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Inorganica Chimica Acta 346 (2003) 7–11
Inorganica Chimica Acta
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Hydrogen-bonded adducts formed from platinum(II) and palladium(II) thiosalicylate complexes $[(Ph_3E)_2M(SC_6H_4CO_2)]$ (E = P, As) and triethylammonium or pyridinium ions; X-ray crystal structure of $[(Ph_3P)_2Pt(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$

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Received 28 April 2002; accepted 23 September 2002

Abstract

One-pot reactions of $[MCl_2(cod)]$ (cod = *cyclo*-octa-1,5-diene; M = Pt, Pd) with two equiv of PPh_3 or $AsPh_3$, one equiv of thiosalicylic acid, and an excess of triethylamine base, followed by the addition of excess $Na[BPh_4]$ to the hot reaction mixture gives complexes $[(Ph_3E)_2M(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ (E = P, As). Analogous pyridinium and platinum–thioglycolate $[(Ph_3P)_2Pt(SCH_2CO_2)]$ derivatives were also prepared. An X-ray crystal structure determination on $[(Ph_3P)_2Pt(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ reveals hydrogen-bonding between the NH proton and the carbonyl group of the thiosalicylate ligand, the major effect of which is to flatten the platinum–thiosalicylate moiety. NMR spectroscopic data indicate that the hydrogen-bonding interaction persists in solution.

Keywords: Platinum(II) complexes; palladium(II) thiosalicylate complexes; Crystal structures

1. Introduction

We have recently reported the syntheses of a series of thiosalicylate complexes of platinum(II), palladium(II), and nickel(II), of the general type $[L_2M(SC_6H_4CO_2)]$, formed by the reaction of a metal dichloride (or in the case of nickel, diacetate) complex $[L_2MCl_2]$ with thiosalicylic acid (2-sulfanylbenzoic acid) and pyridine base [1]. These complexes act as metalloligands (through sulfur) to mercury(II) halides [2]. Subsequently, Thomas and Darkwa have synthesised the complex $[(dppe)Ni(SC_6H_4CO_2)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) from $[(dppe)NiCl_2]$ and thiosalicylic acid with triethylamine base [3]. Another report of the synthesis of this complex has appeared [4]. We have also prepared a series of mixed-ligand platinum(II) and palladium(II) thiosalicylate complexes of the type $[(Ph_3P)(L)M(SC_6H_4CO_2)]$ by reaction of $[MCl_2(cod)]$ with one equivalent of PPh_3 and an excess of a nitrogen donor base (L), such as pyridine (and derivatives thereof) and imidazole.[5] In this contribution, we describe the synthesis of crystalline, hydrogen-bonded adducts of the platinum(II) and palladium(II) complexes $[(Ph_3E)_2M(SC_6H_4CO_2)]$ (**1**, M = Pt; **2**, M = Pd; E = P, As) and $[(Ph_3P)_2Pt(SCH_2CO_2)]$ with triethylammonium and pyridinium cations.

2. Results and discussion

2.1. Synthesis and characterization

The one-pot reactions of the complexes $[MCl_2(cod)]$ (M = Pt, Pd; cod = *cyclo*-octa-1,5-diene) with two equivalents of PPh_3, one equivalent of thiosalicylic acid and an excess of triethylamine in refluxing methanol results in the formation of clear yellow (Pt) or red–

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PII: S0020-1693(02)01380-4

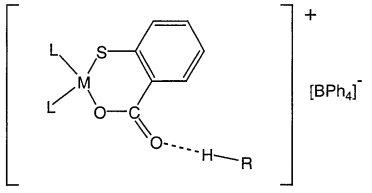
orange (Pd) solutions. When an excess of solid sodium tetraphenylborate is added to these hot solutions, microcrystalline solids **3a** and **3b** are rapidly precipitated. On the basis of NMR spectroscopy, electrospray mass spectrometry, and elemental analysis, these products are formulated as hydrogen-bonded adducts of the thiosalicylate complexes $[(Ph_3P)_2M(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$. The triphenylarsine complex $[(Ph_3As)_2Pt(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ (**3c**), the pyridinium compounds $[(Ph_3P)_2M(SC_6H_4CO_2)\cdots Hpy]^+[BPh_4]^-$ (**3d**, M = Pt; **3e**, M = Pd), and the thioglycolate derivative $[(Ph_3P)_2Pt(SCH_2CO_2)\cdots HNEt_3]^+[BPh_4]^-$ (**4**) can be prepared in the same way. The attempted synthesis of the triphenylarsine palladium analogue $[(Ph_3As)_2Pd(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ gave a deep brown solution, from which no product could be isolated. The use of excess triphenylphosphine in the synthesis of the platinum complex **3a** does not influence the purity of the product formed, however for the palladium–triphenylphosphine complexes, use of excess PPh_3 in the synthesis results in observation of free PPh_3 (δ −5) in the $^{31}P-\{^1H\}$ NMR spectra of the isolated products, and the PPh_3 ligand *trans* to S was seen to be broadened, presumably due to exchange with the free PPh_3. The palladium complexes were therefore synthesised using a stoichiometric amount of the phosphine ligand.

