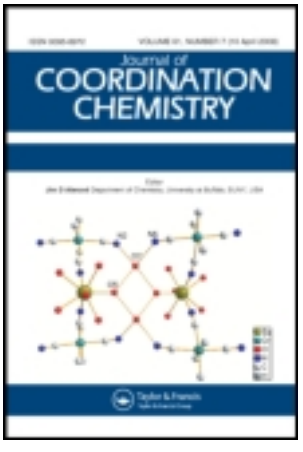

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Further investigations on the methylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

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Further investigations on the methylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$

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The methylation product of the reaction between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and MeI in diethyl ether has been reinvestigated using positive-ion electrospray mass spectrometry and found to be contaminated with the dimethylated iodide-containing complex $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$, which is believed to be formed early in the reaction. New, facile routes to the monomethylated complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ have been developed using mild methylating agents. Heating $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ in neat dimethyl methylphosphonate results in rapid and selective conversion to $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$; methylation with $Me_3S^+OH^-$ in refluxing methanol also affords pure $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$, isolated as its hexafluorophosphate salt. The X-ray structure of the previously reported complex $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ has also been undertaken.

Keywords: Platinum complexes; Thiolate complexes; Methylation reactions; Electrospray ionization mass spectrometry; X-ray crystal structure

1. Introduction

The alkylation of bridging sulfide (S^{2-}) ligands is a versatile method of synthesizing metal–thiolate complexes, using an appropriate alkylating agent. The alkylation chemistry of the dinuclear platinum(II) sulfide complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) [1] is now well established, with a wide range of known mono- and di-alkylated derivatives (scheme 1). A wide variety of alkylating agents have been investigated in such reactions, containing various functionalities, with the products formed being dependent on the alkylating agent used [2, 3].

While the dimethylated complex $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]^{2+}$ (**2**) can be easily prepared by the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with excess dimethyl sulfate [4], the synthesis of the monomethylated complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ (**3**) turns out to be less straightforward. In very early studies on $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, Ugo *et al.* [5] investigated the reactivity with methyl iodide, and found the reaction to be solvent dependent. In diethyl ether it was suggested that the dialkylated product $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]I_2$ was formed, whereas in methanol the reaction proceeded further by losing phosphine to give neutral

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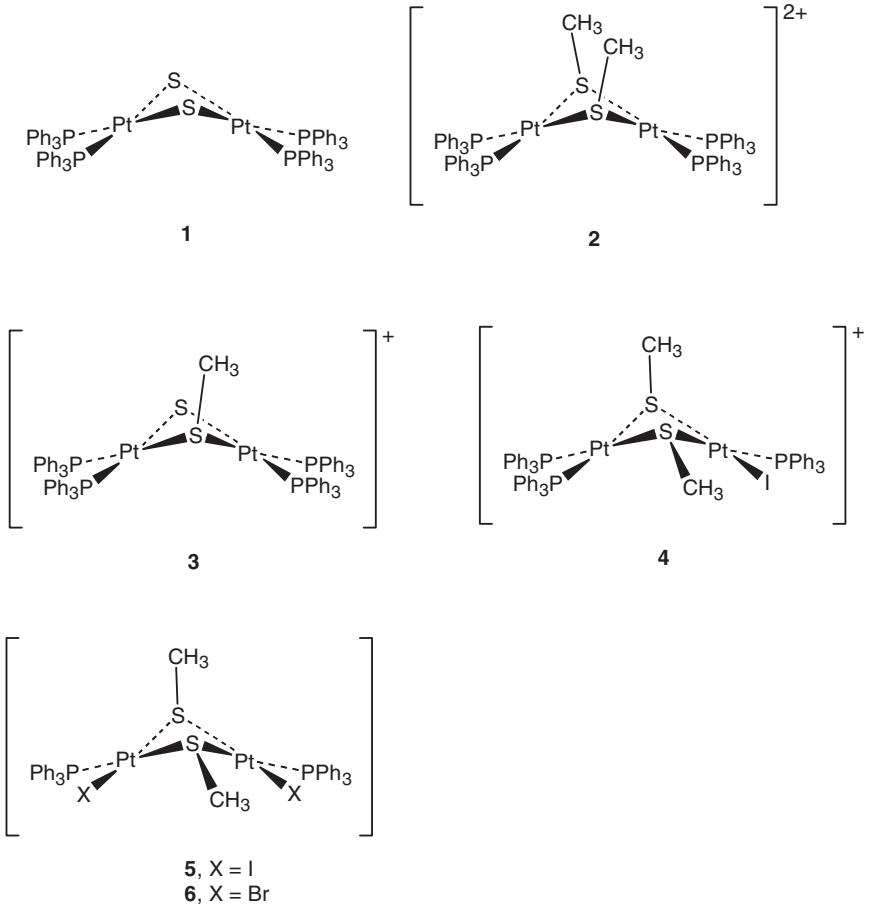

Scheme 1. Structures of the dinuclear platinum(II) complexes.

