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Platinum *bis*phosphine complexes of 1,8-naphthosultone

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ABSTRACT

A series of three platinum(II) *bis*phosphine complexes **1**–**3** [Pt(1-(SO_2),8-(O)-nap)(PR_3)$_2$] (where R_3 = Ph_3, Ph_2Me, Me_2Ph) have been prepared by metathesis from *cis*-[Pt(PR_3)$_2$$Cl_2$)] and the dilithium salt of 1,8-naphthosultone. The novel compounds were fully characterised by X-ray crystallography, multinuclear NMR, IR and MS. The molecular structures of **1**–**3** were compared by measuring the *peri*-distance, splay angle magnitude, *peri*-atom displacement, naphthalene ring torsions, aromatic ring orientations and the geometry around the platinum centre. The platinum metal adopts a distorted square planar geometry in all three complexes which causes deformation of the naphthalene system. The degree of molecular deformation does not decrease upon going from **1** to **3** as anticipated, instead a competition between steric effects and intramolecular interactions causes **3** to display distortion intermediate of **1** and **2**.

1. Introduction

The naphthalene backbone has a unique geometry which allows the study of non-bonded intramolecular interactions [1–4]. Heteroatoms that are substituted at the *peri*-positions (positions 1- and 8- of the naphthalene ring) are forced to occupy space that is closer than the sum of their van der Waals radii, resulting in unique interactions [5,6]. Although steric strain occurs when the hydrogen atoms are replaced by larger heteroatoms, a great array of *peri*-substituted naphthalenes have been prepared [7–11]. Preparation is possible because of the naphthalene unit's ability to relieve strain through distortion. Firstly, attractive interactions can occur which relieve the strain by causing formation of weak or strong bonds between the substituents [5–11]. Secondly, repulsive interactions cause the *peri*-bonds to distort in-plane or out-of-plane or distort the naphthalene backbone away from its normal geometry [5–11]. Furthermore, complexation to a bridging metal species will also relieve strain; with the naphthalene system providing the correct spacial arrangement for bidentate coordination.

In the late 1970's and early 1980's Teo et al. [12–15] coordinated tetrathionaphthalene (TTN), tetrachlorotetrathionaphthalene (TCTTN) and tetrathiotetracene (TTT) to a Pt(PPh_3)$_2$ centre through oxidative addition reactions with [Pt(PPh_3)$_4$]. Due to the structural similarity of these compounds to naphthalene, we used this oxidative reaction to study the coordination chemistry of 1,8-dichalcogen naphthalenes and the oxidised derivatives of naphtho[1,8-*cd*]1,2-dithiole, to platinum *bis*phosphines [16,17]. An alternative metathetical reaction was also utilised where the parent 1,8-dichalcogen naphthalene was reduced with lithium triethylborohydride to form the dilithio-1,8-dichalcogenato naphthalene. The dilithio-species was then reacted with *cis*-[Pt(PR_3)$_2$$Cl_2$] (where R = Ph or Me) in THF at room temperature to yield [Pt(1,8-E_2-nap)(PR_3)$_2$] (where E = S or Se) [16,17]. As a continuation of this work, we chose to study the coordination chemistry of the commercially available 1,8-naphthosultone, which up until now had not been investigated.

Herein we describe the preparation and structural analysis of three platinum *bis*phosphine complexes **1**–**3** [Pt(1-(SO_2),8-(O)-nap)(PR_3)$_2$] (where R_3 = Ph_3, Ph_2Me, Me_2Ph) formed by metathetical methods from 1,8-naphthosultone and *cis*-[PtCl_2(PR_3)$_2$] (R_3 = Ph_3, Ph_2Me, $PhMe_2$).

2. Results and discussion

Compounds **1**–**3** were synthesised and their crystal structures were determined. The three complexes were characterised by multinuclear NMR, IR spectroscopy, mass spectrometry and the homogeneity of the complexes was confirmed by microanalysis.