Interestingly, no immediate precipitation of $[Et_3NH][BPh_4]$ is observed when solid $Na[BPh_4]$ is added to a hot solution of triethylammonium chloride under analogous conditions. This suggests that the hydrogen-bonding interaction with the platinum complex, and the presence of a bulky cation-bulky anion combination are required for crystallisation of the adduct.

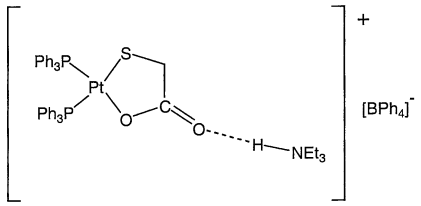
Complexes **3** and **4** are insoluble in water and diethyl ether, are only sparingly soluble in methanol, but are soluble (particularly the triethylammonium adducts) in chloroform and dichloromethane. Melting points are lower than for the parent thiosalicylate complexes, and melting occurs with gas evolution, presumably liberation of triethylamine or pyridine.

The ^1H NMR spectrum of **3a** shows the expected resonances due to the triethylammonium cation, with the integrated spectrum confirming the 1:1 adduct of $[(Ph_3P)_2Pt(SC_6H_4CO_2)]$ and $[Et_3NH][BPh_4]$. Unsurprisingly, solutions of the hydrogen-bonded adducts give very similar $^{31}P-\{^1H\}$ NMR spectra, with similar chemical shifts and coupling constants. The complex $[(Ph_3P)_2Pt(SC_6H_4CO_2)]$ gives two doublets in its $^{31}P-\{^1H\}$ NMR spectrum, at δ 24.48 and 10.15, with ^1J coupling to ^{195}Pt of 2884 and 3899 Hz, respectively, assigned to the PPh_3 ligands *trans* to S and O, respectively [1]. For complex **3a**, values of δ 24.44 and 9.85 were observed, with $^1J(PtP)$ 2886 and 3963 Hz, respectively, with the greatest change in chemical shift and coupling constant occurring for the PPh_3 ligand *trans* to the carboxylate ligand. The carbonyl CO resonance is shifted from δ 166.5 in $[(Ph_3P)_2Pt(SC_6H_4CO_2)]$ [1] to δ 169 in the Et_3NH^+ adduct **3a**, and in a mixture of $[(Ph_3P)_2Pt(SC_6H_4CO_2)]$ with excess $[Et_3NH]Cl$. These data indicate that the hydrogen-bonding interaction persists in solution, and that it most likely involves the carboxylate group.

The positive-ion electrospray (ES) mass spectra of the triethylammonium adducts show adduct ions with both H^+ and the Et_3NH^+ cation at a relatively low cone voltage (20 V). In contrast, no $[M+pyH]^+$ ions were observed for the pyridinium complexes, though $[M+H]^+$ and weak $[M+Et_3NH]^+$ ions (due to adventitious Et_3NH^+ in the spectrometer) were observed. For example, for **3a** the ions $[(Ph_3P)_2Pt(SC_6H_4CO_2)+H]^+$ (m/z 872, 100%) and $[(Ph_3P)_2Pt(SC_6H_4CO_2)+Et_3NH]^+$ (m/z 973, 80%) were both observed at 20 V. However, at 50 V, the only ion observed was $[(Ph_3P)_2Pt(SC_6H_4CO_2)+H]^+$, while at 5 V the Et_3NH^+ adduct ion dominated. Interestingly, for the thioglycolate adduct **4** only a $[M+Et_3NH]^+$ ion (m/z 911) was seen at 20 V, suggesting that the interaction between the platinum complex $[(Ph_3P)_2Pt(SCH_2CO_2)]$ and Et_3NH^+ is stronger than that between the cation and the thiosalicylate complexes, possibly due to greater steric accessibility and/or basicity of the (aliphatic) carbonyl group. The presence of the $[BPh_4]^-$ ion was confirmed in **3a** from the negative ion ES spectrum, which showed a single intense peak at m/z 319.