$[Pt_2(SMe)_2(PPh_3)_2I_2]$. In a subsequent investigation, the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with excess MeI in diethyl ether suspension was shown to give the iodide salt of the monomethylated complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ (**3**), which could be metathesized to the PF_6^- salt [6].

More recently, the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ toward MeI in methanol has been investigated using reaction monitoring by positive-ion electrospray ionization–mass spectrometry (ESI–MS) [7]. The reaction initially gives $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$, which is then followed by dimethylation and subsequent reaction of the resulting dication $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]^{2+}$ with nucleophilic iodide (from MeI), giving the ligand-substituted complex $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$ (**4**) [7], which is related to $[Pt_2(SMe)_2(PPh_3)_2I_2]$ (**5**) reported in the early studies by Ugo *et al.* [5]. ESI–MS [8] has been extensively and successfully applied to study the chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$. The high basicity of this complex (giving $[MH]^+$ ions), and the fact that it typically forms charged reaction products, means that the system is particularly easily studied by this technique. ESI–MS has been used to survey the reaction landscape in the alkylation and

arylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ [7], and these results are now being used to direct subsequent macroscopic syntheses. In this article, a reinvestigation (using ESI–MS) of the methylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ is reported, together with the application of easily handled, mild methylating agents which provide a facile route to the monomethylated complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$.

2. Results and discussion

2.1. *A reinvestigation of the literature route to $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ (3)*

A sample of the monomethylated complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ was prepared as its iodide salt under the reported conditions (reaction time 3 h) by the reaction of a suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with excess MeI in diethyl ether, giving a yellow suspension of the product [6]. Analysis of the isolated product showed $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ (observed m/z 1517.255, Calcd m/z 1517.261) as the dominant ion in the spectrum, together with $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$ observed at m/z 1397.095 (Calcd m/z 1397.098) at about 5% relative intensity. This ion arises from dialkylation followed by the displacement of a phosphine ligand by iodide. While the amount of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$ is small (especially compared to the corresponding reaction in methanol), its presence necessitates purification if a pure sample of $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ is required.

The reasonably successful monomethylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ by MeI in ether is almost certainly due to the much lower solubility of the ionic monomethylated complex compared to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, which prevents significant dialkylation to $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]^{2+}$ (**2**) and $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$ (**3**). When $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ is reacted with MeI in ether for a much longer reaction period (24 h), the composition of the isolated product (as analyzed by ESI–MS) was unchanged compared to the material prepared with a 3 h reaction time, suggesting that the dialkylated compound forms early in the process. Furthermore, when a sample of pure $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]PF_6$ (prepared by methylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ by $Me_3S^+OH^-$, *vide infra*) is stirred with excess MeI in ether for 3.5 h, only a trace of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]^{2+}$ (observed m/z 766.636, Calcd 766.643) was observed, with no $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$. Thus, the observation of dialkylated products in the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with MeI is probably due to a rapid double alkylation reaction involving a small amount of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, which is slightly ether-soluble, before the ionic (and far less reactive) monomethylated complex can precipitate.

2.2. *Synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ using mild methylating agents*

The previously reported method for the synthesis of $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ utilizes MeI in diethyl ether [6]. As MeI is a volatile, toxic substance with possible teratogenic properties [9], and because it generates dimethylated impurities (*vide supra*), we sought to develop an alternative synthesis avoiding this substance. The use of other methyl halides is also not convenient since MeCl and MeBr are gases under ambient conditions. $Me_3PbO_2CCH_3$ has been shown to convert $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ [10], but the high toxicity of organolead compounds makes this

undesirable as a synthetic method. It is noteworthy that the problem is essentially unique to the monomethylated complex, since for higher alkyl derivatives (e.g., ethyl, *n*-butyl) the corresponding alkyl bromides are liquids at room temperature, and are less reactive than the iodides, so selective monoalkylation is more easily accomplished.

