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C–Pt(IV) activation in new trimethylplatinum(IV) complexes: nucleophilic attack at metal–carbon bond

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Abstract

Reaction of the tetranuclear complex $[Me_3PtI]_4$ with the ligand *o*-$Ph_2P(E)C_6H_4SMe$ (E = S, Se) in a 1:4 molar ratio yields the mononuclear neutral complexes $[Me_3PtI\{\eta^2\text{-}MeSC_6H_4P(E)Ph_2\text{-}S,S\}]$ (E = S(**1**), Se(**2**)). Iodide abstraction from these compounds with $AgPF_6$ in the presence of a ligand L (PPh_3, py) leads to cationic complexes of the type $[Me_3Pt(\eta^2\text{-}MeSC_6H_4P(E)Ph_2\text{-}E,S)L]PF_6$ [E = S, L = PPh_3 (**3**), Py (**4**); E = Se, L = Py (**5**)]. However, using complex **2** and the ligand PPh_3 under identical conditions induces a reductive elimination reaction affording the Pt(II) complex $[MePt(\eta^2\text{-}MeSC_6H_4PPh_2\text{-}P,S)(PPh_3)]PF_6$ (**6**). Reactions of complexes **3** and **4** with NaI reveal a nucleophilic attack of the iodide to one of the methyl groups bonded to the platinum center generating a series of subsequent side reactions. Complex $[Me_3Pt\{\eta^2\text{-}MeSC_6H_4P(S)Ph_2\text{-}S,S\}(py)]PF_6\cdot CH_2Cl_2$ (**4**) was additionally characterised by X-ray diffraction. The platinum atom exhibits a distorted octahedral coordination, bonded to three methyl carbon atoms in a facial arrangement; a bidentate chelate S,S′-bonded ligand and a nitrogen atom of the pyridine ligand complete the metal coordination sphere.

Keywords: Phosphino-methylthioether complexes; Trimethylplatinum(IV) complexes; Nucleophilic attack; Reductive elimination; Oxidative addition

1. Introduction

Kinetic and thermodynamic studies of trimethylplatinum(IV) complexes in thermolysis reactions have indicated that the stability of the trimethylplatinum(IV) moiety must have a kinetic origin [1–3]. Early studies involving activation of the C–Pt(IV) bond at platinum(IV) alkyl complexes were made on the basis of thermally induced reductive elimination reactions [4] or by variation of the ligand environment, with the concomitant elimination of ethane [5]. However, studies of reactivity involving direct attack on C–Pt(IV) bonds are scarce. Bercaw and Labinger [6–8] have studied Shilov's systems where an aqueous mixture of $PtCl_4^{2-}/PtCl_6^{2-}$ is capable of functionalizing C–H bonds in alkanes to generate compounds of the type R–Cl or R–OH. Kinetic studies have suggested a nucleophilic attack on the C–Pt(IV) bond as a fundamental step to displace and generate the reaction products. On the other hand, Goldberg et al. [9] have shown that thermolysis of $[Me_3PtI(dppe)]$ results in competitive production of both methyl iodide and ethane with formation of the expected Pt(II) products. Once again, a nucleophilic attack on the proposed intermediate $[Me_3Pt(dppe)(S)]^+$ (S = donor solvent) is invoked to explain the results obtained. In spite of the strong evidence for the existence of these types of intermediates, they have not been isolated and characterised. In this paper we report the preparation of some new trimethylplatinum(IV) complexes of the type $[Me_3PtI(\eta^2\text{-}L_2)]$ {$L_2 = Ph_2P(E)C_6H_4SMe$, E = S (**1**), Se (**2**)} and $[Me_3Pt(\eta^2\text{-}Ph_2P(E)C_6H_4SMe\text{-}E,S)(L)]PF_6$ {E = S, L = PPh_3 (**3**), Py (**4**); E = Se, L = Py (**5**)}. We also present the first example of a nucleophilic attack on C–Pt(IV) bond in a well characterised cationic trimethylplatinum(IV) complex. The crystal structure of complex $[Me_3Pt(\eta^2\text{-}Ph_2P(S)C_6H_4SMe\text{-}S,S')(Py)]$

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$PF_6CH_2Cl_2$, determined by single-crystal X-ray diffraction, is also reported.

2. Experimental

2.1. General

All reactions were carried out by standard Schlenk techniques under a dry nitrogen atmosphere. Reagent grade solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting complex $[Me_3PtI]_4$ [10], $[Me_3PtI\{\eta^2\text{-P,S-}Ph_2PC_6H_4SMe\}]$ [11] and the ligands *o*-(diphenylphosphino)thioanisole (*o*-Ph_2P-C_6H_4SMe) [12] and *o*-(diphenylphosphinosulphide or selenide)thioanisole [*o*-$Ph_2P(E)C_6H_4SMe$, E = S, Se] [13] were synthesised according to literature procedures. Elemental analyses (C, H, N, S) were made with a Fisons EA 1108 microanalyser. Mass spectra were measured on a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode; ions were produced with the standard Cs^+ gun at ca. 30 kV and 3-nitrobenzylalcohol (NBA) was used as the matrix. ^1H- and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker AC-200P spectrometer. Chemical shifts are reported in ppm relative to Me_4Si (^1H) and 85% H_3PO_4 [$^{31}P\{^1H\}$, positive shifts downfield] as internal and external standards, respectively.