Complex	M	L	R
3a	Pt	PPh_3	Et_3N
3b	Pd	PPh_3	Et_3N
3c	Pt	$AsPh_3$	Et_3N
3d	Pt	PPh_3	py
3e	Pd	PPh_3	py



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2.2. Crystal structure of $[(Ph_3P)_2Pt(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ (3a)

Previous crystallographic studies on thiosalicylate complexes of square-planar d^8 metal centres have shown that the metal–thiosalicylate system is very flexible, and a wide range of fold angles between the metal coordination and thiosalicylate planes have been observed. These results have recently been summarized [5]. Since one of the complexes structurally characterised was the complex $[(Ph_3P)_2Pt(SC_6H_4CO_2)]$, a crystal structure determination was carried out on the triethylammonium adduct **3a**, to confirm the hydrogen-bonding aspect, and to directly examine the effect of such hydrogen-bonding on the platinum–thiosalicylate system. Hydrogen-bonding between the triethylammonium cation and a coordinated thiosalicylate ligand has been observed in the dimeric anionic manganese complex $[Et_3NH]_2[\{Mn(SC_6H_4CO_2)(CO)_3\}_2]$, with N–H 0.98 Å and O···H 1.73 Å [6] and in some anionic molybdenum [7] and iron ($[Et_3NH][Fe(SC_6H_4CO_2)_2$(2-methylimidazole)]) complexes [8]. However, this is the first direct comparison for the same molecule with and without H-bonding interactions.

The structure of the H-bonded cation of **3a** is illustrated in Fig. 1. There is the usual square-planar Pt(II) centre, with two *cis*-Ph_3P ligands and the chelating (S,O) thiosalicylate ligand, as in the free complex [1]. In **3a** there is an extra interaction involving H-bonding of $[Et_3NH]^+$ with the C=O of the carboxylate group. Table 1 lists some parameters for the Pt complex in the free (**1**) and H-bonded (**3a**) forms, which on comparison show significant differences. The most dramatic is the fold angle between the plane of the ligand and the Pt coordination plane, 47.2° in **1** and 26.75(7)° in **3a**. As seen earlier in a series of Pt, Pd and Ni thiosalicylate

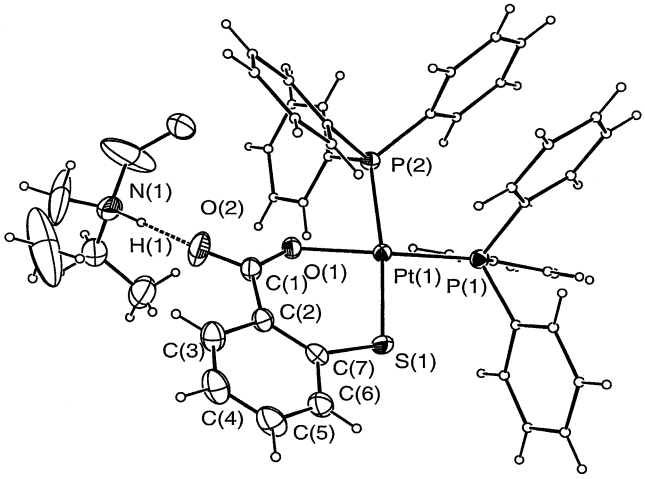

Fig. 1. Molecular structure of the cation $[(Ph_3P)_2Pt(SC_6H_4CO_2)\cdots HNEt_3]^+$ of **3a** [as its BPh_4^- salt] showing the atom numbering scheme.

Table 1
A comparison of structural features for free [1] and H-bonded $[(Ph_3P)_2Pt(SC_6H_4CO_2)]$

	Free (**1**)	H-bonded (in **3a**)
Pt–S (Å)	2.322(2)	2.296(1)
Pt–P(1) (Å)	2.250(1)	2.233(1)
S···O (Å)	2.99	3.114(2)
P–Pt–P (°)	100.46(4)	97.52(4)
Twist angle [a] (°)	21.1	7.6(2)
Pt–O	2.109(3)	2.069(2)
Pt–P(2)	2.303(1)	2.321(1)
S–Pt–O (°)	84.7(1)	90.9(1)
Fold angle [b] (°)	47.2	26.75(7)

[a] The angle between the CO_2 group plane and the plane defined by the rest of the thiosalicylate ligand [5].
[b] The dihedral angle between the Pt coordination plane and the plane of the thiosalicylate ligand [5].