A number of mild methylating agents have recently been developed as reagents for green syntheses. Dimethyl carbonate $(MeO)_2CO$ is one of these, but at reflux temperature (90°C) it acts as a carboxymethylating agent; high temperatures (>160°C, and higher than atmospheric pressures) are required for it to act as a methylating agent [11], which makes it less convenient for laboratory syntheses. Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ in refluxing dimethyl carbonate produced a yellow solution and some pale yellow-brown insoluble matter. ESI–MS analysis of the yellow solution showed a fairly complex mixture of unidentified products, which did not include $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$, so no further studies were carried out with this compound. In contrast, methyl *p*-toluenesulfonate $CH_3C_6H_4SO_2OMe$ behaves like dimethylsulfate [4], resulting in dimethylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ as evidenced by ESI–MS.

Methyl esters of phosphorus acids, such as trimethyl phosphate [$(MeO)_3P{=}O$, TMP] [12] and dimethyl methylphosphonate [$(MeO)_2P(O)Me$, DMMP] [13], are known to have mild methylating properties; DMMP is the preferred reagent because of its lower toxicity [14]. Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with a large excess of DMMP in refluxing methanol showed clean but partial conversion to $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$, as shown by positive-ion ESI–MS. By simply carrying out the reaction in neat DMMP (in the absence of solvent) and using a higher reaction temperature (*ca* 90°C, b.p. 181°C), the reaction proceeds rapidly, giving a clear yellow solution of $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ in DMMP. The product is easily recovered as its hexafluorophosphate salt by the addition of excess NH_4PF_6, water, and methanol, giving $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]PF_6$ as a yellow powder in 89% yield. The ^{31}P-NMR spectrum of the isolated product showed it to contain $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ as the sole platinum-containing product (spectra were compared with an authentic sample of $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]I$ prepared by the literature procedure [6]), though there were several minor singlet peaks which arise from residual organophosphorus compounds. The reaction conditions do not need to be closely controlled; reaction is easily monitored by dissolution of the insoluble $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, while prolonged reaction (e.g., 7 h at *ca* 100°C) still leads to the formation of fairly pure monomethylated product, with only a small quantity of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]^{2+}$ and some other minor unidentified products.

Methylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with trimethylphosphate proceeds similarly, though qualitatively somewhat more quickly; the $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]PF_6$ product was isolated in 87% yield from this reaction, but was found to contain some dimethylated product; no attempts were made to minimize the formation of dimethylated side-products, for example, using lower temperatures or shorter reaction times.

Optimum monomethylation was achieved using the trimethylsulfonium ion Me_3S^+; this is commercially available (as the hydroxide salt) and widely used as a mild methylating agent [15–17] because of the ease of removal of byproducts (Me_2S and H_2O) [18]. Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with excess $Me_3S^+OH^-$ in refluxing methanol for 3 h gave a clear yellow solution containing $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ which was isolated as its hexafluorophosphate salt in 86% yield, and found to have a very high

degree of purity with no dimethylated product observed by ESI–MS. The ^{31}P-NMR spectrum of the product showed a high degree of purity of $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$.

2.3. *Further studies on the methylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with methyl iodide; the X-ray structure of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ (5)*

The cation $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$ (**4**) was previously observed as a dominant ionic product in the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with MeI in methanol [7], but has not been fully characterized. We therefore attempted to isolate this product and fully characterize it. The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with MeI was carried out, leading to the formation of a pale yellow solution, from which the cationic products were precipitated by the addition of excess NH_4PF_6. Analysis by positive-ion ESI–MS showed a mixture of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$ (**4**) and $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]^{2+}$ (**2**). Recrystallization of the sample by vapor diffusion of diethyl ether into a dichloromethane solution of the product initially produced colorless crystals of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4](PF_6)_2$ which were discarded. Continued diffusion of diethyl ether produced well-formed yellow blocks that showed $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$ (observed m/z 1397.095, Cald m/z 1397.098) in the ESI mass spectrum. However, microelemental analysis and NMR (^{31}P and ^{1}H) spectroscopic data together with a single-crystal X-ray diffraction study suggested that the isolated crystals were the known di-iodo complex $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ (**5**), initially reported by Ugo *et al.* [5], from the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with MeI in ethanol. The $^{31}P\{^1H\}$ NMR spectrum showed a single resonance at δ 13.7 showing ^1J(PtP) 3250 Hz, while the ^{1}H-NMR spectrum showed (in addition to PPh_3 resonances) two methyl environments. The first methyl group at δ 3.20 appeared as a triplet due to ^4J(PH) coupling of 5.6 Hz, together with satellites due to ^3J(PtH) coupling of *ca* 37 Hz. The second methyl resonance was observed at δ 1.29 as a singlet, showing coupling only to Pt with ^3J(PtH) *ca* 59 Hz. $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ has been recently prepared by an alternative method involving iodine oxidation of the triangular platinum cluster $[Pt_3(\mu\text{-}SMe)_3(PPh_3)_3]Cl$ [19]. However, the reported ^{1}H-NMR data differ from what we observe, with the two methyl resonances reported at δ 2.75 [^3J(PtH) 36.4, ^4J(PH) 5.3 Hz] and 3.06 [^3J(PtH) 38.4, ^4J(PH) 5.6 Hz]. Ugo *et al.* did not report ^{1}H-NMR data of their product, and the reason for the discrepancy in NMR data is not clear.

