Experimental

Dipotassium tetrachloroplatinate(II) [26], 2-(benzylthio)azobenzene [11] and 2-(benzylsulphinyl)azobenzene [23] were prepared as previously described. Purification of solvents and the preparation of tetraethylammonium perchlorate for electrochemical work were carried out as described previously [27]. All other chemicals and solvents used for the preparative work were of reagent grade, and were used without further purification.

UV-Vis spectra were recorded on a Hitachi spectrophotometer and IR (4000–200 cm^{-1}) spectra on a Perkin–Elmer 783 spectrophotometer. Proton NMR spectra were recorded for $CDCl_3$ solutions on Varian XL 200 and Bruker 270 MHz FT NMR spectrometers. Electrochemical studies were carried out with PAR Model 370-4 electrochemistry apparatus as described elsewhere [28]. Elemental analyses were performed with a Perkin–Elmer 240C elemental analyser.

Synthesis

*Chloro((2-(benzylthio)phenyl)azo)phenyl-C^2,N,S)platinum(II), [Pt(HL^1)Cl] (**1a**)*

To an aqueous solution (10 cm^3) of K_2PtCl_4 (0.10 g, 0.24 mmol) was added slowly a hot ethanolic solution of 2-(benzylthio)azobenzene (0.067 g, 0.22 mmol).

Table 5

Crystallographic data for [Pt(HL^1)Cl$_3$] (**2a**), [Pt(MeL^2)Cl] (**3b**) and [Pd(MeL^1)Cl]

	[Pt(HL^1)Cl$_3$]	[Pt(MeL^2)Cl]	[Pd(MeL^1)Cl]
Formula	$C_{19}H_{15}N_2Cl_3PtS$	$C_{20}H_{17}N_2OClPtS$	$C_{20}H_{17}N_2ClPdS$
Formula weight	604.8	564.0	459.3
Crystal size, mm^3	0.12 × 0.18 × 0.22	0.06 × 0.14 × 0.12	0.11 × 0.13 × 0.27
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$	$P2_1/n$
a, Å	11.773(3)	9.782(8)	11.062(3)
b, Å	11.205(4)	13.932(8)	10.963(4)
c, Å	15.099(7)	14.038(10)	15.409(4)
β, °	99.48(3)	98.76(7)	100.47(2)
V, Å^3	1964.7(12)	1891(2)	1837.6(9)
Z	4	4	4
No. centering reflections	25	15	25
Centering 2θ	$15 < 2\theta < 31°$	$10 < 2\theta < 25°$	$15 < 2\theta < 27°$
D_c, g·cm^{-3}	2.045	1.981	1.660
μ(Mo-K_α), cm^{-1}	77.36	7u.57	12.56
2θ limits	2–52	2–50	2–55
h, k, l range	15, 14, ±19	12, 17, ±17	14, 14, ±20
No. unique reflections	3785	3329	4199
Observed data $I > 3\sigma(I)$	1699	1418	2403
Parameters refined	235	165	226
R [a]	0.0518	0.0550	0.0412
R_w [b]	0.0519	0.055	0.0509
g in weighting scheme [c]	0.000300	0.000500	0.000400
Largest peak in final Fourier map, eÅ^{-3}	0.78	1.00	0.23

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [c] $1/[\sigma^2(|F_o|) + g|F_o|^2]$.

The mixture was stirred for 24 h, then the brown-red solution was evaporated in air and the residue washed thoroughly with water and then with ethanol–water (1 : 1 v/v). The dark brown residue was chromatographed on silica gel with acetonitrile–benzene (1 : 9 v/v) as eluent. A brown band was collected which yielded [Pt(HL^1)Cl] in 74% yield (found: C, 42.65; H, 2.79; N, 5.36. $C_{19}H_{15}N_2SClPt$ calcd.: C, 42.73; H, 2.81; N, 5.25%).

[Pt(MeL^1)Cl (**1b**), [Pt(HL^2)Cl] (**3a**) and [Pt(MeL^2)Cl] (**3b**) were prepared similarly in 70–80% yield (**1b**: found: C, 43.61; H, 2.93; N, 5.29. $C_{20}H_{17}N_2SClPt$ calcd.: C, 43.83; H, 3.10; N, 5.11%. **3a**: found: C, 40.97; H, 2.67; N, 4.98. $C_{19}H_{15}N_2SOClPt$ calcd.: C, 41.49; H, 2.73; N, 5.10%. **3b**: found: C, 42.45; H, 2.98; N, 4.67. $C_{20}H_{17}N_2SOClPt$ calcd.: C, 42.59; H, 3.02; N, 4.97%).