complexes [5], the flattening of the fold angle leads to a decrease in the angle that the carboxylate group is twisted out of the ligand plane (21.1 and 7.6° in **1** and **3a**, respectively), and an increase in the S···O 'bite' of the chelating ligand (2.99 to 3.11 Å). The ligand is apparently also more tightly bound in the H-bonded form since the Pt–O and Pt–S bonds are both shortened [2.069(2) and 2.296(1) Å] relative to the same distances in the free form [2.109(3) and 2.322(2) Å, respectively]. The coordination around platinum is more regularly square in **3a** with P–Pt–P and S–Pt–O angles of 97.52(4) and 90.9(1)°, respectively, compared with 100.46(4) and 84.7(1)° in **1**; however the Pt is less planar in **3a** (rms deviation ±0.08 Å) than in **1** (±0.02 Å).

The H-bonded interaction between the neutral Pt complex and the $[Et_3NH]^+$ cation is defined by N–H and H···O distances of 0.93(3) and 1.79(3) Å, respectively, and a N–H···O angle of 174°, very similar to the cation–anion hydrogen-bonded interactions found for the $[Et_3NH]^+$ salts of the manganese and molybdenum thiosalicylate complexes mentioned earlier [6,7], though the equivalent interaction is more bent (158°) in $[Et_3NH][Fe(SC_6H_4CO_2)_2$(2-methylimidazole)] [8].

The packing in the crystal of **3a** is clearly assisted by a series of edge-face phenyl 'embraces' between the PPh_3 groups and the $[BPh_4]^-$ anions, with B···P distances of 7.6–7.7 Å compared with that of 7.1 Å found for $[Ph_4P][BPh_4]$ [9]. The network of these interactions is complicated but is related to those analysed in detail for other systems (particularly $[PPh_4]^+$ salts) by Scudder and Dance [10].

Although not the original intention of this work, $[Et_3NH][BPh_4]$ acts as an ionic crystallizing aid for neutral thiosalicylate complexes which bear a hydrogen-bond accepting C=O group, and might find application in the crystallization of other H-bond accepting complexes which are difficult to crystallize.

3. Experimental

3.1. Instrumentation

All NMR spectra were recorded in $CDCl_3$ solution on a Bruker AC300P instrument, as follows: ^1H (300.13 MHz), ^{13}C (75.47 MHz), ^{31}P (121.51 MHz). ^1H and ^{13}C NMR spectra were referenced relative to external $SiMe_4$ (δ 0.0), while ^{31}P NMR spectra were referenced relative to external 85% H_3PO_4 (δ 0.0). Electrospray mass spectra were recorded on a VG Platform II instrument, using methanol as the mobile phase and solvent. Assignment of major ions was aided by use of the ISOTOPE program [11] and *m/z* values quoted are for the most intense peak in the isotope distribution envelope of the ion. Melting points were recorded on a Reichert–Jung hotstage apparatus, and are uncorrected.

3.2. Materials and methods

Reactions were carried out in air, in reagent grade methanol, with no further purification. Water was singly distilled prior to use; diethyl ether was of LR grade and used as supplied. The following compounds were used as supplied from commercial sources: $K_2[PtCl_4]$ (Johnson Matthey), thiosalicylic acid (Sigma), thioglycolic acid (BDH), triphenylphosphine (BDH), triphenylarsine (Koch-Light), triethylamine (BDH), triethylammonium chloride (BDH), pyridine (BDH), and sodium tetraphenylborate (BDH). The complexes [$PtCl_2$(cod)] [12] and [$PdCl_2$(cod)] [13] were prepared by the literature methods.

