DALTON

Platinum(II), palladium(II), and nickel(II) thiosalicylate complexes

Louise J. McCaffrey, William Henderson,* Brian K. Nicholson,* Jane E. Mackay and Maarten B. Dinger

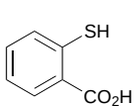
Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

A series of platinum(II), palladium(II) and nickel(II) complexes containing thiosalicylate ligands have been prepared by the reaction of $[MX_2L_2]$ complexes [X = halide or acetate; L or L_2 = ancillary neutral donor ligand such as a tertiary phosphine or cycloocta-1,5-diene (cod)] with thiosalicylic acid in methanol with added pyridine. Displacement of the cod ligand from $[Pt(SC_6H_4CO_2)(cod)]$ with phosphines and phosphites allows the synthesis of additional derivatives. The complexes $[Pt(SC_6H_4CO_2)(PPh_3)_2]$ and $[Ni(SC_6H_4CO_2)(dppp)]$ [dppp = 1,3-bis(diphenylphosphino)propane] have been the subjects of single-crystal X-ray diffraction studies. While both complexes contain the expected approximately square-planar metal co-ordination environments, the plane of the thiosalicylate ligand is inclined at an angle of 45.9° to the platinum co-ordination plane, but at only 9.4° to the nickel plane. The results of an electrospray mass spectrometry study of the thiosalicylate complexes and some related thioglycolate, 2-sulfanylpropionate and salicylate derivatives are discussed in terms of the stabilities of the complexes.

Thiolate ligands (RS^-) display a strong propensity for binding to soft metal centres, and there is a large amount of information on metal–thiolate complexes.[1] Thiolate ligands containing ancillary hard donor atoms (*e.g.* O and N) have attracted interest for their co-ordination chemistry[2] since the combination of hard and soft donor atoms provides a multitude of bonding opportunities to a wide range of transition-metal centres.[3] Thiol-containing amino acids, peptides and proteins are of importance for their ability to bind with metal-based drugs (such as cisplatin *cis*-$[Pt(NH_3)_2Cl_2]$ and auranofin),[4] while functionalised thiols [*e.g.* penicillamine (3-sulfanyl-D-valine)] are used to complex toxic heavy metals in chelation therapy. Platinum, palladium and nickel complexes with $Ph_2PCH_2CH_2EPh_2$ (E = P or As) and some carboxylic- and sulfonic-acid functionalised thiol and dithiol ligands have been studied for their anticancer activity.[5] Sulfanylacetic acid (thioglycolic acid, $HSCH_2CO_2H$) has also shown utility in the coupling of semiconductor TiO_2–PbS nanoparticles.[6]

Thiosalicylic acid (2-sulfanylbenzoic acid), **I**, is a potential source of such a heterodifunctional ligand but transition-metal complexes derived from it have not been investigated in any great detail,[7–9] though there has been recent interest in organometallic complexes.[10,11] Very few platinum, palladium or nickel complexes of the thiosalicylate ligand have been reported previously, and no X-ray structural determinations have been carried out. Some complexes of Pd and Pt containing the thiosalicylate dianion together with 1,10-phenanthroline or 2,2′-bipyridine (bipy) have been reported,[12,13] as have those containing two chelated thiosalicylate ligands;[14] such species in combination with hexylamine have been used as an extractive reagent for palladium analysis.[15]

In this paper we describe the syntheses of some new platinum(II), palladium(II) and nickel(II) complexes containing the thiosalicylate ligand, together with the crystal structures of two selected complexes, to explore the binding of the thiosalicylate ligand to metal centres of different sizes. We have also studied the thiosalicylate and some related complexes by the relatively new technique of electrospray mass spectrometry (ESMS), which provides useful information on the stabilities and fragmentation pathways for the various metallacyclic complexes.



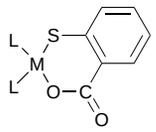
I

Results and Discussion

Syntheses

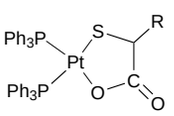
Reactions of the complexes *cis*-$[PtCl_2L_2]$ [L_2 = cycloocta-1,5-diene (cod), dppe; L = PPh_3], $[PdCl_2L_2]$ (L_2 = dppe or dppf; L = PPh_3) and $[NiX_2L_2]$ (L_2 = dppe or dppp; X = Cl or O_2CMe) with 1 mole equivalent of thiosalicylic acid in refluxing methanol with added pyridine base yields the thiosalicylate complexes of platinum **1a**–**1c**, palladium **2a**–**2c**, and nickel **3a**–**3c**, as given in Scheme 1 and the Experimental section. The complexes can be readily isolated, generally as microcrystalline solids, by the addition of water to the reaction mixture. This procedure generally yields pure products (as shown by microanalytical, NMR and ESMS data), since the by-product pyridinium chloride and excess of pyridine are readily removed. Successful alternative methods for synthesizing the triphenylphosphine platinum complex **1b** include the reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with **I** in dichloromethane, with an excess of either pyridine or silver(I) oxide as the base.

The accessibility of the labile cod complex **1a** allows the synthesis of a potentially large number of derivatives by ligand substitution; complexes **1c**–**1h** were prepared in order to demonstrate the general applicability of this route, and to prepare some additional complexes for ESMS study. In order to be able to compare the ESMS behaviour of the related five-membered $Pt(SCC(O)O)$ and six-membered $Pt(SCCC(O)O)$ ring systems, the related triphenylphosphine platinum complexes **4a** and **4b,** respectively containing doubly deprotonated thioglycolic acid and 2-sulfanylpropionic acid ligands were prepared by reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with the acid and pyridine in hot methanol. Complex **4a** has been prepared previously by an alternative route involving silver(I) oxide,[16] but **4b** has not been reported previously. The related platinum salicylate complex **5** was prepared in order to permit a direct comparison of the ESMS

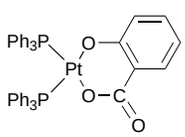


Compound	M	L or L-L
1a	Pt	cod
1b	Pt	PPh_3
1c	Pt	dppe
1d	Pt	dppm
1e	Pt	dppf
1f	Pt	$P(OPh)_3$
1g	Pt	$P(OPr^i)_3$
1h	Pt	pta
2a	Pd	dppe
2b	Pd	dppf
2c	Pd	PPh_3
3a	Ni	dppe
3b	Ni	dppp
3c	Ni	phen
3d	Ni	2 x phen

Scheme 1 Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane; dppm = bis(diphenylphosphino)methane; dppf = 1,1′-bis(diphenylphosphino)ferrocene; pta = triazaphosphaadamantane; phen = 1,10-phenanthroline; dppp = 1,3-bis(diphenylphosphino)propane



4a R = H
4b R = Me



5

properties of complexes containing chelating salicylate and thiosalicylate ligands. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with 1 mol equivalent of salicylic acid in refluxing CH_2Cl_2 with an excess of silver(I) oxide gave **5**; this complex does not appear to have been reported previously. Attempted preparation of **5** from salicylic acid in methanol with pyridine base was unsuccessful.

The thiosalicylate complexes **1**–**3** are all air-stable, and are generally soluble in polar chlorinated hydrocarbon solvents, moderately soluble in lower alcohols, but essentially insoluble in diethyl ether and aliphatic hydrocarbons. However, **1h**, containing triazaphosphaadamantane (pta) ligands is insoluble in methanol and chlorinated solvents, but is slightly soluble in water. Complexes of pta generally show appreciable water solubility, and are attracting considerable interest as a result.[17] The 1,10-phenanthroline complex **3c** shows rather low solubilities in all common solvents.

The platinum–thiosalicylate complexes are typically lemon-yellow to bright yellow, though the platinum–phosphite complexes are very pale yellow or colourless. The palladium and nickel complexes are orange and dark red respectively. The dppf complexes, as a result of the ferrocene moiety, are orange. Melting points and microanalytical data for the various complexes are given in Table 1. The phen nickel complex **3c** could not be obtained analytically pure, and its formulation is thus based upon mass spectrometric analysis. A high nitrogen content possibly suggests the presence of some residual pyridine, possibly co-ordinated.

Crystal structures of the platinum and nickel complexes 1b and 3b

The molecular structure of complex **1b** is shown in Fig. 1, together with the atom numbering scheme, while selected bond lengths and angles are given in Table 2. The molecular structure

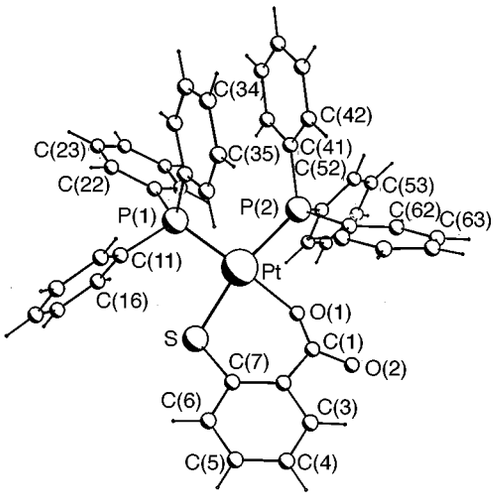


Fig. 1 Molecular structure and atom numbering scheme for $[Pt(SC_6H_4CO_2)(PPh_3)_2]$ **1b**

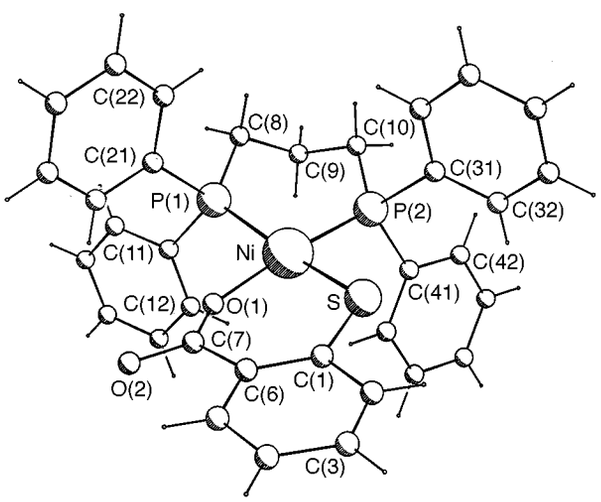


Fig. 2 Molecular structure and atom numbering scheme for $[Ni(SC_6H_4CO_2)(dppp)]$ **3b**

and numbering scheme for complex **3b** are given in Fig. 2, with bond lengths and angles in Table 3. These structures, the first of platinum-triad thiosalicylate complexes, consist of the expected square-planar metal co-ordination with two *cis* phosphine ligands. The thiosalicylate ligands are chelated to the metal *via* the S atom and one of the carboxylate oxygen atoms. However there is a striking difference between the two examples in the dihedral angles between the ligand plane and the co-ordination plane (see below).

