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The arylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

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ABSTRACT

Routes to the synthesis of the mixed sulfide-phenylthiolate complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$ have been explored; reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with excess Ph_2IBr proceeds readily to selectively produce this complex, which was structurally characterised as its PF_6^- salt. Reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with other potent arylating reagents (1-chloro-2,4-dinitrobenzene and 1,5-difluoro-2,4-dinitrobenzene) also produce the corresponding nitroaryl-thiolate complexes $[Pt_2(\mu\text{-}S)\{\mu\text{-}SC_6H_2(NO_2)_2X\}(PPh_3)_4]^+$ (X = H, F). The complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$ reacts with Me_2SO_4 to produce the mixed alkyl/aryl bis-thiolate complex $[Pt_2(\mu\text{-}SMe)(\mu\text{-}SPh)(PPh_3)_4]^{2+}$, but corresponding reactions with the nitroaryl-thiolate complexes are plagued by elimination of the nitroaryl group and formation of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]^{2+}$. $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$ also reacts with Ph_3PAuCl to give $[Pt_2(\mu\text{-}SAuPPh_3)(\mu\text{-}SPh)(PPh_3)_4]^{2+}$.

1. Introduction

The powerful nucleophilicity of the bridging sulfido ligands of the dinuclear complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ [1] was one of the very early characteristics defined for this and the closely-related PMe_2Ph system [2,3]. Reactions with alkyl halides result in alkylation of one or both sulfide ligands, giving mixed thiolate–sulfide complexes of the type $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ or dialkylated bis(thiolate) complexes $[Pt_2(\mu\text{-}SR)_2(PPh_3)_4]^{2+}$ [4,5]. We are currently investigating the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards a wide range of alkyl halides, as a synthetic route towards complexes containing functionalised thiolate ligands [6,7], mixed alkyl-thiolate complexes $[Pt_2(\mu\text{-}SMe)(\mu\text{-}SR)(PPh_3)_4]^{2+}$ [8], and as precursors to organosulfur molecules not easily accessible by other means [9].

In contrast to the range of alkylation reactions of complexes with $[Pt_2(\mu\text{-}S)_2]$ cores now known [1,10], the corresponding arylation chemistry has scarcely been explored. Using electrospray ionisation mass spectrometry we have previously carried out a preliminary investigation of the reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards a small selection of arylating agents [6]. Very recently [10], nucleophilic aromatic substitution (S_NAr) reactions of $[Pt_2(\mu\text{-}S)_2(dppp)_2]$ [dppp = $Ph_2P(CH_2)_3PPh_2$] with perfluorobenzene and perfluoropyridine has been explored by a combination of experimental and theoretical methods. Perfluorobenzene gave the *ortho*-dithiolate complex $[dpppPt(S_2C_6F_4)]$ (together with $[Pt_3(\mu\text{-}S)_2(dppp)_3]^{2+}$), though no intermediates could be experimentally detected. In contrast, perfluoropyridine reacted much more quickly (at 0 °C), giving the mono-arylated *para*-tetrafluoropyridyl derivative $[Pt_2(\mu\text{-}S)\{\mu\text{-}SC_6F_4N\text{-}p)(dppp)_2]^+$.

In this paper we report full details on the synthesis, characterisation, and some aspects of the reactivity of some new dinuclear arylthiolate/sulfide complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ (R = phenyl, 2,4-dinitrophenyl or 5-fluoro-2,4-dinitrophenyl).

2. Results and discussion

2.1. Reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards Ph_2IBr and other phenylating agents; synthesis and characterisation of $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$

Previously we have investigated the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards PhBr and PhI and found that, on a micro-scale, the thiophenolate complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$ is formed [6]. However, attempts at scaling up this reaction to provide a practical synthesis have not been successful for PhBr, with considerable amounts of unreacted $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ always remaining. The use of a large excess of PhBr, and higher boiling solvents (e.g. ethanol) were unsuccessful. The attempted reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards PhF or PhCl in refluxing methanol were also unsuccessful, with no reaction being observed, despite the fact that aryl fluorides are typically the most reactive of the aryl halides in nucleophilic aromatic substitution reactions [10]. However, more success was obtained with PhI in refluxing methanol, which

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resulted in slow reaction and dissolution of the (sparingly soluble) $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to give a clear bright yellow solution which was shown to contain predominantly $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$ by positive-ion ESI MS, where a dominant ion at m/z 1580 was observed. The complex was readily isolated in 56% yield as its yellow hexafluorophosphate salt **1**·PF_6 by addition of excess NH_4PF_6 to the reaction mixture.