2.2. Synthesis of complexes

2.2.1. $[Me_3PtI(\eta^2\text{-}L_2)]$ $\{L_2 = Ph_2P(E)C_6H_4SMe,\ E = S$ (**1**), Se (**2**)$\}$

To a solution of complex $[Me_3PtI]_4$ (100 mg, 0.27 mmol) in chloroform or benzene (25 ml), a stoichiometric amount of the corresponding bidentate ligand [L_2: E = S (92.6 mg); Se (105.4 mg)] was added. The resulting solution was stirred under reflux for 3 h and concentrated under reduced pressure. Addition of *n*-hexane led to the precipitation of a solid, which was filtered off, washed with *n*-hexane and/or diethyl ether and dried under vacuum. Compound **1**: yield, 152 mg (79%). Anal. Calc. for $C_{22}H_{26}IPPtS_2$: C, 37.4; H, 3.7; S, 9.1. Found: C, 37.1; H, 3.9; S, 8.8%. MS (FAB+, *m/s*, %): 580, 68% [M−I], 550, 57% [M−IMe_2]. ^1H NMR ($CDCl_3$): δ 0.75 [s, 3H, ^2J(PtH) = 70.6 Hz, Pt–Me (trans to I)], 1.37 [s, 3H, ^2J(PtH) = 73.0 Hz, Pt–Me (trans to $SPPh_2$)], 1.76 [s, 3H, ^2J(PtH) = 73.7 Hz, Pt–Me (trans to SMe)], 2.59 [s, 3H, SMe, ^3J(PtH) = 11.9 Hz]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, 298 K): δ 34.98 [s, ^2J(PtP) = 48 Hz]. Compound **2**: yield, 140 mg (68%). Anal. Calc. for $C_{22}H_{26}IPPtSSe$: C, 35.0; H, 3.5; S, 4.3. Found: C, 34.8; H, 3.8; S, 4.1%. MS (FAB+, *m/s*, %): 627, 100% [M−I], 597, 74% [M−IMe_2]. ^1H-NMR ($CDCl_3$): δ 0.76 [s, 3H, ^2J(PtH) = 71.0 Hz, Pt–Me (trans to I)], 1.40 [s, 3H, ^2J(PtH) = 72.1 Hz, Pt–Me (trans to $SePPh_2$)], 1.70 [s, 3H, ^2J(PtH) = 73.2 Hz, Pt–Me (trans to SMe)], 2.60 [s, 3H, SMe, ^3J(PtH) = 11.9 Hz]. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 34.98 [s, ^2J(PtP) = 48 Hz, ^1J(PSe) = 632 Hz].

2.2.2. $[Me_3Pt(\eta^2\text{-}Ph_2P(E)C_6H_4SMe\text{-}E,S')(L)]PF_6$ $[E = S,\ L = PPh_3$ (**3**), Py (**4**); E = Se, L = Py (**5**)$]$

A solution of the complex $[Me_3PtI(\eta^2\text{-}Ph_2P(E)\text{-}C_6H_4SMe\text{-E,S}')]$ (E = S, 100 mg 0.15 mmol; E = Se, 106 mg, 0.14 mmol) in a mixture of dichloromethane–acetone (10:10 ml) was treated with $AgPF_6$ (39 mg; 0.15 mmol). After stirring the mixture for 1 h at room temperature (r.t.), the AgI formed was filtered off through Kieselguhr. To the filtrate was added a stoichiometric amount of the corresponding ancillary ligand {L: PPh_3 (**3**), 38.7 mg; Py (**4**), 12 μl; Py (**5**), 11 μl}. The resulting solution was stirred for 1 h and then evaporated to dryness at reduced pressure. The solid residue was extracted with chloroform (3 ml) and the complexes precipitated by adding *n*-hexane. The white solids were collected by filtration, washed with *n*-hexane and/or diethyl ether and dried under vacuum. Compound **3**: Yield, 120 mg (70%). Anal. Calc. for $C_{40}H_{41}P_2PtS_2$: C, 48.6; H, 4.2; S, 6.5. Found: C, 48.4; H, 4.1; S, 6.3%. ^1H-NMR ($CDCl_3$): δ 0.47 [d, 3H, ^3J(PH) = 7.1 Hz, ^2J(PtH) = 56.3 Hz, Pt–Me (trans to PPh_3)], 1.13 [d, 3H, ^2J(PH) = 7.1 Hz, ^2J(PtH) = 68.4 Hz, Pt–Me (trans to $SPPh_2$)], 1.67 [d, 3H, ^3J(PH) = 7.4 Hz, ^2J(PtH) = 69.6 Hz, Pt–Me (trans to SMe)], 1.40 (s, 3H, SMe, ^2J(Pt–H) = 11.1 Hz). $^{31}P\{^1H\}$-NMR($CDCl_3$): δ −8.1 [s, PPh_3, ^1J(PtP) = 952 Hz], 35.0 [s, P, ^2J(PtPA) = 50 Hz], −145 [sept, PF_6^-, ^1J(PF) = 712 Hz]. Compound **4**: yield, 152 mg (80%). Anal. Calc. for $C_{27}H_{31}NPPtS_2$: C, 40.3; H, 3.9; N, 1.7: S, 8.0. Found: C, 40.2; H, 3.8; N, 1.6; S, 7.9%. ^1H-NMR($CDCl_3$): δ 0.80 [s, 3H, ^2J(PtH) = 68.0 Hz, Pt–Me (trans to Npy)], 1.14 [s, 3H, ^2J(PtH) = 68.4 Hz, Pt–Me (trans to $SPPh_2$)], 1.33 [s, 3H, ^2J(PtH) = 68.6 Hz, Pt–Me (trans to SMe)], 2.81 [s, 3H, SMe, ^3J(PtH) = 12.6 Hz]. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 36.2 [s, ^2J(PtP) = 48 Hz], −145 [sept, PF_6^-, ^1J(PF) = 712 Hz]. Compound **5**: yield 120 mg (70%). Anal. Calc. for $C_{27}H_{31}NPPtSSe$: C, 38,1; H, 3.7; N, 1.6; S, 3.8. Found: C, 38.3; H, 3.8; N, 1.4; S, 3.6%. ^1H-NMR($CDCl_3$): δ 0.85 [s, 3H, ^2J(PtH) = 68.2 Hz, Pt–Me (trans to Npy)], 1.16 [s, 3H, ^2J(PtH) = 67.2 Hz, Pt–Me (trans to SMe)], 1.27 [s, 3H, ^2J(PtH) = 70.0 Hz, Pt–Me (trans to $SePPh_2$)], 2.80 [s, 3H, SMe, ^3J(PtH) = 12.7 Hz]. $^{31}P\{^1H\}$-NMR($CDCl_3$): δ 22.1 [s, ^2J(PtP) = 46 Hz, ^1J(PSe) = 596 Hz], −145 [sept, PF_6^-, ^1J(PF) = 712 Hz].