For the platinum complex **1b** the co-ordination sphere shows only minor deviations from planarity, but with angles that differ considerably from 90° [*e.g.* P(1)–Pt–P(2) 100.5°, S–Pt–O(1) 84.7°] reflecting the relative bulk of the Ph_3P ligands and the natural bite of the thiosalicylate group. The anionic ligand itself is virtually planar except for a small twist about the C(1)–C(2) bond which displaces each of O(1) and O(2) *ca.* 0.3 Å from the plane. The Pt–P distance *trans* to the S atom is longer than that opposite the O atom, as expected from *trans*-influence considerations. The C(1)–O(1) distance (formally a single bond) is 1.125(8) Å, unexpectedly shorter than the non-co-ordinated C(1)–O(2) distance of 1.282(7) Å, which is longer than expected for a C=O bond. There is no obvious explanation for these observations and they are perhaps an artifact arising from the location of light atoms adjacent to a heavy Pt atom. For comparison, the same ligand attached *via* the same S,O fashion to manganese[10] showed C–O distances of 1.272(3) and 1.248(3) Å for the co-ordinated and non-co-ordinated oxygen

Table 1 Melting point, infrared spectroscopic and microanalytical data for the platinum, palladium and nickel thiosalicylate complexes

Complex	M.p. (°C)	$\tilde{\nu}_{max}$(C=O region)/cm^{-1}	Analysis (%)[a] C	H	N
1a[b]	Decomp. > 170[c]	1629vs	39.5 (39.55)	3.7 (3.55)	0.0 (0.0)
1b·0.33MeOH[b]	>230	1624vs, 1596m (sh)	58.1 (58.8)	4.05 (4.05)	0.0 (0.0)
1c[b]	174–177	1618w, 1593s, 1578m	51.55 (53.15)	3.85 (3.8)	0.0 (0.0)
1d[b]	>230	1600vs, 1582m	52.55 (52.55)	3.75 (3.6)	0.0 (0.0)
1e[d]	>230	1612s	*e*		
1f[d]	157–160	1624m, 1587m	52.2 (53.35)	3.75 (3.55)	0.3 (0.0)
1g[d]	170–172	1616m	39.1 (39.3)	6.05 (6.05)	0.0 (0.0)
1h[d]	>230	1597s	34.65 (34.5)	4.6 (4.25)	12.15 (12.7)
2a[f]	>230	1612w, 1578vs	58.3 (60.35)	4.45 (4.3)	0.0 (0.0)
2b[b]	Softens and melts > 180	1612vs, 1598s, 1572m (sh)	*e*		
2c[b]	203–205	1618vs, 1582w (sh)	65.95 (65.25)	4.25 (4.4)	0.0 (0.0)
3a·2MeOH[b]	169–173	1618s, 1601s, 1582m (sh)	62.55 (62.6)	4.55 (4.5)	0.0 (0.0)
3b[f]	228–230	1616m (sh), 1600vs	65.3 (65.5)	4.65 (4.85)	0.0 (0.0)
3c[b]	>230	1586m, 1570s	56.35 (58.35)	4.05 (3.1)	8.4 (7.15)
4a[b]	Not determined	1647s, 1617vs	Not determined		
4b[b]	>230	1647m, 1636s, 1618s	56.1 (56.85)	4.34 (4.15)	0.3 (0.0)
5	>230	1618vs, 1590m (sh)	60.05 (60.35)	4.05 (4.0)	0.0 (0.0)

[a] Calculated values are given in parentheses. [b] Prepared by reaction of metal halide or acetate in methanol with pyridine base. [c] With evolution of cod. [d] Prepared by ligand substitution from complex **1a**. [e] Could not be obtained analytically pure. [f] Sample for analysis recrystallised from CH_2Cl_2–diethyl ether.

Table 2 Selected bond lengths (Å) and angles (°) for $[Pt(SC_6H_4CO_2)(PPh_3)_2]$ **1b** with estimated standard deviations in parentheses

Pt–O(1)	2.109(3)	Pt–S	2.322(2)
Pt–P(1)	2.2501(11)	Pt–P(2)	2.3027(11)
C(1)–O(1)	1.125(8)	C(1)–O(2)	1.282(7)
C(1)–C(2)	1.515(8)	C(2)–C(3)	1.417(8)
C(3)–C(4)	1.351(10)	C(4)–C(5)	1.334(11)
C(5)–C(6)	1.357(10)	C(6)–C(7)	1.409(7)
C(2)–C(7)	1.396(7)	C(7)–S	1.778(6)
P(1)–Pt–P(2)	100.46(4)	P(1)–Pt–S	92.66(5)
P(2)–Pt–O(1)	82.15(10)	S–Pt–O(1)	84.73(10)
P(1)–Pt–O(1)	177.39(10)	P(2)–Pt–S	166.68(5)
Pt–S–C(7)	103.7(2)	Pt–O(1)–C(1)	135.8(4)
O(1)–C(1)–O(2)	123.9(6)	O(1)–C(1)–C(2)	121.6(6)
O(2)–C(1)–C(2)	114.4(7)	C(1)–C(2)–C(3)	117.3(6)
C(2)–C(3)–C(4)	121.9(7)	C(3)–C(4)–C(5)	120.3(8)
C(4)–C(5)–C(6)	120.8(7)	C(5)–C(6)–C(7)	121.7(7)
C(6)–C(7)–C(2)	117.7(5)	C(1)–C(2)–C(7)	124.9(6)
C(2)–C(7)–S	124.5(4)	C(6)–C(7)–S	117.9(4)

Table 3 Selected bond lengths (Å) and angles (°) for $[Ni(SC_6H_4CO_2)(dppp)]$ **3b** with estimated standard deviations in parentheses

Ni–O(1)	1.877(2)	Ni–S	2.1686(9)
Ni–P(1)	2.2198(9)	Ni–P(2)	2.1697(8)
C(7)–O(1)	1.290(4)	C(7)–O(2)	1.253(4)
C(6)–C(7)	1.500(5)	C(5)–C(6)	1.412(4)
C(4)–C(5)	1.393(5)	C(3)–C(4)	1.383(5)
C(2)–C(3)	1.375(5)	C(1)–C(2)	1.414(5)
C(1)–C(6)	1.404(4)	C(1)–S	1.754(3)
P(1)–Ni–P(2)	95.63(3)	P(1)–Ni–S	170.99(4)
P(2)–Ni–O(1)	170.73(7)	S–Ni–O(1)	95.11(7)
P(1)–Ni–O(1)	84.35(7)	P(2)–Ni–S	86.36(3)
Ni–S–C(1)	110.8(1)	Ni–O(1)–C(7)	138.4(2)
O(1)–C(7)–O(2)	119.2(3)	O(1)–C(7)–C(6)	121.7(3)
O(2)–C(7)–C(6)	118.9(3)	C(5)–C(6)–C(7)	116.6(3)
C(4)–C(5)–C(6)	121.2(3)	C(3)–C(4)–C(5)	119.5(3)
C(2)–C(3)–C(4)	120.1(3)	C(1)–C(6)–C(7)	121.7(7)
C(6)–C(7)–C(2)	117.7(5)	C(1)–C(2)–C(3)	121.8(3)
C(6)–C(1)–S	127.4(2)	C(2)–C(1)–S	114.1(2)

atoms respectively. However in the molybdenum examples $[Mo(SC_6H_4CO_2)_2O(N_2Ph_2)]$[7] and $[Mo(SC_6H_4CO_2)_2O_2]$[8] the co-ordinated and unco-ordinated C–O distances do not differ significantly from each other.

For the nickel example **3b** the overall structure is similar, though with a small twist from square-planar towards tetrahedral co-ordination giving a dihedral angle of 12.3° between the P(1)NiP(2) and SNiO(1) planes. The P(1)–Ni–P(2) angle is 95.63(3)° and the S–Ni–O(1) angle is 95.11(7)°. The thiosalicylate ligand is planar to within ±0.1 Å, and the C–O distances show the expected pattern with the co-ordinated oxygen atom involved in the longer bond [C(7)–O(1) 1.290(4) Å] while the free C(7)–O(2) bond is shorter [1.253(4) Å]. Similarly to the platinum complex, the longer Ni–P distance is *trans* to the S atom of the thiosalicylate ligand.