A more convenient synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$ is achieved using the more reactive diphenyliodonium salts Ph_2IBr and Ph_2ICl. Iodonium salts have been widely used as arylating agents [11], including the synthesis of organosulfur compounds [12,13], but few applications to the arylation of metal-sulfur bonded species have been reported. A rare example is the self-phenylation of the platinum(II) and palladium(II) bis(dithiooxalate) complexes $(Ph_2I)_2[M(S_2C_2O_2)_2]$, which give polymeric thiophenolate complexes $[M(SPh)_2]_n$ [14]. A preliminary investigation on the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards Ph_2ICl in methanol, using ESI MS, indicated the initial formation of the diphenyliodonium adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4IPh_2]^+$, which smoothly converted to $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$ [6]. When this reaction was carried out on a larger scale in methanol using conveniently-prepared Ph_2IBr, rapid dissolution of the (sparingly soluble) $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ occurred, giving a bright orange-yellow solution. Upon stirring overnight, this converted to a bright yellow solution, which was shown by ESI MS to contain exclusively the desired product cation $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$. The salt **1**·$PF_6$ was isolated in 60% yield by addition of excess NH_4PF_6 to the reaction solution. Dinuclear complexes containing μ-S and μ-SPh ligands supported by metal–metal bonds are well-known [15–17], but analogues unsupported by metal–metal bonds appear to be rather rare [18]; our synthetic procedures clearly define a practical route to such systems.

Crystals of complex **1**·PF_6 suitable for an X-ray crystallographic study were obtained by vapour diffusion crystallisation from dichloromethane–diethyl ether. The structure is shown in Fig. 1 and selected bond parameters are given in Table 1. The cation lies on a two-fold axis, with the phenyl group disordered over the two equivalent sites (i.e. with a 50:50 distribution over the two S atoms), but the structure unequivocally confirms the identity of the complex. The fold angle between the two PtS_2 planes is 146.3° and the S···S separation is 3.105 Å. It is noteworthy that complex **1** exists as the *exo* isomer, analogous to the structure of the methylated species $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ [19], but the opposite of the tetrafluoropyridylthiolate analogue $[Pt_2(\mu\text{-}S)\{\mu\text{-}SC_6F_4N\text{-}p)(dppp)_2]^+$, where the thiolate ligand adopts an *endo* arrangement. In this latter complex it was proposed that π–π stacking and C–F···H–C interactions between the fluorinated pyridyl ring and phenyl rings of the dppp ligands could be responsible for this arrangement. In complex **1**, π–π stacking interactions are presumably much weaker, in the absence of an electron-deficient aromatic ring.

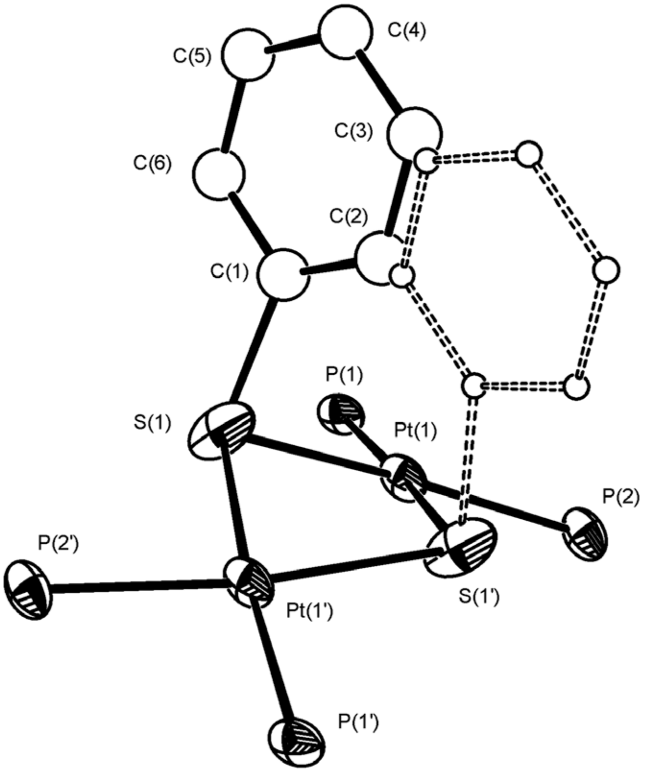

Fig. 1. Molecular structure of the cation of $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]PF_6$ (**1**·PF_6) with triphenylphosphine carbon atoms and the PF_6^- counterion omitted for clarity. The complex is disordered about the two-fold axis; the two components of the disordered phenyl ring are indicated by solid and dotted bonds.