3.3. Synthesis of $[(Ph_3P)_2Pt(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ (**3a**)

A mixture of [$PtCl_2$(cod)] (200 mg, 0.535 mmol), triphenylphosphine (440 mg, 1.679 mmol), thiosalicylic acid (83 mg, 0.539 mmol) and triethylamine (1 ml, excess) in methanol (20 ml) was heated to reflux for 10 min giving a clear, bright yellow solution. Solid $Na[BPh_4]$ (220 mg, 0.643 mmol) was added to the refluxing solution, resulting in the immediate precipitation of yellow microcrystals. After cooling and standing for 12 h, the solid was filtered, washed with cold methanol (5 ml), water (10 ml), methanol (5 ml) and diethyl ether (2 × 5 ml) and dried under vacuum. Yield 562 mg, 81%. M.p. 182–186 °C. *Anal.* Found: C, 67.7; H, 5.5; N, 1.1; S, 2.4. Calc. for $C_{73}H_{70}NBO_2P_2PtS$: C, 67.8; H, 5.5; N, 1.1; S, 2.5%. ES MS: positive ion, cone voltage 20 V, $[(Ph_3P)_2Pt(SC_6H_4CO_2)+H]^+$ (*m/z* 872, 100%), $[(Ph_3P)_2Pt(SC_6H_4CO_2)+Et_3NH]^+$ (*m/z* 973, 80%). Cone voltage 50 V, $[(Ph_3P)_2Pt(SC_6H_4CO_2)+H]^+$ (*m/z* 872, 100%). Negative ion, cone voltage 20 V, $[BPh_4]^-$ (*m/z* 319, 100%). $^{31}P-\{^1H\}$ NMR, δ 24.4 [d, ^1J(PtP) 2886 Hz, ^2J(PP) 22 Hz, P *trans* to S], and 9.9 [d, ^1J(PtP) 3963 Hz, P *trans* to O]; ^1H NMR, δ 7.7–6.8 (m, 54H, Ph), 2.09 [q, CH_2 of Et_3NH^+, J(HH) 7 Hz] and 0.66 [t, CH_3 of Et_3NH^+, J(HH) 7 Hz].

3.4. Synthesis of $[(Ph_3P)_2Pd(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ (**3b**)

Following the method above for **3a**, [$PdCl_2$(cod)] (200 mg, 0.701 mmol), triphenylphosphine (368 mg, 1.404 mmol), thiosalicylic acid (108 mg, 0.701 mmol) and triethylamine (1 ml, excess) gave a bright red solution. Solid $Na[BPh_4]$ (239 mg, 0.699 mmol) was added to the refluxing solution, resulting in the immediate precipitation of orange microcrystals. Yield 557 mg, 66%. M.p. 180–182 °C. *Anal.* Found: C, 72.6; H, 5.8; N, 1.2. Calc. for $C_{73}H_{70}NBO_2P_2PdS$: C, 72.8; H, 5.9; N, 1.2%. ES MS: cone voltage 20 V, $[(Ph_3P)_2Pd(SC_6H_4CO_2)+H]^+$ (*m/z* 783, 75%), $[(Ph_3P)_2Pd(SC_6H_4CO_2)+Et_3NH]^+$ (*m/z* 884, 55%).

3.5. Synthesis of $[(Ph_3As)_2Pt(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ (**3c**)

Following the method above for **3a**, [$PtCl_2$(cod)] (200 mg, 0.535 mmol), triphenylarsine (491 mg, 1.604 mmol), thiosalicylic acid (83 mg, 0.539 mmol) and triethylamine (1 ml, excess) in methanol (20 ml) gave a clear bright yellow solution. Addition of solid $Na[BPh_4]$ (200 mg, 0.585 mmol) gave yellow microcrystals. Yield 574 mg, 78%. M.p. 193–196 °C. *Anal.* Found: C, 63.3; H, 5.0; N, 1.15. Calc. for $C_{73}H_{70}NAs_2BO_2PtS$: C, 63.5; H, 5.1; N, 1.0%. ES MS: cone voltage 20 V, $[(Ph_3As)_2Pt(SC_6H_4CO_2)+H]^+$ (*m/z* 960, 65%), $[(Ph_3As)_2Pt(SC_6H_4CO_2)+Et_3NH]^+$ (*m/z* 1061, 100%).

3.6. Synthesis of $[(Ph_3P)_2Pt(SC_6H_4CO_2)\cdots Hpy]^+[BPh_4]^-$ (**3d**)

Following the method for **3a**, a mixture of [$PtCl_2$(cod)] (200 mg, 0.535 mmol), triphenylphosphine (280 mg, 1.069 mmol), thiosalicylic acid (83 mg, 0.539 mmol) and pyridine (1 ml, excess) in methanol (20 ml), gave a clear, bright yellow solution. Solid $Na[BPh_4]$ (250 mg, 0.731 mmol) was added to the refluxing solution, resulting in the immediate precipitation of yellow microcrystals. Yield 667 mg, 98%. M.p. 162–165 °C. *Anal.* Found: C, 69.0; H, 4.9; N, 1.4. Calc. for $C_{72}H_{60}NBO_2P_2PtS$: C, 68.0; H, 4.8; N, 1.1%. $^{31}P-\{^1H\}$ NMR, δ 23.9 [d, ^1J(PtP) 2840 Hz, ^2J(PP) 21 Hz] and 10.5 [d, ^1J(PtP) 3978 Hz].