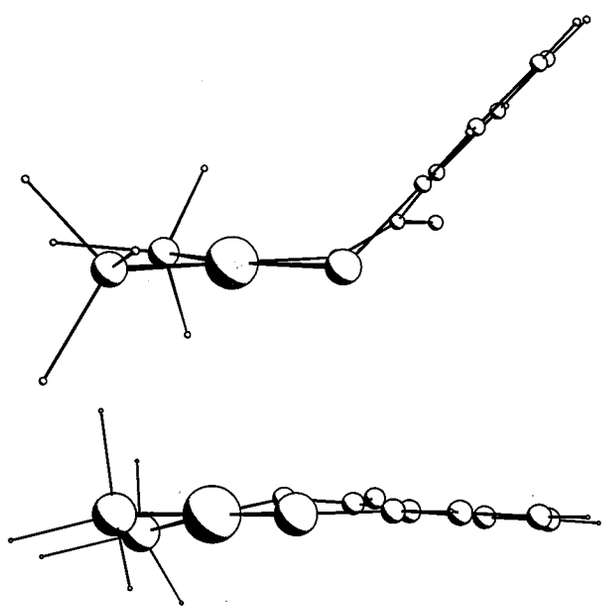


Fig. 3 A comparison of the relative orientation of the thiosalicylate ligands to the platinum (upper) and nickel (lower) co-ordination planes in **1b** and **3b** respectively. For clarity, only the phosphorus-bonded carbon atoms of the phosphine ligands are shown

A comparison of the thiosalicylate ligand in the two examples shows remarkable similarity, despite the different sizes of the metal atoms and the different conformations. In each case there is a relatively acute angle at S (103.7 **1b**, 110.8° **3b**) and a wider one at O (135.8 **1b**, 138.4° **3b**). For both, the S···O(1) 'bite' distance is 2.99 Å which suggests a somewhat rigid ligand, which does not alter to accommodate the different sized metals.

As mentioned above, the most obvious difference between the two complexes is the dihedral angle between the least-squares plane of the ligand and the co-ordination plane, 45.9° for the platinum example **1b** and 9.4° for the nickel example **3b**. This means that the platinum atom is displaced 1.24 Å from the thiosalicylate plane and the nickel atom 0.24 Å. These differences are shown in Fig. 3. If the difference in radii for platinum and nickel is taken as 0.08 Å (based on the difference in the M–P bond lengths) then the Pt–S and Pt–O bonds are apparently longer than expected, since they are 0.15 and 0.23 Å longer than the corresponding Ni–S and Ni–O ones. In the complex $[\overline{Mo(SC_6H_4CO_2)_2}O(N_2Ph_2)]$[7] there are two different thiosalicylate ligands, one coplanar with the co-ordination plane as in the nickel complex **3b**, and one slanted as in the platinum example **1b**. The Mo–S/O distances to the slanted ligand are significantly longer than those to the coplanar ligand, so non-coplanarity appears generally to lead to a less tightly held ligand. For the molybdenum example there are obvious intramolecular interactions leading to the observed conformation, but there is no equivalent explanation for the geometry of the platinum complex **1b**. Whether it is a solid-state effect arising in this particular example, or whether there is a more general cause related to the larger size of the Pt atom, will remain unresolved until a wider range of complexes incorporating the thiosalicylate ligand has been structurally characterised.

IR and NMR characterisation of thiosalicylate complexes

IR spectroscopic data are given in Table 1. All complexes show a strong band or bands due to the co-ordinated carboxylate group. The thiosalicylate complex $[\overline{Pt(SC_6H_4CO_2)}(bipy)]$ has been reported[12] to have a carboxylate stretch at 1680 cm^{-1}. In comparison, two dinuclear molybdenum complexes containing thiosalicylate ligands show ν(C=O) values of 1590 and 1594 cm^{-1}. The cod complex **1a** shows a single strong ν(C=O) stretch at 1629 cm^{-1}. The absence of an S–H vibration (which is at 2520 cm^{-1} for free thiosalicylic acid[12]) is in keeping with the presence of deprotonated co-ordinated thiolate groups in these complexes. The cod complex **1a** shows a weak C=C stretch at 1586 cm^{-1}, a strong C–O stretching band at 1308 cm^{-1}, together with an S–C stretch from the 1,2-disubstituted aromatic ring at 751 cm^{-1}.

The NMR spectroscopic properties of the complexes **1**–**3** are entirely consistent with their formulation as complexes of the thiosalicylate dianion. For the platinum complexes, the presence of the oxygen- and sulfur-donor groups having markedly different *trans* influences is reflected in the values of ^1J(PtP) for the phosphine and phosphite complexes, and in the values of ^1J(PtC) and ^2J(PtH) for the cod complex **1a**. Thus, in the ^{31}P-{^1H} NMR spectrum of the dppe complex **1c**, two resonances at δ 39.8 and 33.0 showing ^1J(PtP) couplings of 2862 and 3699 Hz are assigned to phosphine ligands *trans* to S and O donor atoms respectively. These coupling constants compare favourably with those of $[Pt(SPh)_2(dppe)]$ (3047 Hz)[18] and $[Pt(C_2O_4)(dppe)]$ (3628 Hz).[19] Comparison of **1b** with the triphenylphosphine platinum salicylate complex **5** readily illustrates the large difference in *trans* influences of the phenolate and thiolate groups, with the PPh_3 ligands *trans* to these moieties showing ^1J(PtP) values of 3549 and 2884 Hz respectively.

The other platinum complexes described in this paper show a similar disparity in the magnitudes of the coupling constants for phosphorus atoms *trans* to oxygen and sulfur atoms of the thiosalicylate ligand, and overall the values are similar to those of the related five-membered ring complexes **4a** and **4b**. The ^{31}P resonance at highest δ for the range of platinum complexes **1a**–**1h** and **4a**,**4b** is consistently for the phosphine *trans* to the thiolate ligand. Phosphine ligands in the palladium and nickel complexes (which lack the presence of a useful spin-active nucleus such as ^{195}Pt which gives direct structural information) were assigned on the same basis.

The cod complex **1a**, which contains no aryl protons other than those of the thiosalicylate ligand, was subjected to a full NMR assignment. Complete, unambiguous NMR assignments were made by a combination of HMBC (heteronuclear multiple bond correlation) (long-range), HMQC (heteronuclear multiple quantum coherence) (short-range) and one-dimensional nuclear Overhauser effect (NOE) experiments. Assignments of the aryl protons and carbons are given in the Experimental section. For **1a**, two cod CH and two cod CH_2 resonances were observed; the CH olefinic resonances appear in the ^1H spectrum at δ 5.67 and 4.93, showing couplings to ^{195}Pt of 49.73 and 66.45 Hz respectively. On the basis of these markedly different coupling constants, the resonances can be unambiguously assigned, with the resonance showing the larger coupling constant being *trans* to the carboxylate oxygen. Similarly, two cod CH resonances in the ^{13}C-{^1H} NMR spectrum, at δ 108.96 and 86.7, showing ^1J(PtC) values of 101.1 and 191.2 Hz, are assigned to CH groups *trans* to the sulfur and oxygen atoms respectively.

While the crystal structure determination of the triphenylphosphine complex **1b** revealed a highly non-planar platinum–thiosalicylate system, the ^1H NMR spectrum of the cod complex **1a** suggests that in solution the platinum–thiosalicylate ring system is undergoing ring inversion at room temperature, or is planar; the two possibilities cannot be distinguished. Thus, only two signals are observed for the cod CH groups, and two signals for the cod CH_2 groups (a conformationally rigid structure with a slanted ligand would display four of each). However, low-temperature ^1H NMR (230 K) spectroscopy did not help to distinguish the two possibilities, with negligible broadening of the original two cod CH resonances.

The co-ordinated carboxylate group appears in the ^{13}C-{^1H} NMR spectrum of the cod platinum complex **1a** at δ 166.5; coupling to ^{195}Pt could not be resolved. Similarly, for the phosphine complex **1b**, the carbonyl resonance (δ 168.0) also appeared as a broadened singlet.

Electrospray mass spectrometric study

Electrospray mass spectrometry (ESMS) is increasingly being used as a routine technique for studying a diverse range of inorganic complexes,[20] and we have been investigating the chemistry of a range of metal–thiolate compounds using ESMS.[21] Other metal–thiolate compounds of biochemical importance have also been studied,[22] including biologically active complexes of silver(I),[23] gold(I)[24] and platinum(II).[25] Studies of molybdenum and tungsten 1,2-dithiolene complexes,[26] and metal–dithiocarbamate and related complexes have also appeared.[27]

All of the thiosalicylate complexes described in this paper give excellent positive-ion ESMS spectra, yielding strong $[M + H]^+$ parent ions under a range of cone voltages, and, in most cases additional aggregate ions of the type $[2M + H]^+$ and $[3M + H]^+$. Complexes **1a** and **3a** were particularly noted to form intense aggregate ions, for the first case possibly a consequence of the sterically undemanding ligands permitting close association of molecules. Excellent agreement was observed between the observed and calculated isotope distribution patterns for all major ions. A typical spectrum, that for the dppe platinum complex **1c**, is shown in Fig. 4, together with a comparison of observed and calculated isotope patterns for the parent $[M + H]^+$ ion. At low to moderate cone voltages (20 and 50 V), simple $[M + H]^+$, $[2M + H]^+$ and $[3M + H]^+$ ions were observed, as illustrated in Fig. 4(*a*). Upon further increasing the cone voltage to 80 V, apart from the decreasing intensities of the aggregate ions, the major noticeable difference was the growth of a small ion ascribed to the decarboxylated complex $[M - CO_2 + H]^+$ (*m/z* 702). Decarboxylation of aryl carboxylic acids is a well known fragmentation pathway for this class of compound, and has been described previously in ion-