We tentatively assign the methyl resonance at δ 1.29 to the axial methyl group of **5**, since this chemical shift is similar to that of the axial methyl group in $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$ at δ 1.48. This methyl resonance notably does not show ^4J coupling to ^{31}P. The PPh_3 ligands are *cis* to the axial SCH_3 group (giving C–S–Pt–P torsion angles of 105.00 and -108.39° in the X-ray structure determination, *vide infra*) which, on the basis of Karplus-type relationships observed for vicinal HCCH couplings in organic molecules [20] would be expected to give a small PH coupling. The J(PtH) coupling constant for this axial methyl group (59 Hz) is relatively large, but consistent with larger values of J(PtH) when protons are in axial environments close to nonbonding electron density on a square-planar platinum(II) center. Similar effects have been previously reported in the platinacyclic complex [Pt{CH(COPh)S(O)CH(COPh)}$(PPh_3)_2$] [21], which has a puckered four-membered Pt–CH–S(O)–CH ring, with one CH proton in an axial position (displaying coupling to only the *trans* PPh_3 ligand, and showing a larger ^2J(PtH) coupling) and the equatorial CH proton (showing coupling to both phosphorus nuclei, but a smaller ^2J(PtH) coupling).

Platinum η^3-allyl complexes show the same behavior, where the *anti* hydrogens (analogous to the axial hydrogens in **5**) show greater ^{195}Pt coupling compared to the *syn* hydrogens [22]. The equatorial methyl of **5** is therefore assigned to the resonance at δ 3.20, which is *trans* to the PPh_3 ligands, and shows ^4J(PH) coupling of 5.6 Hz, appearing as a triplet. SELROESY ^{1}H-NMR experiments are consistent with the proposed structure with axial and equatorial methyls, since irradiation of one of the methyl resonances produced no enhancement of the other methyl group.

The observation of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$ in the ESI mass spectrum of the product is worthy of comment. As $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ is neutral, ionization is expected to proceed in a manner analogous to other neutral platinum group metal halide complexes, namely by the loss of a halide anion [23]. However the iodo ligands of **5** are expected to be bonded strongly to platinum, so the complex is likely to have a low ionization efficiency in contrast to cationic complex **4** which, if present only in trace quantities, would have a high ionization efficiency, and dominate the mass spectrum.

Although the structure of the bromo analogue $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2Br_2]$ (**6**) is known [19], the structure of the iodo complex (**5**) has not been reported, so an X-ray structure determination was carried out on the CH_2Cl_2 solvate, which is isomorphous with that of **6**. The structure of **5** is shown in figure 1, together with the atom numbering scheme, while selected bond lengths and angles are given in table 1. The iodide complex has a structure similar to $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2Br_2]$ (**6**), with one SMe group in an axial position and the other in an equatorial position between the two iodo ligands. However, there are some subtle differences between the two structures. The dihedral angles between the two PtS_2 planes are 127.66° and 129.19° in the iodide and bromide complexes, respectively, indicating that the iodide complex is slightly more puckered. Concomitantly, the S···S [2.9673(1) Å] and Pt···Pt [3.2332(1) Å] nonbonding distances in **5** are slightly smaller than those in the bromide [S···S 2.971(3), Pt···Pt 3.247(1) Å]. The higher *trans*-influence [24] of iodide compared to bromide is manifested in the significantly longer Pt–SMe bond distances *trans* to iodide [2.3074(1) and 2.3034(1) Å] in **5** compared to the Pt–SMe bonds *trans* to bromide [2.288(2) and 2.295(2) Å]. However, the Pt–SMe bonds *trans* to PPh_3 are shorter in the iodide complex [2.3609(1) and 2.3635(1) Å] compared to the bromide [2.372(2) and 2.374(3) Å].