Utilising our previously reported metathetical method [16,17], the sulfur-oxygen bond in 1,8-naphthosultone was reduced with two equivalents of lithium triethylborohydride to form a yellow

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solution of the dilithio-species. Subsequent addition of the dilithio-species to a suspension of the appropriate *cis*-dichloro*bis*(phosphine)platinum in THF resulted in the formation of [Pt(1-(SO_2),8-(O)-nap)(PPh_3)$_2$] (**1**), [Pt(1-(SO_2),8-(O)-nap)(PPh_2Me)$_2$] (**2**) and [Pt(1-(SO_2),8-(O)-nap)(PMe_2Ph)$_2$] (**3**) Scheme 1.

The $^{31}P\{^{1}H\}$ NMR spectra of the three complexes (Table 1) all display similar AX patterns with appropriate platinum satellites. For example, the phosphorus resonances and $^{1}J(^{31}P{-}^{195}Pt)$ coupling constants of **1** are $\delta(P_A)$ = 19.1 ppm (2504 Hz) and $\delta(P_X)$ = 10.6 ppm (3876 Hz), which are assigned to the phosphine groups *trans* to the SO_2 group and the oxygen atom, respectively. Complexes **2** and **3** are characterised accordingly (Table 1). In previously characterised [$(PPh_3)_2Pt$] complexes containing (–S(O)R) and –(SR) ligands, the phosphine groups *trans* to the (–S(O)R) group have smaller $^{1}J(^{31}P{-}^{195}Pt)$ coupling constants because of the larger *trans* influence of the (–S(O)R) moiety [16,17].

The *trans* influence, also known as the structural *trans* effect, is defined as the ability of a ligand to weaken the bond *trans* to itself [18–21]. The *trans* influence is a thermodynamic concept and must not be mistaken for the *trans* effect which is a kinetic concept. The *trans* effect, otherwise known as the kinetic *trans* effect, describes the ability of a ligand to alter the lability of a ligand *trans* to itself [18–21]. If the ligand is a strong σ-donor ligand or π-acceptor ligand then it increases the rate of substitution of a ligand that lies *trans* to itself [22].

With regards to *trans* influence, ligands that are poor π-acceptors, e.g. halides, are less competitive than phosphorus ligands for electron back-donation and therefore have lower *trans* influence, this results in larger coupling constants. In contrast, ligands that are strong π-acceptors, e.g. phosphorus ligands, are more competitive with other phosphorus ligands for electron back-donation and hence have higher *trans* influence. This results in smaller $^{1}J(^{31}P{-}^{195}Pt)$ coupling constants. In the case of the ‘sultone’ complexes **1** to **3** the (–S(O)R) group is a stronger π-acceptor than the oxygen atom resulting in the SO_2 group having a larger *trans* influence than the oxygen atom and hence the smaller $^{1}J(^{31}P{-}^{195}Pt)$ coupling constant value has been assigned to the phosphine group *trans* to the SO_2 group.

It has been shown that higher $^{1}J(^{31}P{-}^{195}Pt)$ coupling constants are observed for more electron withdrawing R groups, with $^{1}J(^{31}P{-}^{195}Pt)$ decreasing as phenyl groups are replaced with electron donating methyl groups [22]. It can be seen from Table 1 that there is a steady decrease in value for $^{1}J(^{31}P_X{-}^{195}Pt)$ coupling constant as the phenyl groups are replaced by methyl groups, as expected. This effect is less apparent for the signals associated with the phosphorus *trans* to the SO_2 group. The $^{2}J(^{31}P_A{-}^{31}P_X)$ values of 19–21 Hz are indicative of unsymmetrically substituted *cis*-platinum diphosphine complexes [16,17].

It was also noted, when the products were left overnight in chlorinated solvent, the solution changed colour from yellow to green. ^{31}P NMR of the green solution showed degradation of product, with the only peaks being those from the appropriate platinum chloro phosphine complex. Similar behaviour was also observed with the platinum complexes of naphthalene-1,8-dichalcogens and the oxidised derivatives of naphtho[1,8-*cd*]-1,2-dithiole [16,17]. The authors found that addition of small quantities of triethylamine to work-up and NMR solvents prevented decomposition; leading them to conclude that free hydrogen chloride in the solvent was causing decomposition. The same can be concluded in this instance.

Table 1
$^{31}P\{^{1}H\}$ NMR data for complexes **1** to **3**.