2.2.3. $[MePt(\eta^2\text{-}Ph_2PC_6H_4SMe\text{-P,S}')(PPh_3)]PF_6$ (**6**)

A solution of the complex $[Me_3PtI\{\eta^2\text{-P,S-}Ph_2PC_6H_4SMe\}]$ (100 mg 0.15 mmol) in dichloromethane (10 ml) was added a solution of $AgPF_6$ (38 mg; 0.15 mmol) in acetone (10 ml). After stirring the

mixture for 1 h at r.t. The AgI formed was filtered off through Kieselguhr. To the filtrate, PPh_3 (38.7 mg; 0.148 mmol) was added and the mixture stirred for 1 h at r.t. The resulting solution was evaporated to a small volume (ca. 2 ml) and the complex precipitated by adding diethyl ether or *n*-hexane. The white solid was filtered off, washed with *n*-hexane and/or diethyl ether and dried under vacuum. Yield: 66 mg (48%). Anal. Calc. for $C_{38}H_{35}F_6P_3PtS$: C, 49.3; H, 3.8; S, 3.5. Found: C, 49.2; H, 3.9; S, 3.3%. ^{1}H NMR ($CDCl_3$): δ 0.67 [dd, 3H, $^3J(P_A–H) = {}^3J(P_B–H) = 6.9$ Hz, $^2J(PtH) = 72$ Hz, Pt–Me (trans to SMe)], 2.0 [s, 3H, SMe, $^3J(Pt–H) = 22.3$ Hz]. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 24.8 [d, P, $^2J(PP) = 401$ Hz, $^1J(PtP) = 2886$ Hz], 46.9 [d, PPh_3, $^2J(PP) = 401$ Hz, $^1J(PtP) = 2836$ Hz], −145 [sept, PF_6^-, $^1J(PF) = 712$ Hz].

2.2.4. Reaction of complexes [$Me_3Pt(\eta^2$-$Ph_2P(E)C_6H_4SMe$-S,S′)(L)]PF_6 (3, 4) with NaI

To a solution of the complex **3** or **4** (100 mg; 0,10 mmol) in acetone (5 ml), a stoichiometric amount of NaI (15 mg; 0.10 mmol) was added and the mixture stirred for 4 h at r.t. The mixture was evaporated to dryness and the residue extracted with chloroform (5 ml). The solid ($NaPF_6$) was filtered off through Kieselguhr. The solution was concentrated to a small volume (ca. 2 ml) and the addition of *n*-hexane caused the precipitation of a white solid, which was filtered off, washed with *n*-hexane and dried under vacuum.

2.2.5. Crystal structure determination of [$Me_3Pt\{\eta^2$-$Ph_2P(S)C_6H_4SMe$-S,S′}(Py)]$PF_6 \cdot CH_2Cl_2$ (4)

Suitable crystals for the X-ray structure determination of complex **4** were grown by slow diffusion of diethyl ether into a dichloromethane solution. A single crystal of approximate dimensions $0.60 \times 0.40 \times 0.06$ mm was used for the intensity data collection, performed at 297(2) K on a Siemens R3m/V four-circle diffractometer, in $\theta/2\theta$ scan mode, up to $2\theta = 55.0°$, using graphite-monochromated Mo–K_α radiation ($\lambda =$ 0.71073 Å). Lattice constants were determined by least-squares fit of 58 reflections within the range $5 \leq \theta \leq 15°$. Semi-empirical corrections, via Ψ-scans, were applied for absorption. The structure was solved by Patterson and refined on F^2 by full-matrix least-squares methods using SHELXL-97 [14]. A riding model was applied to hydrogen atoms, placed geometrically at idealized positions, with C–H distances of 0.96 Å and isotropic $U = 1.2\ U_{eq}$ of parent atoms. Relevant crystal data and refinement parameters are summarised in Table 1.