3. Experimental

3.1. *Materials and methods*

ESI mass spectra were recorded on a Bruker MicrOTOF mass spectrometer. Samples of the isolated products were analyzed as solutions (*ca* 0.1 mg mL^{-1}), prepared by dissolving a small quantity of sample in a few drops of dichloromethane, followed by dilution with methanol. Confirmation of species was facilitated by comparing observed and calculated isotope distribution patterns, the latter was obtained from instrument-based software, or an internet-based program [25]. The m/z values are of the most abundant isotopomer in the isotope envelope of the ion.

Elemental analyses were obtained by the Campbell Microanalytical Laboratory at the University of Otago, Dunedin, New Zealand. $^{31}P\{^1H\}$ NMR spectra were recorded

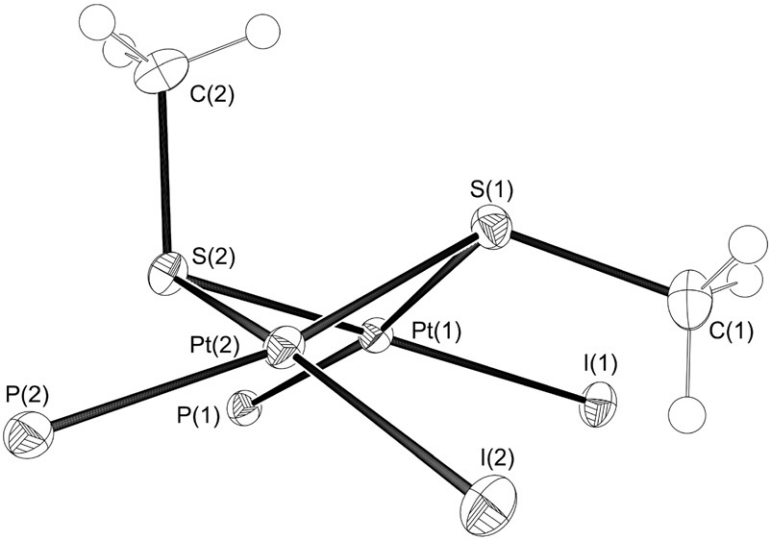

Figure 1. ORTEP diagram of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ (**5**). Thermal ellipsoids are at the 50% probability level. Phenyl rings of the triphenylphosphine ligands have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ (**5**) with estimated standard deviations in parentheses.

Pt(1)–P(1)	2.2590(11)	Pt(1)–S(2)	2.3074(10)
Pt(1)–S(1)	2.3609(10)	Pt(1)–I(1)	2.6105(3)
Pt(1)–Pt(2)	3.2332(2)	Pt(2)–P(2)	2.2650(11)
Pt(2)–S(2)	2.3034(11)	Pt(2)–S(1)	2.3635(10)
Pt(2)–I(2)	2.6206(3)	S(2)–C(2)	1.822(5)
S(1)–C(1)	1.809(5)	P(1)–Pt(1)–S(2)	89.12(4)
S(2)–Pt(1)–S(1)	78.92(4)	P(1)–Pt(1)–I(1)	96.25(3)
S(1)–Pt(1)–I(1)	95.76(3)	P(2)–Pt(2)–S(2)	94.23(4)
S(2)–Pt(2)–S(1)	78.95(4)	P(2)–Pt(2)–I(2)	92.22(3)
S(1)–Pt(2)–I(2)	96.03(3)	C(2)–S(2)–Pt(2)	108.18(16)
C(2)–S(2)–Pt(1)	105.02(16)	Pt(2)–S(2)–Pt(1)	89.05(4)
C(1)–S(1)–Pt(1)	114.26(16)	C(1)–S(1)–Pt(2)	114.53(16)
Pt(1)–S(1)–Pt(2)	86.37(3)		

in $CDCl_3$ solution on a Bruker AVIII 400 under Topspin 3.0 software, or an AVII 300 under Topspin 2.1 software.