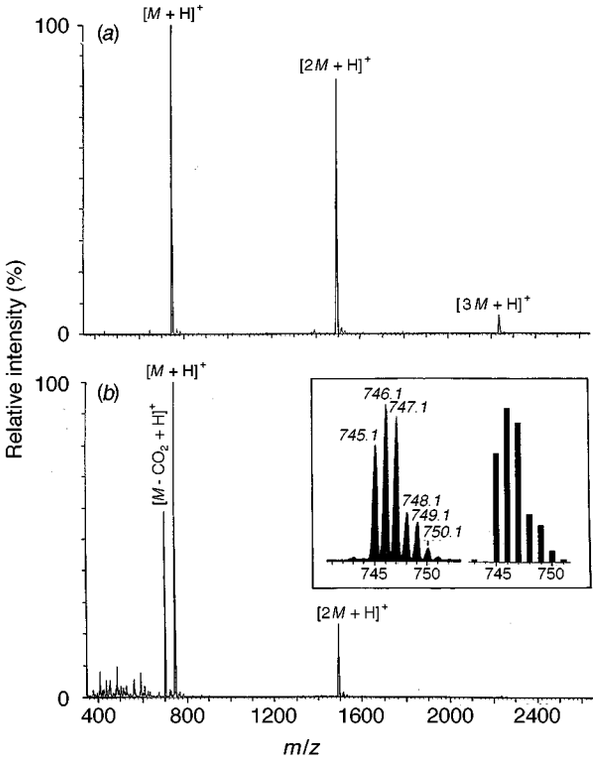


Fig. 4 Positive-ion ESMS spectrum of the dppe platinum thiosalicylate complex **1c** at cone voltages of (*a*) 50 V, showing the $[M + H]^+$ parent together with $[2M + H]^+$ and $[3M + H]^+$ 'aggregate' ions, and (*b*) 150 V, demonstrating the high stability of the complex. Partial fragmentation by decarboxylation is indicated by the $[M - CO_2 + H]^+$ ion at *m/z* 702. The inset shows a comparison of observed and calculated isotope distribution patterns for the $[M + H]^+$ ion

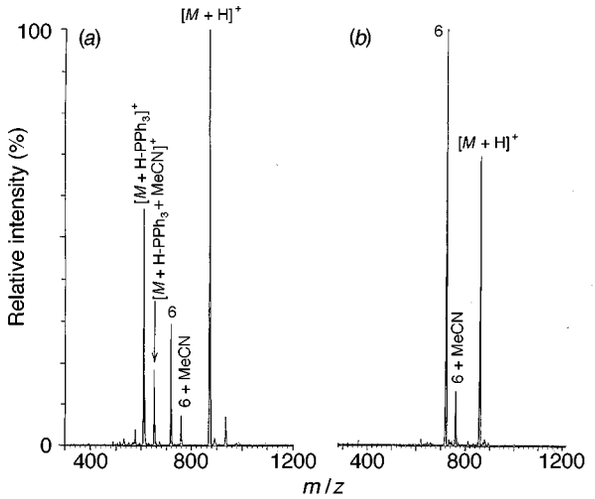
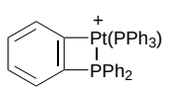


Fig. 5 Comparison of the ESMS spectra (cone voltage 80 V, *m/z* range 300–1200) for the triphenylphosphine platinum thiosalicylate (*a*) and salicylate (*b*) complexes **1b** and **5** respectively, indicating ion assignments, and showing the formation of the orthometallated species **6**. The spectra clearly show different fragmentation pathways and stabilities of the two related complexes



6

spray spectra.[28] At the very high cone voltage of 150 V, $[M + H]^+$ remained the most intense ion, followed by $[M - CO_2 + H]^+$ (59%) and $[2M + H]^+$ (23%), while a number of very minor ions were observed at *m/z* <600, Fig. 4(*b*). For the pta complex **1h** a simple spectrum, with little evidence for fragmentation, was observed at a cone voltage of 200 V, the maximum for the instrument employed. These observations indicate remarkable stability of these thiosalicylate complexes.

It is interesting to compare the triphenylphosphine platinum salicylate complex **5** and the thiosalicylate complex **1b** towards cone voltage-induced fragmentation. A comparison of the ESMS spectra of **5** and **1b** at a cone voltage of 80 V is shown in Fig. 5. For **5**, strong $[M + H]^+$ and weaker $[2M + H]^+$ ions are exclusively observed at 20 V, however increasing the cone voltage to 50 V begins to effect fragmentation and formation of the cyclometallated species **6**, observed previously when triphenylphosphine platinum complexes are subjected to high cone voltages.[29] At 80 V **6** is the most abundant ion. Only a very small ion is observed at *m/z* 812 at 80 V, corresponding to the decarboxylated species $[M + H - CO_2]^+$. However, for the thiosalicylate complex **1b** at 80 V, the $[M + H]^+$ ion remains the base peak; the most intense fragment ion is $[M + H - PPh_3]^+$ (*m/z* 610), formed by loss of the monodentate phosphine ligand and the ion **6** at *m/z* 718 is relatively weak (*ca.* 30% relative intensity). Since no PPh_3 loss is observed for the salicylate complex, it seems reasonable that it is the PPh_3 ligand *trans* to the (higher *trans* influence) S atom which is displaced.

The platinum–oxygen bonds in the salicylate complex **5** are expected to be weaker than the platinum–sulfur bond of **1b**; dissociation of a Pt–O bond will generate a vacant co-ordination site, promoting cyclometallation of one of the phosphine ligands. The different fragmentation routes for the dppe and triphenylphosphine complexes **1c** and **1b** respectively can also be rationalised in terms of the far greater difficulty for the chelated dppe ligand (when compared to PPh_3) to undergo cyclometallation of a phenyl ring. Decarboxylation thus provides the dominant fragmentation pathway for complex **1c** at very high cone voltages.

It is also interesting to compare the behaviour of the five-membered ring cyclic thiolate complexes **4a** and **4b** towards cone voltage-induced fragmentation. The spectra recorded at 80 V show generally similar behaviour to that of the salicylate complex **5**, with the cyclometallated species **6** (*m/z* 718) being the principal fragment ion, in association with its acetonitrile adduct at *m/z* 759. However ions formed by loss of a PPh_3 ligand were only of minor importance; for **4b** the ion $[M + H - PPh_3]^+$ was tentatively assigned as a weak ion at *m/z* 562. There is however one significant difference in the fragmentation behaviour of complexes **4** compared to those of the thiosalicylate **1b** and salicylate **5** complexes. For **4a** a relatively weak ion was observed at *m/z* 764, and a corresponding ion observed at *m/z* 778 for **4b**, indicating the presence of a CHR group (R = H or Me) in this fragment ion. The isotope distribution pattern clearly shows the species from **4a** to have *m/z* 764; the ion formed by simple decarboxylation, *viz.* $[\mathbf{4a} - CO_2 + H]^+$, would have *m/z* 766. While ESMS does not give direct structural information, one possibility for these species is that they are the cyclometallated complex **6**, but additionally containing CHRS ligands, which may be co-ordinated thioformaldehyde or thioacetaldehyde respectively, for R = H and Me. The absence of related ions for the thiosalicylate complex can be explained on the basis that formation of a C=S bond from the thiosalicylate ligand would necessarily result in loss of aromatic character of the phenyl ring of this group. Little appears to be known about platinum–thioformaldehyde species, though they have been observed as intermediates in the decomposition of MeSH on Pt(111) surfaces.[30] Thioformaldehyde co-ordinated to copper has been observed previously in ES studies of copper–amino acid complexes.[31]

The site of protonation in ESMS analyses of the various complexes described herein is undoubtedly one of the carboxylate oxygen atoms, most likely the carbonyl. Addition of a small quantity of KCl to the ESMS sample of the triphenylphosphineplatinum complex **1b** yields additional ions at *m/z* 910/911 and 1782, assigned as $[M + K]^+$ and $[2M + K]^+$

respectively, in the spectrum recorded at 20 V. Upon decreasing the cone voltage to 5 V, the intensity of the potassium adducts increased.

The ESMS technique can be used to identify impurities present in samples of the thiosalicylate complexes. The initial synthesis of the (phen)Ni complex **3c** used a 1:1 molar ratio of nickel to phen; the resulting product was isolated as brown microcrystals, poorly soluble in all common organic solvents and thus characterisation by NMR spectroscopy could not be readily achieved. The ESMS of this product (apparently 'insoluble' in the MeCN–water solvent mixture) showed peaks due to the expected $[M + H]^+$ and $[2M + H]^+$ ions, together with a peak at *m/z* 571 which is readily identified as the bis(phenanthroline) species $[Ni(SC_6H_4CO_2)(phen)_2 + H]^+$. However, attempted synthesis of this complex (**3d**) using appropriate mole ratios was unsuccessful, as evidenced by elemental microanalytical data. However the product did show increased amounts of **3d** in the ESMS spectrum. Thus it appears that a trace impurity of the more soluble **3d** in **3c** can be solubilised in ESMS studies.

Ligand-substitution reaction of complex 1b with 2,6-xylyl isocyanide

When complex **1b** is treated with an excess of 2,6-xylyl isocyanide in refluxing dichloromethane only one phosphine is replaced by isocyanide. Crystallisation by addition of light petroleum yielded a pale yellow microcrystalline solid which was shown by ^{31}P-{^{1}H} and ^{1}H NMR spectroscopy to be a mixture of isomers **7a** and **7b** in approximately 4:1 ratio. The major isomer **7a** [δ(^{31}P) 16.4] contains the phosphine *trans* to the thiolate ligand, with the characteristic value (see below) of ^1J(PtP) of 2535 Hz. The minor isomer **7b** [δ(^{31}P) 6.4] has the phosphine *trans* to carboxylate, with a correspondingly larger value of ^1J(PtP) (3605 Hz). The ^{1}H NMR spectrum of this mixture of isomers showed two methyl resonances of the isocyanide ligands (isomer **7a**, δ 2.00; **7b**, δ 2.02). No attempt has been made to separate these isomers.

Conclusion

A wide range of platinum(II), palladium(II) and nickel(II) complexes containing thiosalicylate dianion ligands can be conveniently prepared by reaction of the appropriate metal halide or acetate complex with thiosalicylic acid in methanol with pyridine base. Crystal structure analyses show that distinct conformational differences are possible for the thiosalicylate ligand in related compounds. Electrospray mass spectrometry provides a very rapid, convenient, and informative technique for probing the stabilities and fragmentation pathways for related complexes.

Experimental

General experimental procedures were similar to those described in other recent publications from these laboratories.[29] All complexes described in this work are air-stable, and reactions were carried out without regard for the exclusion of air. Methanol, diethyl ether and light petroleum (b.p. 40–60 °C) were LR grade, while dichloromethane was distilled from CaH_2 prior to use.