Table 1
Crystal data and refinement parameters for [$Me_3Pt(\eta^2$-$Ph_2P(S)C_6H_4SMe$-S,S′)(Py)]$PF_6 \cdot CH_2Cl_2$

Empirical formula	$C_{28}H_{33}Cl_2F_6NP_2PtS_2$
Formula weight	889.60
Temperature (K)	293(2)
Wavelength (Å)	Mo–K_α (0.71073)
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.449(3)
b (Å)	11.551(3)
c (Å)	14.685(3))
α (°)	80.15(2)
β (°)	72.01(2)
γ (°)	66.44(2)
Volume (Å^3)	1690.6(7)
Z	2
Density$_{calc}$ (Mg m^{-3})	1.748
Absorption coefficient (mm^{-1})	4.580
$F(000)$	872
Index ranges	$-5 \leq h \leq 14$, $-13 \leq k \leq 15$, $-18 \leq l \leq 19$
Reflections collected	7787
Independent reflections	7218 ($R_{int} = 0.0182$)
Data/restraints/parameters	7218/0/379
Final R indices[$I < 2s(I)$]	$R = 0.0378$, $wR = 0.0968$
R indices (all data)	$R = 0.0482$, $wR = 0.1006$
Goodness-of-fit on F^2	1.000
Largest difference peak and hole (e Å^{-3})	1.03/−1.229

3. Results and discussion

3.1. Synthesis of complexes

The tetranuclear complex [Me_3PtI_4] reacted in chloroform solution with sulfur or selenium derivatives of *o*-(methylthio)phenyl{diphenylphosphine) (*o*-$Ph_2P(E)$-C_6H_4SMe) in a 1:4 molar ratio, to give neutral complexes of the type [$Me_3PtI(\eta^2$-$Ph_2P(E)C_6H_4SMe$-E,S)] [E = S(**1**), Se(**2**)].

Complexes **1** and **2** reacted in dichloromethane–acetone with silver hexafluorophosphate to form silver iodide and, most probably, the solvated complex [$Me_3Pt(\eta^2$-$Ph_2P(E)C_6H_4SMe$-E,S)(Solvent)]$^+$. This intermediate further reacts with one equivalent of an ancillary ligand L (PPh_3, py), to give cationic complexes of the type [$Me_3Pt(\eta^2$-$Ph_2P(E)C_6H_4SMe$-E,S)L]PF_6 [E = S, L = PPh_3 (**3**), py(**4**), E = Se, L = py(**5**)]. Interestingly, when the reaction is carried out with complex **2** and the ligand PPh_3, the resulting solid does not show the presence of Se, and the analytical results indicate that the isolated complex corresponds to the cationic compound [$MePt(\eta^2$-$Ph_2PC_6H_4SMe$-P,S)(PPh_3)]PF_6 (**6**). Complex **6**, most probably arises from a reaction involving the loss of selenium and a reductive elimination producing C_2H_6.

In order to prove the reductive elimination process [9,15,16], we carried out the reaction of the [$Me_3PtI(\eta^2$-$Ph_2PC_6H_4SMe$-P,S)] [11] with $AgPF_6$ in the presence of PPh_3. Indeed, under these conditions we observed the formation of complex **6** upon elimination of ethane, confirming our hypothesis. NMR spectra are in agreement with the formulation of complex **6**. Complexes **1**–**6** were isolated as air stable solids and characterised by elemental analysis, mass and NMR spectroscopy. All chemical shifts and coupling constants are summarised in Table 2 (^{1}H) and Table 3 (^{31}P).

3.2. Solution NMR studies of complexes (*1*–*6*)

The ^{1}H-NMR spectra of the complexes **1** and **2** showed a singlet signal at δ 2.6 ppm, which was assigned to protons of the SMe group on the basis of the small value of the coupling constants [^3J(PtH) = 11.9 Hz]. Also, the ^{1}H-NMR spectra of these complexes are quite simple, assignment of the signals is not trivial due to the marked similarity of the coupling constant values ^2J(PtH), in particular the methyl groups in positions trans to sulfur atoms on complex **1**. The assignment of the signals was performed with the aid of NOEDIFF-NMR experiments and by comparison with known values for similar platinum(IV) complexes [11,17,18]. The NOE result indicates that the highest field signal at δ 0.75 ppm corresponds to the methyl group in trans position to the iodide atom. The signals at δ 1.37 and 1.76 ppm were assigned to the methyl groups in trans position to the SPh_2 group and to the SMe group, respectively. For complex **2**, the NOE effect was not observed due to the low interaction (< 1%) [19]. For this reason, in this case the assignment of the signals was made on the basis of chemical shifts and coupling constant of complex **1**, and on reported data for analogous complexes [13,20]. The ^{31}P{^{1}H}-NMR spectra of complexes **1** and **2** showed a singlet resonance at δ 34.98 and 21.32 ppm, respectively, both with a coupling constant ^2J(PtP) = 48 Hz. These results are in agreement with those observed for other similar compounds [21,22]. Moreover, the spectrum of complex **2** showed the corresponding satellites due to ^{31}P–^{77}Se coupling [^1J(PSe) = 632 Hz] [13,21,23,24].