*Trichloro(((2-(benzylthio)phenyl)azo)phenyl-*C^2,N,S*)platinum(IV), [Pt(HL^1)Cl$_3$] (**2a**)*

To an acetonitrile solution (50 cm^3) of Pt(HL^1)Cl (0.10 g, 0.19 mmol) was added dropwise 20 cm^3 of acetonitrile saturated with chlorine. The mixture was stirred for 0.5 h and then evaporated in the air. The solid was dissolved in dichloromethane and the solution (10 cm^3) chromatographed on silica gel with benzene as eluent. An orange yellow band was collected and yielded 0.080 g (70%) of [Pt(HL^1)Cl$_3$] (found: C, 37.34; H, 2.52; N, 4.70. $C_{19}H_{15}N_2SCl_3Pt$ calcd.: C, 37.72; H, 2.48; N, 4.63%).

[Pt(MeL^1)Cl$_3$] (**2b**), [Pt(HL^2)Cl$_3$] (**4a**) and [Pt(MeL^2)Cl$_3$] (**4b**) were prepared

Table 6

Atomic coordinates (×10^4) for [Pt(HL^1)Cl$_3$]

Atom	*x*	*y*	*z*
Pt	2891(1)	1199(1)	1055(1)
S	197894)	369(5)	−381(3)
Cl(1)	1140(3)	829(4)	1571(3)
Cl(2)	4655(3)	1541(4)	586(3)
Cl(3)	2384(4)	3178(5)	779(3)
N(1)	3878(13)	−731(16)	2150(10)
N(2)	3326(11)	−454(15)	1374(10)
C(1)	4103(15)	294(20)	2670(13)
C(2)	3700(13)	1415(18)	2323(10)
C(3)	3890(16)	2426(20)	2836(13)
C(4)	4494(20)	2249(25)	3717(13)
C(5)	4890(17)	1192(31)	4059(13)
C(6)	4666(18)	194(25)	3550(14)
C(7)	3015(16)	−1417(16)	748(12)
C(8)	2345(13)	−1149(19)	−75(12)
C(9)	2002(20)	−2077(24)	−674(14)
C(10)	2321(20)	−3245(24)	−469(17)
C(11)	2961(18)	−3472(17)	343(17)
C(12)	3329(16)	−2634(19)	982(13)
C(13)	2862(15)	623(18)	−1248(12)
C(14)	2277(16)	192(19)	−2143(12)
C(15)	1234(17)	659(21)	−2560(13)
C(16)	690(18)	236(22)	−3372(13)
C(17)	1193(22)	−648(26)	−3792(14)
C(18)	2247(19)	−1095(22)	3445(13)
C(19)	2761(17)	−686(19)	−2597(13)

similarly in 60–70% yield (**2b**: found: C, 38.61; H, 2.80p N, 4.32. $C_{20}H_{17}N_2SCl_3Pt$ calcd.: C, 38.81; H, 2.75; N, 4.53%. **4a**: found: C, 36.49; H, 2.50; N, 4.32. $C_{19}H_{15}N_2SOCl_3Pt$ calcd.: C, 36.75; H, 2.42; N, 4.51%. **4b**: found: C, 37.64; H, 2.59; N, 4.37. $C_{20}H_{17}N_2SOCl_3Pt$ calcd.: 37.83; H, 2.68; N, 4.91%).

Reaction of [Pd(MeL^1)Cl] with chlorine

Chlorine gas was passed slowly into an acetonitrile solution (50 cm^3) of Pd(MeL^1)Cl (0.10 g, 0.22 mmol) for 0.5 h and the mixture then stirred for an additional 1 h. The orange yellow solution was evaporated in air and the residue washed thoroughly with water. The aqueous extract contained chloro-coordinated palladium(II). The residue from water was dissolved in dichloromethane (10 cm^3) and chromatographed on silica gel with benzene as eluent. An orange yellow band was collected and yielded 0.060 g (71%) of 2-(benzylthio)azo-*o*,*o*′-dichloro-*p*-toluene (found: C, 61.85; H, 3.90; N, 7.51. $C_{20}H_{16}N_2SCl_2$ calcd.: C, 62.03; H, 4.14; N, 7.24%).