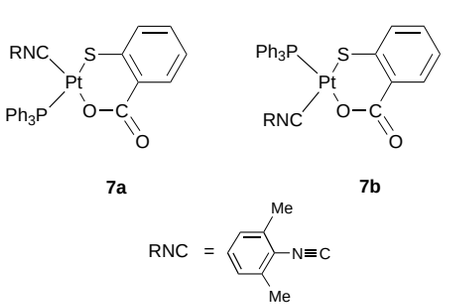
The following compounds were used as supplied from commercial sources: thiosalicylic acid (Sigma), triisopropyl phosphite, triphenyl phosphite, bis(diphenylphosphino)methane, 1,3-bis(diphenylphosphino)propane, and 1,1′-bis(diphenylphosphino)ferrocene (Aldrich), 2-sulfanylpropionic acid (thiolactic acid) (Koch-Light), thioglycolic acid, salicylic acid, nickel(II) acetate tetrahydrate and 1,10-phenanthroline monohydrate (BDH), and triphenylphosphine (Pressure Chemical Co.). Triazaphosphaadamantane was prepared by the literature procedure[32] and was a gift from Dr. K. Fisher, University of New South Wales, Australia. The complexes $[PtCl_2(cod)]$,[33] $[PdCl_2(cod)]$,[34] $[NiCl_2(dppe)]$,[35] 2,6-xylyl isocyanide[36] and 1,2-bis(diphenylphosphino)ethane[37] were prepared by the literature procedures. Phosphine complexes *cis*-$[PtCl_2(PPh_3)_2]$, $[PdCl_2(PPh_3)_2]$, $[PdCl_2(dppe)]$ and $[PdCl_2(dppf)]$ were prepared by substitution of the cod ligand of $[MCl_2(cod)]$ (M = Pt or Pd) with the stoichiometric amount of phosphine, in dichloromethane solution, followed by precipitation with light petroleum.[38] Other chemicals used in this work were of at least reagent grade and used as supplied.

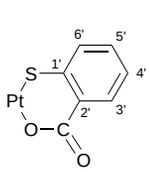
Electrospray mass spectra were recorded on a VG Platform II instrument in MeCN–water (1:1) solution, in positive-ion mode. Other ESMS experimental details were as described previously.[39] Confirmation of all species was accomplished by comparison of the observed and calculated isotope patterns, the latter being obtained by use of the ISOTOPE program.[40] The *m/z* values refer to the most intense peak (or peaks) in the isotope distribution pattern for that ion. The NMR spectra were recorded in $CDCl_3$ solution unless otherwise stated, on a Bruker AC300 spectrometer (^{1}H, 300.13; ^{13}C, 75.47; ^{31}P, 121.51 MHz). The HMBC, HMQC and NOE data for the cod complex **1a** were recorded in $CDCl_3$ solution on a Bruker DRX spectrometer at 400.13 MHz.

Microanalytical data (Campbell Microanalytical Laboratory, University of Otago), melting points (Reichert Thermovar hotstage apparatus) and selected IR spectroscopic data (Perkin-Elmer 1600 Series FTIR, KBr discs) for the various thiosalicylate complexes are presented in Table 1.

Syntheses

[Pt(SC$_6$H$_4$CO$_2$)(cod)] 1a. The complex $[PtCl_2(cod)]$ (279 mg, 0.746 mmol) and compound **I** (115 mg, 0.747 mmol) were mixed in methanol (20 cm^3), giving a yellow suspension. Pyridine (10 drops) was added, and the mixture refluxed for 20 min, giving a clear bright yellow solution. Water (80 cm^3) was added and the mixture allowed to crystallise. The lemon-yellow microcrystalline product was filtered off, washed with water (10 cm^3), diethyl ether (10 cm^3), and vacuum dried. Yield 212 mg, 62%. NMR: ^{1}H (400.13 MHz), δ 8.22 [dd, 1 H, H$^{3'}$, ^3J(H$^{3'}$H$^{4'}$) 7.74, ^4J(H$^{3'}$H$^{5'}$) 1.86], 7.34 [dd, 1 H, H$^{6'}$, ^3J(H$^{6'}$H$^{5'}$) 7.62, ^4J(H$^{6'}$H$^{4'}$) 1.39], 7.19 [td, 1 H, H$^{4'}$, ^3J(H$^{4'}$H$^{3'/5'}$) 7.28, ^4J(H$^{4'}$H$^{6'}$) 1.83], 7.15 [td, 1 H, H$^{5'}$, ^3J(H$^{5'}$H$^{4'/6'}$) 7.74, ^4J(H$^{5'}$H$^{3'}$) 1.46], 5.67 [s, br, 2 H, cod C*H*=CH *trans* S, ^1J(PtH) 49.73], 4.93 [s, br, 2 H, cod C*H*=CH *trans* O, ^1J(PtH) 66.45], 2.70–2.63 (*m*, 4 H, cod CH_2) and 2.41–2.28 (*m*, 4 H, cod CH_2); ^{13}C-{^{1}H} (75.47 MHz), δ 166.5 (s, C=O), 137.9 [s, C$^{1'}$, *J*(PtC) 22.9], 133.5 (s, C$^{3'}$), 130.8 [s, C$^{2'}$, ^3J(PtC) not discernible], 130.2 [s, C$^{6'}$, ^3J(PtC) 59.9], 130.1 (s, C$^{4'}$), 124.6 (s, C$^{5'}$), 109.0 [s, cod *C*H=CH *trans* S, ^1J(PtC) 101.1], 86.7 [s, cod *C*H=CH *trans* O, ^1J(PtC) 191.2], 31.3 (s, cod *C*H$_2$) and 28.6 (s, cod CH_2). ESMS (cone voltage 20 V); $[M + H]^+$ (*m/z* 456, 100), $[2M + H]^+$ (911, 62) and $[3M + H]^+$ (1366/1367, 7%).





[Pt(SC$_6$H$_4$CO$_2$)(PPh$_3$)$_2$] 1b·0.33MeOH. The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] (220 mg, 0.278 mmol) and compound **I** (43 mg, 0.279 mmol) in methanol (25 cm^3) with pyridine (10 drops) were refluxed for 20 min giving a clear bright yellow solution. After cooling and adding water (70 cm^3), the resulting lemon-yellow microcrystalline precipitate was filtered off and washed as above to give 207 mg (84%) of product, after vacuum drying. NMR: ^{31}P-{^{1}H}, δ 24.48 [d, PPh$_3$ *trans* S, ^1J(PtP) 2884, ^2J(PP) 22.3] and 10.15 [d, PPh$_3$ *trans* O, ^1J(PtP) 3899 Hz]; ^{13}C-{^{1}H}, δ 168.0 (s, C=O) and 140.4–123.4 (m, Ph). The complex crystallises with 0.33 mol of methanol per mol of complex, shown by ^{1}H NMR spectroscopy. ESMS: (cone voltage 20 V), [*M* + H]$^+$ (*m/z* 872, 100) and [2*M* + H]$^+$ (1744, 5); (cone voltage 80 V), [*M* + H − PPh$_3$]$^+$ (610, 28), [*M* + Na − PPh$_3$]$^+$ (632, 11), [*M* + H − PPh$_3$ + MeCN]$^+$ (651, 8), [**6**] (718, 12), [**6** + MeCN] (759, 2), [*M* + H]$^+$ (872, 100), [2*M* − PPh$_3$ + H]$^+$ (1481, 3) and [2*M* + H]$^+$ (1744, 18%); (with added KCl, cone voltage 20 V), [*M* + H]$^+$ (872), [*M* + K]$^+$ (910/911), [2*M* + H]$^+$ (1744) and [2*M* + K]$^+$ (1783).

Alternative syntheses. (*a*) The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] (400 mg, 0.506 mmol) and compound **I** (78 mg, 0.506 mmol) were dissolved in dichloromethane (30 cm^3) to give a cloudy colourless solution. Upon addition of pyridine (10 drops) the mixture rapidly yielded a clear bright yellow solution. Ethanol (30 cm^3) was added, and the mixture allowed to evaporate to dryness to yield a yellow crystalline solid which was washed with water (2 × 20 cm^3) and dried to give 408 mg (93%) of crude bright yellow crystalline product. The complex was recrystallised from dichloromethane–diethyl ether, yield 368 mg.

(*b*) To a solution of [PtCl$_2$(cod)] (120 mg, 0.321 mmol) in dichloromethane (10 cm^3) were added in succession, with stirring, triphenylphosphine (200 mg, 0.763 mmol), compound **I** (40 mg, 0.260 mmol) and silver(I) oxide (320 mg, excess). The mixture was refluxed for 2 h, cooled to room temperature, filtered to remove the silver salts, and the yellow filtrate evaporated to dryness. Recrystallisation from dichloromethane–light petroleum yielded 130 mg of crude product. Slow recrystallisation by diffusion of hexane into a chloroform solution gave well formed yellow crystals suitable for an X-ray diffraction study.

[Pt(SC$_6$H$_4$CO$_2$)(dppe)] 1c. The complex [PtCl$_2$(dppe)] (100.1 mg, 0.151 mmol) and compound **I** (21.2 mg, 0.138 mmol) in methanol (20 cm^3) with pyridine (10 drops) were refluxed for 20 min giving a clear pale yellow solution. Work-up as for **1a** gave **1c** as a pale yellow solid (67.3 mg, 66%). NMR: ^{31}P-{^{1}H}, δ 39.8 [d, P *trans* S, ^1J(PtP) 2861.9, ^2J(PP) 11.0] and 33.0 [d, P *trans* O, ^1J(PtP) 3698.7 Hz]. ESMS: (cone voltage 20 V), [*M* + H]$^+$ (*m/z* 746, 100), [2*M* + H]$^+$ (1491, 42%) and [3*M* + H]$^+$ (2237, 2%); (cone voltage 50 V), [*M* + H]$^+$ (746, 100), [2*M* + H]$^+$ (1491, 82) and [3*M* + H]$^+$ (2237, 6); (cone voltage 150 V), [*M* − CO$_2$ + H]$^+$ (702, 59), [*M* + H]$^+$ (746, 100) and [2*M* + H]$^+$ (1491, 23%). Spectra at cone voltages of 50 and 150 V are illustrated in Fig. 5.