3.7. Synthesis of $[(Ph_3P)_2Pd(SC_6H_4CO_2)\cdots Hpy]^+[BPh_4]^-$ (**3e**)

Following the method for **3a**, a mixture of [$PdCl_2$(cod)] (200 mg, 0.701 mmol), triphenylphosphine

(367 mg, 1.401 mmol), thiosalicylic acid (109 mg, 0.708 mmol) and pyridine (1 ml, excess) in methanol (30 ml), gave a clear, red–orange solution. Solid $Na[BPh_4]$ (239 mg, 0.699 mmol) was added to the refluxing solution, resulting in the immediate formation of orange microcrystals. Yield 680 mg, 82%. M.p. 159–161 °C. *Anal.* Found: C, 72.9; H, 5.0; N, 1.3. Calc. for $C_{72}H_{60}NBO_2P_2PdS$: C, 73.1; H, 5.1; N, 1.2%.

3.8. Synthesis of $[(Ph_3P)_2Pt(SCH_2CO_2)\cdots HNEt_3]^+[BPh_4]^-$ (**4**)

A mixture of $[PtCl_2(cod)]$ (200 mg, 0.535 mmol), triphenylphosphine (280 mg, 1.069 mmol), thioglycolic acid (10 drops, excess) and triethylamine (1 ml, excess) was heated to reflux for 10 min in methanol (20 ml), giving a clear, bright yellow solution. Solid $Na[BPh_4]$ (183 mg, 0.535 mmol) was added to the refluxing solution. On cooling, pale yellow microcrystals were deposited, which were filtered, washed with methanol (5 ml), water (5 ml), methanol (5 ml), and diethyl ether (5 ml), and dried under vacuum. Yield 165 mg, 25%. M.p. 187–191 °C. *Anal.* Found: C, 66.6; H, 5.6; N, 1.1. Calc. for $C_{68}H_{68}NBO_2P_2PtS$: C, 66.3; H, 5.6; N, 1.1%. ES MS: cone voltage 20 V, $[(Ph_3P)_2Pt(SCH_2CO_2)+Et_3NH]^+$ (*m*/*z* 911, 55%). $^{31}P-\{^1H\}$ NMR, δ 22.1 [d, ^1J(PtP) 2871 Hz, ^2J(PP) 22 Hz] and 11.8 [d, ^1J(PtP) 3795 Hz].

3.9. X-ray crystal structure of $[(Ph_3P)_2Pt(SC_6H_4CO_2)\cdots HNEt_3]^+[BPh_4]^-$ (**3a**)

Crystals of **3a** were obtained from CH_2Cl_2–Et_2O. Crystal and intensity data were collected on a Siemens SMART CCD diffractometer using standard procedures. An empirical correction for absorption was carried out with SADABS [14]; all other calculations were carried out with the SHELX-97 programs [15]. Refinement was based on F^2. One of the ethyl groups of the $[Et_3NH]^+$ cation was disordered, with the CH_2 carbon over two equal sites. The hydrogen atoms were included in calculated positions, except for those on the disordered group, which were omitted.

3.9.1. Crystal data

$C_{73}H_{70}BNO_2P_2PtS$, M_r 1293.2, triclinic, space group $P\bar{1}$, $a = 13.487(6)$, $b = 14.525(6)$, $c = 17.372(7)$ Å, $\alpha = 72.749(4)$, $\beta = 70.543(4)$, $\gamma = 89.399(4)^\circ$, $U = 3050(2)$ Å^3, $D_{calc} = 1.408$ g cm^{-3}, $Z = 2$, $F(000)$ 1320, μ(Mo Kα) 2.435 mm^{-1}, $T_{max,\,min}$ 1.000, 0.772. A total of 40 049 reflections, 12 970 unique ($R_{int} = 0.0306$) were collected at 163 K, for $2 < \theta < 27^\circ$. Final $R_1 = 0.0261$ [$I > 2\sigma(I)$], $wR_2 = 0.0671$ (all data), GoF = 1.059, final Δe +1.21/−1.50.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 192640 for compound **3a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the University of Waikato for financial support of this work. The New Zealand Lottery Grants Board is thanked for a grant in aid towards the mass spectrometer, and the generous loan of platinum from Johnson Matthey plc is acknowledged. Professor Ward Robinson and Dr. Jan Wikaira (University of Canterbury) are thanked for collection of the X-ray data set.

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