X-Ray crystal structure and analysis

Crystals suitable for X-ray work were grown by slow diffusion of hexane into dichloromethane solutions at 298 K. Data collection was performed on a Nicolet

Table 7

Atomic coordinates (×10^4) for [Pt(MeL^2)Cl]

Atom	*x*	*y*	*z*
Pt	957(1)	212(1)	2304(1)
S	−393(6)	1445(4)	1573(5)
Cl	2272(7)	1131(4)	3445(5)
O(1)	105(17)	2235(9)	1043(11)
N(1)	101(20)	−1541(12)	1367(14)
N(2)	−169(20)	−631(13)	1377(14)
C(1)	1195(23)	−1777(16)	2009(16)
C(2)	1838(21)	−1061(15)	2675(15)
C(3)	2911(23)	−1346(17)	3339(15)
C(4)	3281(24)	−2318(22)	3427(20)
C(5)	2643(34)	−2997(20)	2821(21)
C(6)	1601(30)	−2749(17)	2067(22)
C(7)	4465(34)	−2579(22)	4253(24)
C(8)	−1287(22)	−250(19)	753(15)
C(9)	−1533(20)	708(15)	797(14)
C(10)	−2632(26)	1117(17)	155(18)
C(11)	−3457(24)	530(15)	−483(16)
C(12)	−3218(24)	−444(15)	−519(17)
C(13)	−2142(24)	−844(15)	112(16)
C(14)	−1485(22)	1993(15)	2359(15)
C(15)	−2129(23)	1290(13)	2932(16)
C(16)	−1488(26)	938(17)	3787(19)
C(17)	−2128(25)	331(18)	4388(17)
C(18)	−3477(27)	−2(17)	4035(19)
C(19)	−4124(25)	345(19)	3185(18)
C(20)	−3482(23)	967(15)	2631(16)

Table 8

Atomic coordinates ($\times 10^4$) for [Pd(MeL^1)Cl]

Atom	*x*	*y*	*z*
Pd	4503(1)	2471(1)	3274(1)
S	3325(1)	4281(2)	3281(1)
Cl	4222(2)	2264(2)	1766(1)
N(1)	5470(4)	1852(5)	5064(3)
N(2)	4748(4)	2590(5)	4570(3)
C(1)	5986(5)	1043(6)	4550(4)
C(2)	5668(5)	1099(6)	3616(4)
C(3)	6196(5)	275(6)	3130(4)
C(4)	6970(5)	658(6)	3537(4)
C(5)	7244(5)	−717(6)	4459(4)
C(6)	6762(5)	125(7)	4962(4)
C(7)	7526(6)	−1587(7)	3003(4)
C(8)	4151(5)	3502(6)	4990(3)
C(9)	3434(5)	4362(6)	4455(3)
C(10)	2870(6)	5286(6)	4830(4)
C(11)	2978(6)	5362(7)	5733(4)
C(12)	3678(6)	4494(7)	6256(4)
C(13)	4266(6)	3599(6)	5897(4)
C(14)	1669(5)	4053(6)	2876(4)
C(15)	1067(5)	3102(6)	3339(4)
C(16)	1127(6)	1883(7)	3125(4)
C(17)	528(7)	1023(7)	3520(5)
C(18)	−145(7)	1341(9)	4136(5)
C(19)	−217(6)	2532(10)	4385(5)
C(20)	392(6)	3439(8)	3979(4)

*R*3*m*/*V* automated diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Crystal data and data collection parameters are listed in Table 5.

Intensities were corrected for Lorentz and polarization effect. An empirical absorption correction was made on the basis of ψ-scans [29]. All calculations, data reduction, and structure solution were carried out on a MicroVAX II computer with the SHELXTL-PLUS programs [30]. The positions of metal atom in both [Pt(HL^1)Cl$_3$] and [Pt(MeL^2)Cl] were determined by heavy atom methods. All nonhydrogen atoms were located from subsequent difference Fourier maps. All nonhydrogen atoms were treated anisotropically for [Pt(HL^1)Cl$_3$]. For [Pt(MeL^2)Cl], the atoms within the coordination sphere and those constituting the *ortho*-metallated benzene ring were treated anisotropically. The structure of [Pd(MeL^1)Cl] was solved by direct methods and all the nonhydrogen atoms were refined anisotropically. For all three complexes hydrogen atoms were included at calculated positions with fixed thermal parameters. Atomic coordinates are collected in Tables 6–8.

Tables of H-atom coordinates and thermal parameters, complete lists of bond distances and angles, and lists of structure factors are available from the authors.

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