[Pd(SC$_6$H$_4$CO$_2$)(dppe)] 2a. The complex [PdCl$_2$(dppe)] (232 mg, 0.403 mmol) and compound **I** (63 mg, 0.409 mmol) in methanol (25 cm^3) yielded a bright orange suspension. Pyridine (10 drops) was added and the mixture refluxed for 1 h. After cooling, water (70 cm^3) was added and the bright orange microcrystalline precipitate filtered off, washed with water (10 cm^3) and diethyl ether (10 cm^3), and dried. Yield 222 mg. NMR: ^{31}P-{^{1}H} [CDCl$_3$ plus 10% (CD$_3$)$_2$SO], δ 59.9 [d, P *trans* S, ^2J(PP) 28.3 Hz] and 45.4 (d, P *trans* O). ESMS (cone voltage 20 V); [*M* + H]$^+$ (*m/z* 657, 100), [2*M* + H]$^+$ (1315, 33) and [3*M* + H]$^+$ (1971, 2%). A sample for elemental analysis and m.p. determination was recrystallised as orange needles from CH$_2$Cl$_2$–diethyl ether.

[Pd(SC$_6$H$_4$CO$_2$)(dppf)] 2b. The complex [PdCl$_2$(dppf)] (50.9 mg, 0.070 mmol) and compound **I** (10.8 mg, 0.070 mmol) in methanol (20 cm^3) with pyridine (10 drops) yielded a deep orange solution. Work-up gave a deep orange solid product (20.3 mg, 36%). NMR: ^{31}P-{^{1}H}, δ 37.7 [d, PPh$_2$ *trans* S, ^2J(PP) 29.7 Hz] and 22.8 (d, PPh$_2$ *trans* O). ESMS (cone voltage 20 V): [*M* + H]$^+$ (*m/z* 813, 100) and [2*M* + H]$^+$ (1627, 23%).

[Pd(SC$_6$H$_4$CO$_2$)(PPh$_3$)$_2$] 2c. The complex [PdCl$_2$(PPh$_3$)$_2$] (200.3 mg, 0.285 mmol) with compound **I** (44.0 mg, 0.285 mmol) gave **2c** (143 mg, 64%) as a fine salmon-red powder. NMR: ^{31}P-{^{1}H}, δ 36.5 [d, PPh$_3$ *trans* S, ^2J(PP) 34.4 Hz] and 25.2 (d, PPh$_3$ *trans* O). ESMS (cone voltage 20 V): [*M* + H]$^+$ (*m/z* 783, 100) and [2*M* + H]$^+$ (1567, 5%).

[Ni(SC$_6$H$_4$CO$_2$)(dppe)] 3a. The complex [NiCl$_2$(dppe)] (110 mg, 0.208 mmol) and compound **I** (32 mg, 0.208 mmol) in methanol (15 cm^3) were treated with pyridine (10 drops) to give an orange-red solution, which was briefly brought to reflux. After cooling and adding water (40 cm^3) the deep red microcrystals were filtered off, washed with water (10 cm^3) and diethyl ether (10 cm^3) and dried. Yield 100 mg (79%). NMR: ^{31}P-{^{1}H}, δ 57.2 [d, P *trans* S, ^2J(PP) 59.5 Hz] and 42.1 (d, P *trans* O); ^{1}H, δ 8.11–6.98 (m, 24 H, Ph) and 2.42–2.03 (m, 4 H, dppe CH$_2$). ESMS (cone voltage 20 V): [*M* + H]$^+$ (*m/z* 609, 92), [2*M* + H]$^+$ (1219, 100) and [3*M* + H]$^+$ (1827, 5%).

[Ni(SC$_6$H$_4$CO$_2$)(dppp)] 3b. The complex Ni(O$_2$CMe)$_2$·4H$_2$O (179 mg, 0.719 mmol) and dppp (297 mg, 720 mmol) were dissolved in methanol (20 cm^3) with warming to give an orange-red solution. Compound **I** (111 mg, 721 mmol) was added, resulting in the formation of a deep blood-red solution. Pyridine (10 drops, excess) was added and the mixture briefly brought to reflux. After cooling, the deep brick-red microcrystals were filtered off, washed with cold methanol (2 cm^3) and diethyl ether (5 cm^3) and dried. Yield 440 mg (98%). NMR: ^{31}P-{^{1}H}, δ 18.8 [d, P *trans* S, ^2J(PP) 97.3 Hz] and 1.0 (d, P *trans* O). ESMS (cone voltage 20 V): [*M* + H]$^+$ (*m/z* 623, 100) and [2*M* + H]$^+$ (1247, 28%).

[Ni(SC$_6$H$_4$CO$_2$)(phen)] 3c. The complex Ni(O$_2$CMe)$_2$·4H$_2$O (294 mg, 1.193 mmol) and 1,10-phenanthroline monohydrate (234 mg, 1.181 mmol) were dissolved in methanol (30 cm^3) giving a light purple solution. Compound **I** (182 mg, 1.182 mmol) was added giving an immediate tan precipitate. After addition of pyridine (10 drops) and refluxing for 1 h the dark red-brown microcrystalline product was filtered off, washed with water (10 cm^3) and diethyl ether (10 cm^3) and dried. Yield 475 mg. ESMS (cone voltage 20 V): [*M* + H]$^+$ (*m/z* 391, 100), [**3d** + H]$^+$ (571, 59) and [2*M* + H]$^+$ (781, 19%).

Attempted preparation of [Ni(SC$_6$H$_4$CO$_2$)(phen)$_2$] 3d. Following the method above, using Ni(O$_2$CMe)$_2$·4H$_2$O (150.3 mg, 0.604 mmol), 1,10-phenanthroline monohydrate (239.2 mg, 1.207 mmol) and compound **I** (93.4 mg, 0.606 mmol) gave a deep brown solution upon addition of pyridine and refluxing for 20 min. Addition of water (80 cm^3) gave a dark brown solid which was filtered off, washed and dried as above to give 113.1 mg of product. Elemental microanalysis gave values (C, 56.45; H, 4.0; N, 8.4%) identical to those given for complex **3c** (Table 1). ESMS (cone voltage 20 V): [*M* + H]$^+$ as the base peak (*m/z* 571); [**3c** + H]$^+$ (391) and [(**3c**)$_2$ + H]$^+$ (781) also observed with intensities around 20%.

[Pt(SCH$_2$CO$_2$)(PPh$_3$)$_2$] 4a. The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] (259 mg, 0.328 mmol) was suspended in methanol (20 cm^3), thioglycolic acid (eight drops, excess) and pyridine (10 drops) added, and the mixture refluxed for 1 h to give a pale yellow suspension. Water (50 cm^3) was added, and the product filtered

off, washed with water (10 cm^3), diethyl ether (10 cm^3) and dried to give a pale yellow powder. Yield 236 mg (89%). NMR: ^{31}P-{^{1}H}, δ 22.1 [d, Ph_3P *trans* S, ^1J(PtP) 2868, ^2J(PP)] and 12.1 [d, PPh_3 *trans* O, ^1J(PtP) 3766]; lit.,[16] ^1J(PtP) 2898 and 3743 Hz. ESMS (cone voltage 20 V): $[M + H]^+$ (*m/z* 810, 100) and $[2M + H]^+$ (1620, 14); (cone voltage 80 V), [**6**] (718, 40), [**6** + MeCN] (759, 31), [**6** + H_2CS] (764, 15), $[M + H]^+$ (810, 100) and $[2M + H]^+$ (1620, 38%).

[Pt(SCHMeCO$_2$)(PPh$_3$)$_2$] 4b. Following an analogous procedure for the synthesis of **4a** above, complex **4b** was formed as a pale yellow microcrystalline solid in 82% yield. NMR: ^{31}P-{^{1}H}, δ 22.2 [d, PPh_3 *trans* S, ^1J(PtP) 2849, ^2J(PP) 22.2] and 12.5 [d, PPh_3 *trans* O, ^1J(PtP) 3790]; ^{1}H, δ 7.54–7.11 (m, 30 H, PPh_3), 3.76 [q, 1 H, CH, ^3J(HH) 7.16], and 1.49 [d, 3 H, Me, ^3J(HH) 7.16 Hz]. ESMS (cone voltage 20 V), $[M + H]^+$ (*m/z* 824, 100) and $[2M + H]^+$ (1648, 14); (cone voltage 80 V, *m/z* 500–1000), $[M + H - PPh_3]^+$ (562, 9), [**6**] (718, 100), [**6** + MeCN] (759, 23), [**6** + MeCHS] (778, 9), $[M + H]^+$ (824, 100%).

[Pt(OC$_6$H$_4$CO$_2$)(PPh$_3$)$_2$] 5. The complex *cis*-[$PtCl_2(PPh_3)_2$] (200 mg, 0.253 mmol) with salicylic acid (35 mg, 0.254 mmol) in dichloromethane (30 cm^3) and an excess of silver(I) oxide were refluxed for 3 h. Filtration to remove silver salts gave a very pale yellow solution, which was evaporated to dryness and the residue recrystallised twice from dichloromethane–light petroleum to give off-white microcrystals of **5** (148 mg, 69%). NMR: ^{31}P-{^{1}H}, δ 13.4 [d, PPh_3 *trans* CO_2, ^1J(PtP) 3929.1, ^2J(PP) 26.9] and 7.6 [d, PPh_3 *trans* O, ^1J(PtP) 3549.0 Hz]. ESMS: (cone voltage 20 V), $[M + H]^+$ (*m/z* 856, 100) and $[2M + H]^+$ (1712, 13); (cone voltage 50 V), $[\mathbf{6}]^+$ (718, 21), [**6** + MeCN] (759, 3), $[M + H]^+$ (856, 100) and $[2M + H]^+$ (1712, 47); (cone voltage 80 V), [**6**] (718, 100), [**6** + MeCN] (759, 13), $[M + H]^+$ (856, 70) and $[2M + H]^+$ (1712, 24%).