The $^{31}P\{1H\}$ NMR spectrum of **1**·PF_6 showed two multiplets (due to PP coupling) at δ 28.4 and 26.7, showing ^1J(PtP) coupling constants of 2613 and 3291 Hz, respectively, consistent with PPh_3 ligands *trans* to rather different *trans* influence S and SPh ligands, respectively. These coupling constants are similar to those of monoalkylated derivatives, such as 2579 and 3319 Hz in $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2CH_2CN)(PPh_3)_4]^+$ [7]. As expected, the ^1H NMR spectrum provided no useful information, showing only a complex set of phenyl resonances.

The positive-ion ESI mass spectrum of **1**·PF_6 in CH_2Cl_2–MeOH showed the parent cation at low to moderate cone voltages e.g. 50 V, Fig. 2a. Upon increasing the cone voltage to 90 V (Fig. 2b) a number of fragment ions are formed. The two most intense ions, at m/z 1317 and 1055, are formed by loss of one and two PPh_3 ligands from the parent $[M]^+$ ion; this is typical behaviour for this general class of complex. The identity of some additional lower intensity ions is of interest. The ion $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_2]^+$ at m/z 1055 can fragment by loss of sulfur to give $[Pt_2(\mu\text{-}SPh)(PPh_3)_2]^+$ at m/z 1023, or by loss of benzene to give an ion at m/z 977. One possibility for the latter ion is that it contains a cyclometallated PPh_3 ligand, *viz* $[Pt_2S_2(PPh_3)(Ph_2PC_6H_4)]^+$, this being a common fragmentation pathway in ESI MS of Pt–PPh_3 complexes [20]. Other low intensity ions at m/z 1207 and 1131 are tentatively assigned as $[Pt_2(\mu\text{-}S)(Ph_2PC_6H_4)(PPh_3)_2]^+$ and $[Pt_2(\mu\text{-}S)(Ph_2P)(PPh_3)_2]^+$. The former ion is formed by elimination of PhSH from $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_3]^+$, while the latter is from elimination of PhSPh. $[Pt_2(\mu\text{-}SPh)(PPh_3)_2]^+$ is directly analogous to a range of dinuclear Pt(I) complexes with μ-thiolate ligands that have been reported in the literature, e.g. $[Pt_2(\mu\text{-}SMe)(PPh_3)_3(CO)]^+$ [21] and $[Pt_2(\mu\text{-}SMe)(\mu\text{-}Ph_2PCH_2PPh_2)L_2]^+$ [L = PPh_3, $P(p\text{-}C_6H_4F)_3$ or P^nBu_3] [22]. Loss of S from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ by reductive carbonylation is known to form dinuclear Pt(I) species $[Pt_2(\mu\text{-}S)(CO)_x(PPh_3)_{4-x}]$ [23], so the formation of $[Pt_2(\mu\text{-}SPh)(PPh_3)_2]^+$ is not unreasonable given that high cone voltage conditions present a reducing environment that often results in metal-based reduction processes [24].

Other potential routes to $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]^+$ **1** have been explored, with variable success. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with one mole equivalent of $Na_2S\cdot 9H_2O$ and excess PhSH in methanol

Table 1
Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)(\mu\text{-}SPh)(PPh_3)_4]PF_6$ (**1**·PF_6).

Pt(1)–P(1)	2.2690(16)	Pt(1)–P(2)	2.2935(15)
Pt(1)–S(1)	2.3249(16)	Pt(1)–S(1)#1	2.3601(17)
S(1)–C(1)	1.995(8)	S(1)–Pt(1)#1	2.3601(17)
P(1)–Pt(1)–P(2)	98.13(6)	P(1)–Pt(1)–S(1)	92.21(6)
P(2)–Pt(1)–S(1)	169.66(6)	P(1)–Pt(1)–S(1)#1	175.22(6)
P(2)–Pt(1)–S(1)#1	86.64(6)	S(1)–Pt(1)–S(1)#1	83.02(8)
C(1)–S(1)–Pt(1)	93.6(4)	C(1)–S(1)–Pt(1)#1	103.0(4)
Pt(1)–S(1)–Pt(1)#1	91.58(6)		

Symmetry code: #1 1-*x*, *y*, 1.5-*z*.