The ^{1}H-NMR spectra of the complexes **3**–**5** showed three signals in the δ 0.5–1.3 ppm region, with intensity relation 1:1:1, corresponding to non-equivalent protons of methyl groups bonded to platinum center. The

Table 2
^{1}H-NMR chemical shifts (δ ppm) and coupling constants (Hz) of platinum complexes [a]

Complex	Pt–Me	^3J(Pt–H)	trans atom	SMe	^3J(Pt–H)
1	0.75(s)	70.6	I	2.59(s)	11.9
	1.37(s)	73.0	S		
	1.76(s)	73.7	SMe		
2	0.76(s)	71.0	I	2.60(s)	11.9
	1.40(s)	72.1	Se		
	1.70(s)	73.1	SMe		
[$Me_3PtI(PSMe)$] [11]	0.70(d) [b]	70.0	I	2.79(bs)	[e]
	1.47(d) [c]	58.7	P		
	1.68(d) [d]	71.7	SMe		
3	0.47(d) [f]	56.3	PPh_3	1.40(s)	11.1
	1.13(d) [g]	68.4	S		
	1.67(d) [h]	69.6	SMe		
4	0.80(s)	68.0	N(py)	2.81(s)	12.6
	1.14(s)	68.4	S		
	1.33(s)	68.6	SMe		
5	0.85(s)	68.2	N(py)	2.80(s)	12.7
	1.16(s)	67.2	SMe		
	1.27(s)	70.0	Se		
6	0.67(dd) [i]	72.0	SMe	2.00(s)	22.3

[a] Measured in $CDCl_3$ at room temperature. Chemical shifts relative to Me_4Si as internal standard. s, singlet; d, doublet; dd, doublet of doublets. All complexes show multiplet in the region 6.88–7.94 ppm corresponding to phenyl groups of the ligands.
[b] ^3J(PH) = 7.2 Hz.
[c] ^3J(PH) = 7.6 Hz.
[d] ^3J(PH) = 7.5 Hz.
[e] ^3J(Pt–H) = not observed.
[f] ^3J(PH) = 7.1. Hz.
[g] ^3J(PH) = 7.1 Hz.
[h] ^3J(PH) = 7.4 Hz.
[i] ^3J(PAH) = ^3J(PBH) = 6.9 Hz.

Table 3
^{31}P-NMR chemical shifts (δ ppm) and coupling constants (Hz) of platinum complexes [a]

Complex	P	$^1J_{Pt-P}$	$^2J_{Pt-P}$
1	35.0(s)		48
2	21.3(s) [b]		48
[$Me_3PtI(PSMe)$] [11]	14.8(bs) [c]	[d]	
(233 K)	19.0(s)	1184	
	13.6(s)	1206	
3	−8.1(s) [e]	952	
	35.0(s)		50
4	36.2(s) [e]		48
5	22.1(s) [e,f]		46
6	24.8(d) [e,g]	2886	
	46.9(d)	2836	-

[a] Measured in $CDCl_3$ at room temperature. Chemical shifts relative to H_3PO_4 (85%) as standard. s, singlet; d, doublet.
[b] $^1J_{P-Se} = 632$ Hz.
[c] At room temperature (295 K) a very broad singlet was observed. On cooling this signal splits into two sharp singlet signals at 233 K, due to the existence of a fluxional process showed by the methyl group of the methylthioether moiety.
[d] Not observed.
[e] $\delta_P = -145$ ppm (sept, $J_{P-F} = 712$ Hz).
[f] $^1J_{P-Se} = 596$ Hz.
[g] $^2J_{Pa-Pb} = {}^2J_{Pb-Pa} = 401$ Hz.

assignment of the signals was made on the basis of the P–H coupling values (Table 2) [13,22,25,26]. Moreover, the spectra showed a singlet signal in the δ 1.4–2.8 ppm region, attributed to protons of the methylthioether group. The $^{31}P\{^1H\}$-NMR spectra of these complexes showed a singlet signal assigned to the phosphorus atom of the chalcogenide ligand [13], along with the corresponding satellites due to $^{31}P-^{195}Pt$ coupling, and the $^{31}P-^{77}Se$ coupling for complex **5** [23,24]. Additionally, the spectrum of complex **3** exhibited a singlet signal at high field (δ −8.1 ppm) assigned to the phosphorus atom of the triphenylphosphine ligand [27a] (Table 2).

The ^{1}H-NMR spectrum of the complex **6** showed a doublet of doublets and a singlet signal in 1:1 intensity, at δ 0.67 and 2.0 ppm, respectively. The high field signal is assigned to a methyl group bonded to the Pt center, coupled with two different phosphorus atoms and the low field signal corresponding to protons of the MeS group. Furthermore, the $^{31}P\{^1H\}$-NMR spectrum exhibited two doublets signals at δ 24.8 [^1J(PtP) = 2886 Hz] and 46.9 [^1J(PtP) = 2836 Hz] ppm, assigned to the P atoms of the triphenylphosphine (L) and the *o*-$Ph_2PC_6H_4SMe$ (L_2) ligands, respectively. The high value observed for the coupling constant, $^2J(P_LP_{L2}) = 401$ Hz, confirms that the phosphorus atoms are in trans positions [27,28].

3.3. Analysis of mass spectra of complexes (*1–5*)

Fast atom bombardment (FAB) mass spectroscopy of complexes **1** and **2** show the highest peaks with *m/z* at 580 and 627 corresponding to the fragment $[M-I]^+$ and less intense peaks with *m/z* at 550 and 597 corresponding to fragment $[M-IMe_2]^+$, respectively [29]. These results are in accord with the experimental preparative methods since the fragments [$Me_3Pt(\eta^2$-$Ph_2P(S)$-$C_6H_4SMe)]^+$ should be stable species in order to generate **3**, **4** and **5**. Thus, the great abundance of the cationic fragment $[M-I]^+$ indicates their high stability and discards that the elimination reaction for complex **2** takes place in the metathesis step. On the other hand, the mass spectrum of complex [$Me_3PtI(\eta^2$-$Ph_2PC_6H_4$-SMe-P,S)] has the highest peak at *m/z* 518, corresponding to the fragment $[M-IMe_2]^+$, indicating that the most probable fragmentation mechanism would involve the loss of ethane from the cationic intermediary $[M-I]^+$, where a weak trans influence exists.

