003) 158.
[26] S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp (Eds.), The XTAL 3.7 System, University of Western Australia, 2000.
[27] F.R. Hartley, S.G. Murray, W. Levason, H.E. Soutter, C.A. McAuliffe, Inorg. Chim. Acta 35 (1979) 265.
[28] G. Marangoni, B. Pitteri, V. Bertolasi, P. Gilli, Inorg. Chim. Acta 234 (1995) 173.
[29] R.J.H. Clark, F.P. Fanizzi, G. Natile, C. Pacifico, C.G. van Rooyen, D.A. Tocher, Inorg. Chim. Acta 235 (1995) 205.
[30] L. Canovese, F. Visentin, G. Chessa, F. Visentin, G. Chessa, P. Uguagliati, G. Bandoli, Organometallics 19 (2000) 461.
[31] Canovese et al., J. Organomet. Chem. 650 (2002) 43.
[32] Gosavi et al., Inorg. Chim. Acta 357 (2004) 1781.