Ligand displacement reactions of [Pt(SC$_6$H$_4$CO$_2$)(cod)] 1a: general method

Complex **1a** and the potential ligand were dissolved in a small quantity of dichloromethane (*ca.* 0.5–1 cm^3), and the mixture swirled to dissolve the reactants. Sufficient light petroleum was slowly added to effect crystallisation of the product. The supernatant was removed by a Pasteur pipette, the solid washed with a small quantity of light petroleum, and dried. For the pta complex methanol was used as the solvent; the product crystallised spontaneously and was washed with light petroleum to remove cod.

With triphenylphosphine. Complex **1a** (25 mg, 0.055 mmol) and PPh_3 (29 mg, 0.111 mmol) gave **1b** as bright yellow crystals (45 mg, 94%). The identity and purity of the product was confirmed by ^{31}P-{^{1}H} NMR spectroscopy.

With dppe. Complex **1a** (40.1 mg, 0.088 mmol) with dppe (41.1 mg, 0.103 mmol) gave **1c** as a pale yellow powder (58.0 mg, 88%). The identity and purity of the product was confirmed by ^{31}P-{^{1}H} NMR spectroscopy.

With dppm. Complex **1a** (40.1 mg, 0.088 mmol) with dppm (33.8 mg, 0.088 mmol) gave **1d** as a pale yellow powder (59.3 mg, 92%). NMR: ^{31}P-{^{1}H}, δ −48.8 [d, PPh_2 *trans* S, ^1J(PtP) 2372.6, ^2J(PP) 73.4] and −55.2 [d, PPh_2 *trans* O, ^1J(PtP) 3180.5]; ^{1}H, δ 8.26–7.05 (m, 24 H, Ph) and 4.32 [t, CH_2, dppm, *J*(PH) 10.9 Hz, *J*(PtH) not resolved]. ESMS (cone voltage 20 V): $[M + H]^+$ (*m/z* 732, 100), $[M + Na]^+$ (754, 7), $[3M + Na + H]^{2+}$ (1109, 5, assignment tentative), $[2M + H]^+$ (1463, 57) and $[2M + Na]^+$ (1485, 5%).

With dppf. Complex **1a** (40.1 mg, 0.088 mmol) with dppf (48.8 mg, 0.088 mmol) gave **1e** as an orange crystalline solid (65.9 mg, 83%). NMR: ^{31}P-{^{1}H}, δ 22.0 [d, PPh_2 *trans* S, ^1J(PtP) 2947.1, ^2J(PP) 22.9] and 9.4 [d, PPh_2 *trans* O, ^1J(PtP) 3962.5 Hz]; ^{1}H, δ 7.94–6.96 (m, 24 H, Ph), 5.29 (s, 1 H, CH_2Cl_2), 4.56 (m, 2 H, C_5H_4), 4.44 (s, br, 2 H, C_5H_4), 4.29 (s, br, 2 H, C_5H_4), 3.89 (m, 2 H, C_5H_4). ESMS: (cone voltage 20 V), $[M + H]^+$ (*m/z* 902, 100), $[3M + 2NH_4]^{2+}$ (1370, 5), $[2M + H]^+$ (1804, 24) and $[2M + NH_4]^+$ (1821, 5); (cone voltage 80 V), $[M + H]^+$ (902, 100) and $[2M + H]^+$ (1804, 38%).

With triphenyl phosphite. Complex **1a** (42 mg, 0.092 mmol) with triphenyl phosphite (five drops, excess) gave pale yellow crystals of **1f** (75 mg, 84%). NMR: ^{31}P-{^{1}H}, δ 91.0 [d, P *trans* S, ^1J(PtP) 4520.6, ^2J(PP) 55.0] and 58.8 [d, P *trans* O, ^1J(PtP) 6071.9 Hz]. ESMS (cone voltage 20 V): $[M + H]^+$ (*m/z* 968, 100) and $[2M + H]^+$ (1936, 15%).

With triisopropyl phosphite. Complex **1a** (100 mg, 0.219 mmol) with triisopropyl phosphite (five drops, excess) gave colourless needles of **1g** (53 mg, 32%). NMR: ^{31}P-{^{1}H}, δ 91.3 [d, P *trans* S, ^1J(PtP) 4603, ^2J(PP) 48.7] and 59.6 [d, P *trans* O, ^1J(PtP) 5928 Hz]; ^{1}H, δ 8.05–7.00 (m, 4 H, Ph), 5.01 [m, 6 H, CH, $P(OPr^i)_3$] and 1.37 [t, 18 H, Me, $P(OPr^i)_3$]. ESMS (cone voltage 20 V): $[M + H]^+$ (*m/z* 764, 100) and $[2M + H]^+$ (1527, 13%).

With pta. Complex **1a** (23.2 mg, 0.051 mmol) with pta (16.1 mg, 0.102 mmol) in methanol gave **1h** as a pale yellow microcrystalline solid (25.9 mg, 77%). ^{31}P-{^{1}H} NMR [$(CD_3)_2SO$ + 10% water], δ −49.6 [d, P *trans* S, ^1J(PtP) 2612, ^2J(PP) 25.1] and −63.9 [d, P *trans* O, ^1J(PtP) 3525 Hz]. ESMS: (cone voltage 60 V), $[M + H]^+$ (*m/z* 662, 100), $[2M + H]^+$ (1323, 70), plus unidentified ion at *m/z* 338; (cone voltage 200 V), $[M + H]^+$ (662, 100), $[2M + H]^+$ (1323, 38%), with several minor ions all with intensities < 10% of $[M + H]^+$.

Preparation of isomers of [Pt(SC$_6$H$_4$CO$_2$)(PPh$_3$)(CNC$_6$H$_3$Me$_2$-2,6)] 7

A solution of complex **1b** (40.6 mg, 0.047 mmol) and 2,6-$Me_2C_6H_3NC$ (12.1 mg, 0.092 mmol) in dichloromethane (*ca.* 20 cm^3) was refluxed for 45 min. Addition of light petroleum (*ca.* 70 cm^3) followed by slow evaporation at room temperature caused the crystallisation of 12.8 mg (37%) of pale yellow microcrystals. ^{31}P-{^{1}H} NMR showed the presence of two compounds containing a single PPh_3 ligand, δ 16.4 [^1J(PtP) 2535] and 6.4 [^1J(PtP) 3605 Hz], due to PPh_3 ligands *trans* to S and O respectively, in isomers **7a** and **7b**. ESMS (cone voltage 20 V): $[Ph_3PO + H]^+$ (*m/z* 279, 20), $[M + H]^+$ (741, 100) and $[2M + H]^+$ (1481, 78%).

Crystallography

Yellow crystals of complex **1b** were obtained from the slow diffusion of hexane into a $CHCl_3$ solution, and red crystals of **3b** formed on slow evaporation of a $CDCl_3$ solution. Preliminary precession photography indicated both formed crystals of monoclinic symmetry. The unit-cell dimensions and intensity data were obtained on a Siemens SMART diffractometer. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS.[41]

The structures were solved by automatic interpretation of a Patterson map[42] and developed routinely. In the final cycles of least-squares refinement based on F^2 against all data all non-hydrogen atoms were treated anisotropically and hydrogen atoms were included in their calculated positions.[43]

Crystal data and refinement for complex 1b. $C_{43}H_{34}O_2P_2PtS$, M_r 871.79, monoclinic, space group $P2_1/n$, $a = 11.4545(2)$, $b = 18.2049(3)$, $c = 17.2872(3)$ Å, $\beta = 91.750(1)°$, $U = 3603.2(1)$ Å^3, $D_c = 1.607$ g cm^{-3}, $Z = 4$, $F(000)$ 1728, μ(Mo-Kα) = 4.078 mm^{-1}. Crystal size 0.28 × 0.20 × 0.14 mm.

A total of 22 044 reflections were collected at 291 K in the range $1.6 < \theta < 28.2°$, corresponding to 8096 unique data ($R_{int} = 0.0328$), $T_{max,min}$ 0.6655, 0.4918. The refinement converged with $R1 = 0.0353$ [for 6817 data with $I > 2\sigma(I)$], $R1 = 0.0477$, $wR2$ 0.0763, goodness of fit 1.100 (all data). The largest features in a final difference map were +1.118 and −0.779 e Å^{-3}.

Crystal data and refinement for complex 3b. $C_{34}H_{30}NiO_2P_2S\cdot 0.66CDCl_3$, M_r 623.32 (excluding solvent of crystallisation), monoclinic, space group $P2_1/n$, $a = 15.5756(1)$, $b = 13.5031(1)$, $c = 16.2162(1)$ Å, $\beta = 104.377(1)°$, $U = 3303.76(3)$ Å^3, $D_c = 1.396$ g cm^{-3}, $Z = 4$, $F(000)$ 1432, μ(Mo-Kα) = 0.94 mm^{-1}. Crystal size 0.80 × 0.76 × 0.18 mm.

A total of 19 054 reflections were collected at 203 K in the range $1.6 < \theta < 28.2°$, corresponding to 7646 unique data ($R_{int} = 0.0425$), $T_{max,min}$ 0.9024, 0.6321. The refinement was complicated by disorder of the $CDCl_3$ of crystallisation, which was modelled as four half-weighted chlorine atoms. Convergence gave $R1 = 0.0533$ [for 5385 data with $I > 2\sigma(I)$], $R1 = 0.0824$, $wR2$ 0.1509, goodness of fit 1.025 (all data). The largest features in a final difference map were +1.033 and −0.617 e Å^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc.*, *Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/538.