Product	Chemical Shifts [ppm]		Coupling Constants [Hz]		
	$\delta(^{31}P_A)$	$\delta(^{31}P_X)$	$^{1}J(P_A{-}Pt)$	$^{1}J(P_X{-}Pt)$	$^{2}J(P_A{-}P_X)$
1	19.1	10.6	2504	3876	19
2	3.0	−2.4	2537	3700	19
3	−9.6	−17.6	2504	3603	21

2.1. X-ray investigations

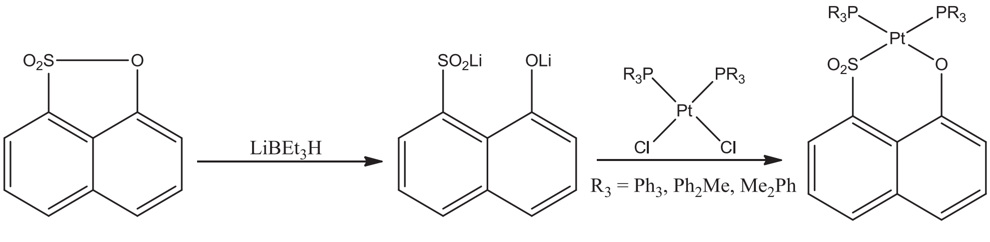
In order to analyse the impact on the *peri*-naphthalene system caused by forming platinum complexes, the crystal structure of 1,8-naphthosultone (**L**) was first studied.

The crystal structure of 1,8-naphthosultone shows a *peri* sulfur-oxygen bond distance of 1.6407(14) Å. This is shorter than the 2.44 Å [23] *peri*-distance in unsubstituted naphthalene; which is expected as there is a bond between the *peri*-substituents. However, it is longer than the typical sulfur-oxygen bond in a (C–O–SO_2–C) system (1.577 Å) [24] due to the rigid naphthalene C_2 backbone causing the sulfur-oxygen bond to be stretched. The *peri*-angles in naphthalene are 118.3(1)°, 120.6(1)° and 118.3(1)° with the sum being 357.2° [6]. In 1,8-naphthosultone the sum of the bay angles is 333.31(12)°; less than those of naphthalene confirming a favourable interaction is occurring between the *peri*-atoms resulting in a *peri*-bond. Little distortion of the naphthalene carbon skeleton is observed with torsion angles deviating by 0.62° and 0.86° from the ‘ideal’ 180°. Minor out-of-plane distortion is also observed with the oxygen atom sitting 0.018(1) Å above the naphthyl plane. The sulfur atom, however, essentially lies on the naphthyl plane Figs. 1 and 2, Table 2.

Single crystals were obtained for **1**, **2** and **3** by diffusion of hexane into saturated dichloromethane solutions. Both **1** and **2** crystallise with two dichloromethane molecules per platinum molecule. The molecular structures of **1**, **2** and **3** are shown in Figs. 4–6, respectively. In all three structures, as expected from the NMR studies, the 1,8-naphthosultone acts as a bidentate ligand, coordinating to the platinum via the sulfur and the oxygen atom to form a six-membered chelate ring. The central platinum metal adopts a distorted square planar geometry in each case, with angles deviating significantly from the ideal (90°).

The Tolman cone angles for PPh_3, PPh_2Me and $PPhMe_2$ are 145°, 136° and 122°, respectively [25]. Therefore, one would anticipate a steady contraction in the P-Pt-P angle on going from **1** to **3** and this is observed.

In **1** the P(1)–Pt(1)–P(2) angle of 99.73(5)° is enlarged to greater than the ideal 90° in order to accommodate the bulky *cis*-triphenylphosphine groups. The same applies to the P(1)–Pt(1)–P(2) angle of 98.71(11)° in **2**. However, it is less enlarged than that of **1** due to



Scheme 1. Reaction route for synthesis of [Pt(1-(SO_2),8-(O)-nap)(PPh_3)$_2$] (**1**), [Pt(1-(SO_2),8-(O)-nap)(PPh_2Me)$_2$] (**2**) and [Pt(1-(SO_2),8-(O)-nap)(PMe_2Ph)$_2$] (**3**).