Alkylation of platinum(II) chalcogenide complex [Pt₂(µ-S)₂(PPh₃)₄] with 1-chloro-2-isocyanatoethane and isonicotinylhydrazide derivatives

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Abstract
The reaction of the platinum(II) chalcogenide complex [Pt₂(µ-S)₂(PPh₃)₄] with electrophiles, 1-chloro-2-isocyanatoethane and isonicotinylhydrazide derivatives, CICH₂CH₂NH(C(O)Py)∙(CH₂CH₂)₂O, CICH₂CH₂NH(C(O)Py)∙(CH₂CH₂)₂S, or Na₂S∙9H₂O, gave the corresponding monocationic complexes, [Pt₂(µ-S)(μ-SCH₂CH₂NH(C(O)Py)∙(CH₂CH₂)₂O)(PPh₃)₄]⁺, [Pt₂(µ-S)(μ-SCH₂CH₂NH(C(O)Py)∙(CH₂CH₂)₂S)(PPh₃)₄]⁺ and the corresponding isonicotinylhydrazide derivative [Pt₂(µ-S)(μ-SCH₂C(NH(C(O)Py)∙(CH₂CH₂)₂NCH₃))(PPh₃)₄]⁺. The products were isolated as the [BPh₄] and [PF₆] salts and characterized by electrospray ionization mass spectrometry, IR, ¹H and 3¹P[¹H] NMR spectroscopic techniques.

Keywords: alkylation, platinum (II), complex, alkylation, thiolate ligand.

Introduction
The rich chemistry exhibited by the neutral chalcogenide complex [Pt₂(µ-S)₂(PPh₃)₄] (I) is mainly due to the exceptional nucleophilicity of the bridging sulfide centres. This accounts for its reactivity towards metal fragments [1-9], leading to the formation of multi-metallic sulfide-bridged aggregates. It also reacts with appropriate alkylation agents [10-13], to form thiolate ligand bonded to platinum. Similar chemical reactivity has been reported for the selenium analogue [14,15] and other closely related complexes with different terminal phosphate ligands [16-18]. Alkylation of the sulfide centre(s) of I is an excellent synthetic route to incorporating any suitable thiolate ligand groups on the platinum complex.

Electrospray ionisation mass spectrometry has been used as the main monitoring tool to incorporate a wide range of organic functionalities [10] into [Pt₂(µ-S)₂] core of I through monoalkylation. Alkylation reaction of I has been experimentally found to be consistent with the expected Sₛ₂ mechanism for an alkylation reaction [19]. Any desired functionality can be incorporated into I through a suitable electrophile. Using the ESI-MS, undesired side reactions can be eliminated and cationic derivatives of the type [Pt₂(µ-S)(µ-SR)(PPh₃)₄]⁺ can easily be synthesized.

The catalytic potential of using this method in the generation of organosulfur molecules has been reported [20]. The applicability of the alkylation derivative can therefore be tailored to incorporate target functionality into I. Also monoalkylated complex of I can act as cationic ligand [21, 22]. Therefore, more functionalised derivatives of [Pt₂(µ-S)₂(PPh₃)₄] which could aid the incorporation of metal fragments through the unalkylated sulfide centre or the donor atoms of incorporated group can be generated. Incorporated functional groups with donor atoms can react with platinum atom in I to give unexpected product [12, 23]. Therefore pre-investigation of the reactivity of functionalised alkylation agents toward I is necessary as a means of generating other novel molecules.

We are interested in extending the investigation of the reactivity of functionalized electrophiles with I and expanding the scope of possible application of monoalkylated derivatives of I as a synthetic template. In this contribution we wish to report the synthesis and characterization of the products of alkylation of I with electrophiles derived from 1-chloro-2-isocyanatoethane and isonicotinylhydrazide.