Table 4
Selected bond lengths (Å) and angles (°) for complex [$Me_3Pt(C_6H_5N)\{\eta^2$-$Ph_2P(S)C_6H_4SMe$-S,S′}]$PF_6 \cdot CH_2Cl_2$

Bond lengths			
Pt–S(1)	2.490(2)	Pt–S(2)	2.482(1)
Pt–N	2.204(4)	Pt–C(1)	2.061(6)
Pt–C(2)	2.073(5)	Pt–C(3)	2.069(6)
P(1)–S(1)	1.996(2)	P(1)–C(11)	1.804(5)
P(1)–C(21)	1.815(5)	P(1)–C(31)	1.818(4)
S(2)–C(4)	1.803(5)	S(2)–C(36)	1.784(5)
Bond angles			
C(1)–Pt–C(3)	88.6(3)	C(1)–Pt–C(2)	86.3(3)
C(2)–Pt–C(3)	88.0(3)	C(1)–Pt–N	90.4(2)
C(3)–Pt–N	178.0(2)	C(2)–Pt–N	90.1(2)
C(1)–Pt–S(2)	96.5(2)	C(3)–Pt–S(2)	87.7(2)
C(2)–Pt–S(2)	174.9(2)	S(2)–Pt–N	94.2(1)
C(1)–Pt–S(1)	173.5(2)	C(3)–Pt–S(1)	90.7(2)
C(2)–Pt–S)1)	87.2(2)	S(1)–Pt–N	90.1(1)
S(2)–Pt–S(1)	90.0(1)	C(11)–P(1)–C(21)	107.5(2)
C(11)–P(1)–C(31)	107.4(2)	C(21)–P(1)–C(31)	106.9(2)
C(11)–P(1)–S(1)	113.0(2)	C(21)–P(1)–S(1)	109.2(2)
C(31)–P(1)–S(1)	112.6(2)	P(1)–S(1)–Pt	108.6(1)
C(36)–S(2)–C(4)	104.6(2)	C(36)–S(2)–Pt	106.0(2)
C(4)–S(2)–Pt	112.5(2)		

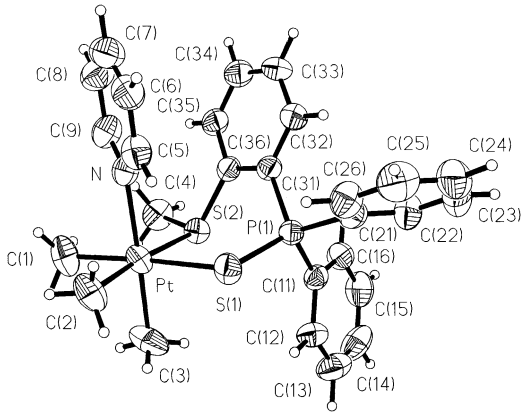


Fig. 1. ORTEP view of the structure of the complex cation **4** with atom numbering scheme.

3.4. Crystal structure determination of [$Me_3Pt\{\eta^2$-$MeSC_6H_4P(S)Ph_2$-S,S}(py)]$PF_6\cdot CH_2Cl_2$ (4)

An ORTEP drawing of the cationic complex **4** with the labeling of the atoms is shown in Fig. 1. Relevant bond distances and angles are given in Table 4. The platinum atom shows a distorted octahedral coordination and is bonded to three methyl carbon atoms in a facial arrangement, to a nitrogen atom of the pyridine ligand and to two sulfur atoms from the *o*-$Ph_2P(S)C_6H_4SMe$ bidentate ligand.

The Pt–C(Me) bond distances [2.061(6), 2.073(5) and 2.069(6) Å] compare well with similar distances found in related Me_3Pt(IV) derivatives such as [$Me_3PtI\{(MeS)_4$-$(CH)_2\}$][average: 2.046(36) Å] [17] [$(Me_3PtI)_2(Me_2Se_2)$] [average: 2.070(3) Å] [30] [Me_3PtI(terpy)] [average: 2.053(10) Å] [31] and [Me_3PtI(dmpbipy)] [average: 2.056(9) Å] [29b]. The Pt–N bond distance [2.204(4) Å] is similar to the Pt–N distances found in the complexes [Me_3PtI(terpy)] [average: 2.207(8) Å] [31] and [Me_3PtI(dmpbipy)] [average: 2.212(7) Å] [29b]. The Pt–S bond lengths [2.490(2) and 2.482(1) Å] are larger to those exhibited by related Pt(IV) or Ir(III) complexes [18a,32–34].

On the other hand, in the bidentate *o*-$Ph_2P(S)C_6H_4SMe$ ligand the P–S distance [1.996(2) Å] compares well with those found in the related Pt(II) and Ir(III) complexes containing phosphinesulfide derivatives as ligands, [$PtCl_2\{PPh_2N(Ph)P(S)Ph_2\}]H_2O$ [2.003(3) Å] [35], *trans*-[$Me_2PtBr_2\{o$-$Ph_2P(S)C_6H_4SMe$-S,S′}] [1.986(2) Å] [13] and [$(\eta^5$-$C_5Me_5)Ir\{P(O)$-$(OMe)_2\}\{\eta^2$-$(SPPh_2)_2CH_2$-S,S}]BF_4 [2.001(2) Å] [34].