Acknowledgements

The University of Waikato and the New Zealand Lottery Grants Board are acknowledged for financial support of this work. We thank Assoc. Professor C. E. F. Rickard and Dr. L. J. Baker (University of Auckland) for collection of the X-ray data sets, Johnson-Matthey plc for a generous loan of platinum metal salts, and Wendy Jackson for technical assistance. Dr. R. A. Thomson is thanked for literature searches and the low-temperature proton NMR spectrum.

References

1 J. R. Dilworth and J. Hu, *Adv. Inorg. Chem.*, 1993, **40**, 411; P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121; I. G. Dance, *Polyhedron*, 1986, **5**, 1037.
2 C. G. Kuehn and S. S. Isied, *Prog. Inorg. Chem.*, 1980, **27**, 153.
3 D. D. Perrin and I. G. Sayce, *J. Chem. Soc. A*, 1967, 82; L. F. Larkworthy and D. Sattari, *J. Inorg. Nucl. Chem.*, 1980, **42**, 551; J.-C. Shi, T.-B. Wen, Y. Zheng, S.-J. Zhong, D.-X. Wu, Q.-T. Liu, B.-S. Kang, B.-M. Wu and T. C. W. Mak, *Polyhedron*, 1997, **16**, 369; N. Ueyama, K. Taniuchi, T. Okamura, A. Nakamura, H. Maeda and S. Emura, *Inorg. Chem.*, 1996, **35**, 1945; S.-J. Chang, H.-J. Liu, C.-T. Chen, W.-E. Shih, C.-C. Lin and H.-M. Gau, *J. Organomet. Chem.*, 1996, **523**, 47; M. Köckerling and G. Henkel, *Chem. Ber.*, 1993, **126**, 951; T. Kiss, P. Buglyó, G. Micera, A. Dessi and D. Sanna, *J. Chem. Soc., Dalton Trans.*, 1993, 1849; W. Clegg, N. Duran, K. A. Fraser, P. González-Duarte, J. Sola and I. C. Taylor, *J. Chem. Soc., Dalton Trans.*, 1993, 3453.
4 E. L. M. Lempers and J. Reedijk, *Adv. Inorg. Chem.*, 1991, **37**, 175; K. A. Mitchell and C. M. Jensen, *Inorg. Chem.*, 1995, **34**, 4441; D. H. Brown and W. E. Smith, *Chem. Soc. Rev.*, 1980, **9**, 217.
5 P. S. Jarrett, O. M. N. Dhubhghaill and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, 1993, 1863.
6 Y. Sun, E. Hao, X. Zhang, B. Yang, M. Gao and J. Shen, *Chem. Commun.*, 1996, 2381.
7 J. Li-Kao, O. Gonzalez, R. Mariezcurrena, R. Baggio, M. T. Garland and D. Carrillo, *Acta Crystallogr., Sect. C*, 1995, **51**, 2486.
8 J. Li-Kao, O. Gonzalez, R. F. Baggio, M. T. Garland and D. Carillo, *Acta Crystallogr., Sect. C*, 1995, **51**, 575.
9 See, for example, S. Mitra, H. Biswas and P. Bandyopadhyay, *Polyhedron*, 1997, **16**, 447; J. S. Bashkin, J. C. Huffman and G. Christou, *J. Am. Chem. Soc.*, 1986, **108**, 5038; M. E. Bodini and M. A. Del Valle, *Polyhedron*, 1990, **9**, 1181; K. Hegetschweiler, T. Keller, M. Baumle, G. Rihs and W. Schneider, *Inorg. Chem.*, 1991, **30**, 4342.
10 C. V. Depree, L. Main, B. K. Nicholson and K. Roberts, *J. Organomet. Chem.*, 1996, **517**, 201.
11 E. W. Ainscough, A. M. Brodie, R. K. Coll, A. J. A. Mair and J. M. Waters, *J. Organomet. Chem.*, 1996, **509**, 259; W. Schneider, A. Bauer and H. Schmidbaur, *Organometallics*, 1996, **15**, 5445.
12 L. Kumar, K. H. Puthraya and T. S. Srivastava, *Inorg. Chim. Acta*, 1984, **86**, 173.
13 S. Shukla, S. S. Kamath and T. S. Srivastava, *J. Photochem. Photobiol. A*, 1989, **47**, 287; A. K. Paul, R. Venkatesen and T. S. Srivastava, *J. Photochem. Photobiol. A*, 1991, **56**, 399; K. H. Puthraya and T. S. Srivastava, *J. Indian Chem. Soc.*, 1985, **62**, 843.
14 C. Nair and H. L. Nigam, *Indian J. Chem.*, 1974, **12**, 769.
15 A. K. Chhakkar and L. R. Kakkar, *Fresenius, Z. Anal. Chem.*, 1993, **347**, 483.
16 R. D. W. Kemmitt, S. Mason, J. Fawcett and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1993, 1165.
17 F. Joó, L. Nádasdi, A. Cs. Bényei and D. J. Darensbourg, *J. Organomet. Chem.*, 1996, **512**, 45; D. J. Darensbourg, N. W. Stafford, F. Joó and J. H. Reibenspies, *J. Organomet. Chem.*, 1995, **488**, 99; D. J. Darensbourg, F. Joó, M. Kannisto, A. Kathó, J. H. Reibenspies and D. J. Daigle, *Inorg. Chem.*, 1994, **33**, 200.
18 C. Eaborn, K. J. Odell and A. Pidcock, *J. Organomet. Chem.*, 1979, **170**, 105.
19 G. K. Anderson and G. J. Lumetta, *J. Organomet. Chem.*, 1985, **295**, 257.
20 C. E. C. A. Hop and R. Bakhtiar, *J. Chem. Educ.*, 1996, **73**, A162; R. Colton, A. D'Agostino and J. C. Traeger, *Mass Spectrom. Rev.*, 1995, **14**, 79.
21 G. A. Bowmaker, I. G. Dance, R. K. Harris, W. Henderson, I. Laban, M. L. Scudder and S.-W. Oh, *J. Chem. Soc., Dalton Trans.*, 1996, 2381; T. Løver, G. A. Bowmaker, W. Henderson and R. P. Cooney, *Chem. Commun.*, 1996, 683; W. Henderson, C. O. Miles and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1995, 889.
22 A. J. Canty, R. Colton, A. D'Agostino and J. C. Traeger, *Inorg. Chim. Acta*, 1994, **223**, 103; X. Yu, M. Wojciechowski and C. Fenselau, *Anal. Chem.*, 1993, **65**, 1355.
23 K. Nomiya, Y. Kondoh, H. Nagano and M. Oda, *J. Chem. Soc., Chem. Commun.*, 1995, 1679.
24 H. E. Howard-Lock, D. J. LeBlanc, C. J. L. Lock, R. W. Smith and Z. Wang, *Chem. Commun.*, 1996, 1391.
25 A. Bernareggi, L. Torti, R. M. Facino, M. Carini, G. Depta, B. Casetta, N. Farrell, S. Spadacini, R. Ceserani and S. Tognella, *J. Chromatogr. B*, 1995, **669**, 247.
26 P. Falaras, C.-A. Mitsopoulou, D. Argyropoulos, E. Lyris, N. Psaroudakis, E. Vrachnou and D. Katakis, *Inorg. Chem.*, 1995, **34**, 4536.
27 A. M. Bond, R. Colton, Y. A. Mah and J. C. Traeger, *Inorg. Chem.*, 1994, **33**, 2548; A. M. Bond, R. Colton, D. A. Fiedler, J. E. Kevekordes, V. Tedesco and T. F. Mann, *Inorg. Chem.*, 1994, **33**, 5761; R. Colton, J. C. Traeger and V. Tedesco, *Inorg. Chim. Acta*, 1993, **210**, 193; A. M. Bond, R. Colton, A. D'Agostino, J. Harvey and J. C. Traeger, *Inorg. Chem.*, 1993, **32**, 3952; A. M. Bond, R. Colton, J. C. Traeger and J. Harvey, *Inorg. Chim. Acta*, 1993, **212**, 233; T. J. Cardwell, R. Colton, N. Lambropoulos, J. C. Traeger and P. J. Marriott, *Anal. Chim. Acta*, 1993, **280**, 239.
28 K. W. M. Siu, G. J. Gardner and S. S. Berman, *Org. Mass Spectrom.*, 1989, **24**, 931.
29 J. Fawcett, W. Henderson, R. D. W. Kemmitt, D. R. Russell and A. Upreti, *J. Chem. Soc., Dalton Trans.*, 1996, 1897; W. Henderson, J. Fawcett, R. D. W. Kemmitt, P. McKenna and D. R. Russell, *Polyhedron*, 1997, **16**, 2455.
30 R. J. Koestner, J. Stohr, J. L. Gland, E. B. Kollin and F. Sette, *Chem. Phys. Lett.*, 1985, **120**, 285.
31 C. L. Gatlin, F. Turecek and T. Vaisar, *J. Mass Spectrom.*, 1995, **30**, 1617.
32 D. J. Daigle, A. B. Peppermann, jun. and S. L. Vail, *J. Heterocycl. Chem.*, 1974, **17**, 407.
33 J. X. McDermott, J. W. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
34 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 52.
35 G. Booth and J. Chatt, *J. Chem. Soc.*, 1965, 3238.
36 I. Ugi, R. Meyr, M. Lipinski, F. Bodesheim and F. Rosendahl, *Org. Synth.*, 1973, **Coll. Vol. V**, 300.
37 J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.

38 G. K. Anderson, H. C. Clark and J. A. Davies, *Inorg. Chem.*, 1981, **20**, 3607.
39 W. Henderson and G. M. Olsen, *Polyhedron*, 1996, **15**, 2105.
40 L. J. Arnold, *J. Chem. Educ.*, 1992, **69**, 811.
41 R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.
42 G. M. Sheldrick, SHELXS 86, Program for solving crystal structures, University of Göttingen, 1986
43 G. M. Sheldrick, SHELXL 93, Program for refining crystal structures, University of Göttingen, 1993.

Received 24*th February* 1997; *Paper* 7/01294B