Methyl iodide, potassium iodide, dimethyl carbonate, methyl *p*-toluenesulfonate, and trimethyl phosphate were obtained from BDH and used as supplied. DMMP (Albright & Wilson Ltd, now Rhodia), ammonium hexafluorophosphate (Aldrich), and trimethylsulfonium hydroxide (0.25 mol L^{-1} solution in methanol, Fluka) were also used as supplied.

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) [5, 26] was prepared by the literature procedure. $[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]I$ was prepared according to the literature procedure of Mingos *et al.* [6] by the addition of excess methyl iodide to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ in a stirred diethyl ether suspension.

3.2. *Synthesis of [Pt_2(μ-S)(μ-SMe)(PPh_3)$_4$]PF_6 (3·PF_6) using $Me_3S^+OH^-$*

To a suspension of [Pt_2(μ-S)$_2$(PPh_3)$_4$] (100 mg, 0.066 mmol) in methanol (30 mL), $Me_3S^+OH^-$ solution (0.25 mol L^{-1}, 1 mL) was added and the mixture was refluxed for 3 h to give a clear yellow solution that had a distinctive odor of Me_2S. After cooling to room temperature, NH_4PF_6 (300 mg, 1.84 mmol) was added to give a yellow precipitate. After the addition of water (10 mL) to assist precipitation, the product was filtered, washed with water (10 mL), and dried under vacuum to give [Pt_2(μ-S)(μ-SMe)(PPh_3)$_4$]PF_6 (95 mg, 86%). Found (%): C 51.95; H 3.76; and N <0.3. $C_{73}H_{63}F_6P_5Pt_2S_2$ requires C 52.69; H 3.82. ESI–MS [Pt_2(μ-S)(μ-SMe)(PPh_3)$_4$]$^+$ (m/z 1517.255, 100%, Calcd m/z 1517.261). $^{31}P\{^1H\}$ NMR δ 24.9 [m, ^1J(PtP) 3225 and 2591 Hz].

3.3. *Synthesis of [Pt_2(μ-S)(μ-SMe)(PPh_3)$_4$]PF_6 (3·PF_6) using DMMP*

A suspension of [Pt_2(μ-S)$_2$(PPh_3)$_4$] (187 mg, 0.124 mmol) in DMMP (8 mL) was heated to 90°C with stirring for 20 min to give a clear yellow solution. After cooling to room temperature, NH_4PF_6 (300 mg, 1.84 mmol) was added, followed by water (50 mL) and methanol (10 mL) to give a yellow precipitate. The product was filtered, washed with water (10 mL), and dried under vacuum to give [Pt_2(μ-S)(μ-SMe)(PPh_3)$_4$]PF_6 (184 mg, 89%) as a light yellow powder that was characterized by ESI–MS and $^{31}P\{^1H\}$ NMR spectroscopy.

3.4. *Prolonged reaction of [Pt_2(μ-S)$_2$(PPh_3)$_4$] in DMMP*

[Pt_2(μ-S)$_2$(PPh_3)$_4$] (*ca* 30 mg) in DMMP (5 mL) was heated to *ca* 100°C for 7 h, giving a clear yellow solution. The product was isolated by addition of excess NH_4PF_6 and water, and characterized by positive-ion ESI–MS.

3.5. *Synthesis of [Pt_2(μ-S)(μ-SMe)(PPh_3)$_4$]PF_6 (3·PF_6) using trimethyl phosphate*

A suspension of [Pt_2(μ-S)$_2$(PPh_3)$_4$] (152 mg, 0.101 mmol) in trimethyl phosphate (6 mL) was heated to *ca* 80°C for 15 min to give a clear yellow solution. After cooling to room temperature, NH_4PF_6 (300 mg, 1.84 mmol) and water (60 mL) were added to give a yellow precipitate. The product was filtered, washed with water (2 × 20 mL) and dried under vacuum to give [Pt_2(μ-S)(μ-SMe)(PPh_3)$_4$]PF_6 (146 mg, 87%) as a light yellow powder that was characterized using ESI–MS and ^{31}P-NMR.

3.6. *Reactivity of [Pt_2(μ-S)(μ-SMe)(PPh_3)$_4$]PF_6 toward MeI*

To a stirred suspension of 44 mg of the pure platinum complex (prepared from Me_3SOH above) in diethyl ether (25 mL), MeI (15 drops, large excess) was added dropwise and the mixture was stirred for 3.5 h. The pale yellow solid was recovered by filtration, washed with diethyl ether to remove excess MeI, and air dried. The product was characterized by ESI–MS in CH_2Cl_2–MeOH solution.