3.5. Reactivity of the cationic complexes 3 and 4 with NaI

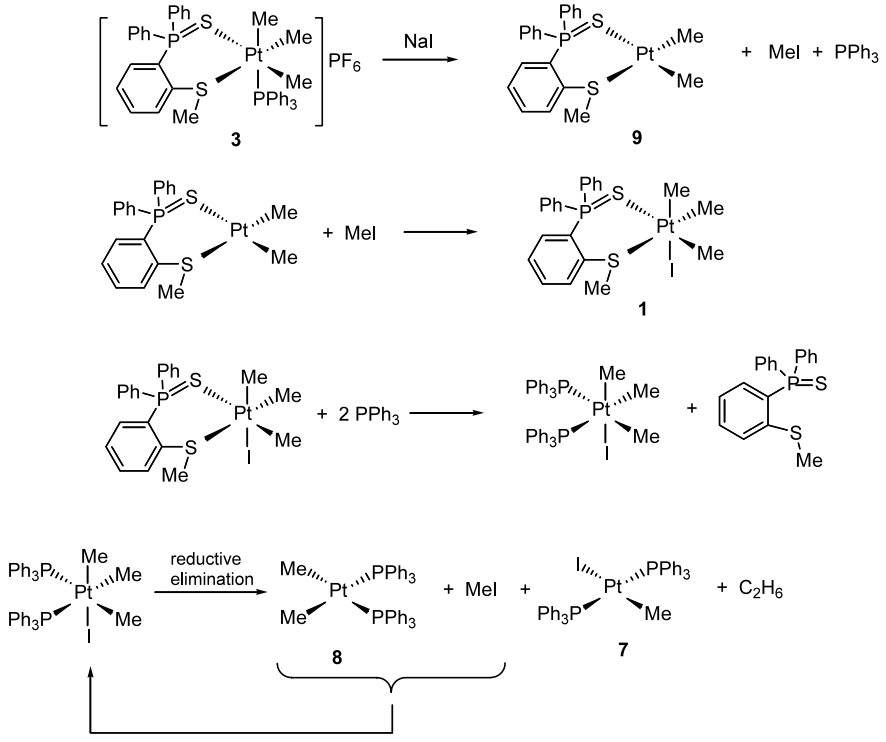
The ligand (*o*-methylthiophenyl)diphenylphosphine has been studied mainly from the perspective of the reactivity of the S–Me bond towards nucleophilic attack. It has been observed that once coordinated, the methyl group possesses increased electrophilicity and upon reaction with nucleophiles such as I^- and SCN^-, MeI and MeSCN are formed, respectively [36].

In the light of these results it seemed to us that the reactivity of complexes **3** and **4** towards selected nucleophiles should follow a similar pathway. In this context, iodide appeared to be a suitable nucleophile to study the reactivity of **3** and **4** based on previous reports for the (*o*-methylthiophenyl)diphenylphosphine ligand coordinated to palladium [36]. Thus, the stoichiometric reaction of **3** with NaI was carried out in acetone solution at room temperature. After 1 h, the solvent was removed in vacuo and the crude product was extracted into chloroform followed by filtration of the solids and crystallization by diffusion with *n*-hexane. Unexpectedly, ^{1}H-NMR analysis of the obtained product shows only one triplet signal centered at 0.07 ppm with satellites corresponding to the coupling between ^{195}Pt–^1H, indicating the presence of only one type of hydrogen atom. Furthermore, the $^{31}P\{^1H\}$-NMR spectrum shows a singlet with a chemical shift at 27.0 ppm and a ^{31}P–^{195}Pt coupling of $^1J = 3072.5$ Hz, indicating again the presence of only one species. No evidence was found for the expected demethylated ligand. Finally, by comparison with the literature [37], the obtained product was identified as *trans*-[$MePt(PPh_3)_2I$] (**7**). Analysis of the supernatant revealed the presence of cis-[$Me_2Pt(PPh_3)_2$] (**8**) [38] [$Me_3PtI(\eta^2$-$Ph_2P(S)C_6H_4SMe$-S,S)] (**1**) and free *o*-$Ph_2P(S)C_6H_4SMe$. The ^{1}H-NMR analysis of initial reaction mixture gives the following percentages: **1** (35.8%), $Ph_2PC_6H_4SMe$ (33.5%), **8** (25.7%) and **7** (5.0%). These results are summarised in Scheme 1.

Based on these results, the expected nucleophilic attack at the methyl group of the *o*-$Ph_2P(S)C_6H_4SMe$ ligand can be discounted as a plausible mechanism. However, a reasonable mechanism could involve nucleophilic attack at a methyl group in the coordination sphere of the platinum atom (Scheme 1). Nucleophilic attack of the I^- anion at one methyl group in the complex **3** generates MeI and the corresponding Pt(II) complex [$Me_2Pt(\eta^2$-$Ph_2P(S)C_6H_4SMe$-S,S)] (**9**), in addition to free triphenylphosphine. Therefore, two processes can take place: (1) displacement of the labile *o*-$Ph_2P(S)C_6H_4SMe$ ligand in **9** by the better donor PPh_3 or; (2) oxidative addition of the generated MeI to **9**.

The first approach involves a divergent pathway to account for all the observed species and seems less probable [39]. For the second pathway, if the oxidative addition of MeI on **9** as the first step is assumed, quantitative formation of **1** can be accounted for. Then, ligand displacement by PPh_3 in **1** takes place and generates free *o*-$Ph_2P(S)C_6H_4SMe$ and the unstable intermediate '[$Me_3Pt(PPh_3)_2I$]' which reductively eliminates both MeI and C_2H_6 to give **8** and **7**. However, the time evolution of the NMR spectra of the reaction shows an increase of the concentration of complex **7** due to the subsequent reaction of complex **8** with MeI to give '[$Me_3Pt(PPh_3)_2I$]', as shown in Scheme 1. Puddephatt and co-workers [3a] originally observed this behavior in the reaction between $[MePtI]_4$ and PPh_3 which was confirmed by us. Identical results are obtained from the reaction between **1** and two equivalents of PPh_3.