3.7. *Attempted synthesis of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]PF_6$ (4·PF_6) using methyl iodide*

To a stirred suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) (375 mg, 0.250 mmol) in methanol (30 mL), methyl iodide (1.5 mL, large excess) was added to give a clear pale yellow solution. After stirring for 2 h, the solution was slightly more yellow and very slightly cloudy. Potassium iodide (400 mg, excess) was added and the mixture was stirred for 1 h. The solution was filtered to remove a small amount of an insoluble bright yellow solid. To the resulting light yellow filtrate NH_4PF_6 (300 mg, 1.84 mmol) was added to give a pale yellow precipitate. Water (5 mL) was added to assist precipitation. The product was filtered, washed with water (10 mL), and dried under vacuum to give a light yellow solid (293 mg), shown to contain $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]^+$ and $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4]^{2+}$ by ESI–MS.

Crystallization of the product by vapor diffusion of diethyl ether into a dichloromethane solution initially produced colorless crystals of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_4](PF_6)_2$ which were identified using ESI–MS and subsequently discarded. Continued diffusion of diethyl ether into the supernatant produced well-formed yellow crystals that were found to be $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ (**5**). Found (%): C 37.42; N 2.97; and N <0.3. $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ ($C_{38}H_{36}I_2P_2Pt_2S_2$ requires C 36.13; H 2.87; $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_3I]PF_6$ ($C_{56}H_{51}F_6IP_4Pt_2S_2$) requires C 43.57; H 3.33. $^{31}P\{^1H\}$ NMR, δ 13.7 [s, ^1J(PtP) 3250]. ^{1}H-NMR, δ 7.43-7.28 (m, Ph), 3.20 [t, SCH_3, ^4J(PH) 5.6, ^3J(PtH) *ca* 37] and 1.29 [s, SCH_3, ^3J(PtH) *ca* 59].

Table 2. Crystal, collection, and refinement data for the X-ray structure determination of $[Pt_2(\mu\text{-}SMe)_2(PPh_3)_2I_2]$ (**5**).

Empirical formula	$C_{38}H_{36}I_2P_2Pt_2S_2{\cdot}CH_2Cl_2$
Formula weight	1347.63
Temperature (K)	89(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P-1$
Unit cell dimensions (Å, °)	
a	11.3382(4)
b	13.6640(5)
c	14.2272(5)
α	98.072(2)
β	111.811(2)
γ	92.492(2)
Volume (Å^3), Z	2015.09(12), 2
Calculated density (g cm^{-3})	2.221
Absorption coefficient (mm^{-1})	8.811
F(000)	1260
Crystal size (mm^3)	$0.26 \times 0.18 \times 0.10$
Reflections collected/unique	47,713/9571 [R(int) = 0.0399]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.482
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9571/0/442
Goodness-of-fit on F^2	1.019
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0251$, $wR_2 = 0.0659$
R indices (all data)	$R_1 = 0.0286$, $wR_2 = 0.0678$
Largest difference peak and hole (e Å^{-3})	+1.3 and −2.4

3.8. *X-ray structure determination of [$Pt_2(\mu$-SMe)$_2$(PPh_3)$_2I_2$] (5)*

Yellow block crystals of **5** were obtained by the procedure described above, one crystal was selected for the study. X-ray data were collected on a Bruker Apex II CCD diffractometer at the University of Auckland and were corrected for absorption by a multi-scan method (SADABS) [27]. The structure was solved and refined with SHELX97 [28]. Crystal, collection, and refinement data are summarized in table 2.

4. Conclusions

This study has identified facile synthetic methods for mild monomethylation of $[Pt_2(\mu\text{-S})_2(PPh_3)_4]$ which gives $[Pt_2(\mu\text{-S})(\mu\text{-SMe})(PPh_3)_4]^+$ in high yield and purity, obviating the need for toxic and volatile methyl halides. The dimethylated product $[Pt_2(\mu\text{-SMe})_2(PPh_3)_2I_2]$, formed by the prolonged reaction of $[Pt_2(\mu\text{-S})_2(PPh_3)_4]$ with methyl iodide, has now been fully characterized (including an X-ray structure determination) and found to contain axial and equatorial SMe groups in a puckered $Pt_2(SMe)_2$ core.

Supplementary material

CCDC no. 829102 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Center, *via* www.ccdc.cam.ac.uk/data_request/cif.

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