Based on these results, the reactivity of the pyridine derivative **4** towards I^- was also investigated. In this particular case, given the differences between PPh_3 and Py as ligands and assuming a similar mechanism to that depicted in Scheme 2, pyridine is expected to stabilize the compound [$Me_3Pt(Py)_2I$] (**11**) [40], eliminating the possibility for reductive elimination, as observed for **3**. Indeed, under identical reaction conditions, complex **4** reacts in similar manner, and the expected species **1**, **11**

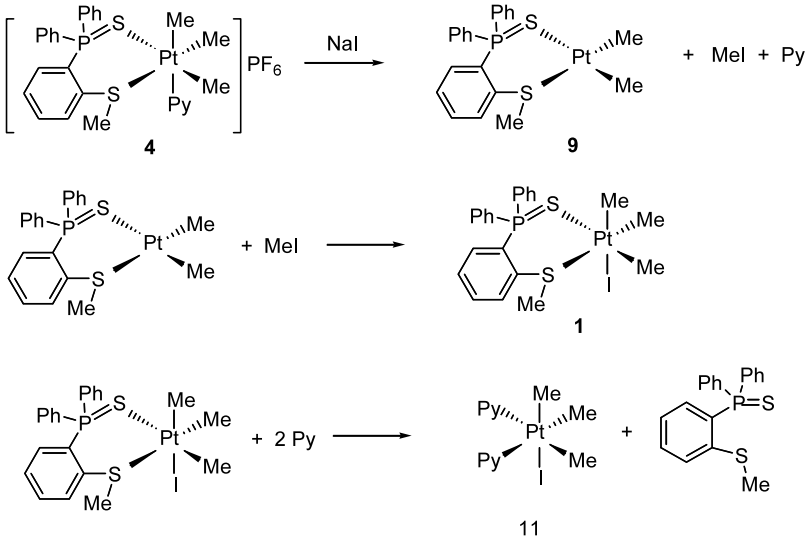


Scheme 1.

and free *o*-$Ph_2P(S)C_6H_4SMe$ are observed in the NMR spectrum (see Scheme 2).

Nucleophilic attack at a methyl group in Pt(IV) alkyl complexes has been suggested previously [6,9,41,42]. Bercaw and co-workers in the context of the activation of C–H bonds in alkanes by Pt(IV) systems, have postulated the attack of chloride or water to platinum alkyl species as the key step in generating the corresponding alkyl chloride or alcohol, respectively [6,41,43].

In the same way, Goldberg et al. have invoked a nucleophilic attack by iodide to the intermediate $[Me_3Pt(dppe)]^+$ during the thermolysis of $[Me_3Pt(dppe)I]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) to generate $[Me_2Pt(dppe)]$ and MeI [9]. More recently, the same authors have reported similar results for the thermolysis of $[Me_3Pt(dppe)(OAc)]$ [42]. In most cases, nucleophilic attack at a pentacoordinated intermediate has been postulated. However, given the donor nature of the solvents used, it is not possible to exclude a six-



Scheme 2.

coordinate solvated species as the key reactive intermediate.

We believe that in our case the nucleophilic attack takes place directly at a methyl group in the six coordinated species **3** and **4**. Although the reactions are carried out in acetone solution (a potential donor), the possibility of phosphine dissociation seems unlikely. No signs of fluxionality are observed either in the ^{1}H-NMR or ^{31}P{^{1}H}-NMR spectra when they are recorded in d_6-acetone under the conditions that the reaction is carried out. Attempts to detect the proposed intermediate **9** (see Scheme 2) by NMR were unsuccessful since the reaction occurs very rapidly on the NMR time scale. In the same way, efforts to synthesise this compound by reaction of the ligand *o*-$Ph_2P(S)C_6H_4SMe$ with the dimeric complex [{$Me_2Pt(\mu\text{-}SMe_2)$}$_2$], have also been unsuccessful.

In conclusion, the synthesis of novel both neutral and cationic trimethylplatinum(IV) complexes has been reported, and we have also shown the first example of an external nucleophilic attack on a well characterized cationic trimethylplatinum(IV) complex. Studies on analogous systems to extend the scope of this mode of reactivity are currently in progress.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 201190 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44-1223-336033; e-mail: deposit @ccdc.can.ac.uk or www: http://www:ccdc.cam.ac.uk).

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[39] If displacement of the ligand takes place as the first step, 0.5 equivalents of complex **9** react with 1 equivalents of PPh_3 to give complex **8** along with 0.5 equivalents of free SPSMe ligand. This balance leaves 0.5 equivalents of **9** which can oxidatively add to 0.5 equivalents of MeI yielding **1**. The remaining 0.5 equivalents of MeI can react with 0.5 equivalents of the previously formed **8** and establish an equilibrium given rise to **10** (see above and Ref. [3a]). In this case we are assuming that the formation of **8** and **10** from '$Me_3Pt(PPh_3)_2I$' follows a pathway similar to that observed in the case of $[Me_3Pt(dppe)I]$ when subjected to thermolysis [9]. We prefer the simpler and straightforward second approach.
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