Experimental
1-Chloro-2-isocyanatoethane, morpholine, 1-methylpiperazine, and sodium tetraphenylborate (NaBPh₄) and isonicotinylhydrazide, [PtCl₃(PPh₃)₃]. Na₂S∙9H₂O and NH₄PF₆ were supplied by Sigma-Aldrich. Reaction solvents: Benzene (Sigma-Aldrich), methanol (Caledon Chemicals), dichloromethane (Sigma-Aldrich) and diethyl ether (EMD Chemicals) were of laboratory reagent grade and used without further purification. Complex [Pt₂(µ-S)₂(PPh₃)₄] I was synthesized by metathesis of cis-[PtCl₂(PPh₃)₂] with Na₂S∙9H₂O in benzene [28,29] and obtained at a yield of 88%. ESI-MS; +20 V distilled MeOH: m/z 1503 [M + H]⁺. CICH₂CH₂NH(C(O)Ph)(CH₂CH₂)₂NCH₃ 3 was originally
Elemental analyses of vacuum dried sample of the compounds were performed on a Perkin-Elmer 2400 CHN elemental analyzer. NMR spectra were recorded in CDCl₃ solution, unless otherwise stated. ¹H NMR (CDCl₃, 300 MHz): δH = 3.65 (2H, t, CH₂), 3.57 (2H, m, CH₂), 3.67 (4H, m, CH₂), 2.20 (4H, m, CH₂), 7.26 (1H, s, NH). ESI-IR (KB): ν(C-H) 2930.93 cm⁻¹, ν(C=O) 1693.56 cm⁻¹, ν(NH) 3430.30 cm⁻¹, ν(C-Cl) 1450 cm⁻¹, ν(Ph) 1450 cm⁻¹.

Synthesis of CICH₂CH₂NHC(O)(N(CH₂CH₂)₃)₂-NCH₃
HN(CH₂CH₂)₂NCH₃ (200 mg, 0.002 mol) was added to a solution of CICH₂CH₂NCO (200 mg, 0.002 mol) in diethyl ether (30 mL) in a 100 mL round bottomed flask and the mixture stirred for 5 min. A quantitative precipitate of the product was formed after storing in the freezer overnight. The product was filtered and washed with ether (20 mL) and dried under vacuum to give CICH₂CH₂NHC(O)(N(CH₂CH₂)₃)₂-NCH₃ (370 mg, 96%). M.p. 182-185°C. Anal Calc. (%) for C₃₅H₇₄N₉O₅: C 61.64; H, 4.53; N, 1.40; found: C 40.34, H 6.29, N 14.41. ESI-MS: m/z: [M+Na]⁺, 215.63. ¹H NMR (CDCl₃, 300 MHz): δH = 3.65 (2H, t, CH₂), 3.57 (2H, m, CH₂), 3.67 (4H, m, CH₂), 2.20 (4H, m, CH₂), 7.26 (1H, s, NH).

Synthesis of [Pt₂(μ-S)(μ-SCH₂CH₂NHC(O)(N(CH₂CH₂)₃)₂O)(PPh₃)₄]₂(BPh₄), 2b-BPPh₄
To an orange suspension of [Pt₂(μ-S)(PPh₃)₄]₂ (50 mg, 0.033 mmol) in methanol (25 mL) was added excess CICH₂CH₂NHC(O)(N(CH₂CH₂)₃)₂O (7.63 mg, 0.040 mmol, 1.2 mol equiv.) in a 100 mL round bottomed flask. The mixture was stirred at room temperature for 1 h to give a clear pale yellow solution. The solution was gravity filtered to remove traces of solid matter and excess NaBPPh₄ (14 mg) was added followed by distilled water (5 mL). The resulting yellow precipitates were filtered, washed with water (4 x 10 mL) and diethyl ether (4 x 10 mL) and dried in air, giving 2b-BPPh₄ (46%, 69%) M.p. 280-282°C. Anal. Calc. for C₁₀₃H₇₂BN₄O₈P₄BP₄S₈ (Mw = 1979.86): C, 62.36; H, 4.93; N, 1.41. Found: C, 61.64; H; 4.53; N, 1.40. ESI-MS m/z 1660.6, ([M⁺] 100%). ³¹P(¹H) NMR: δ = 23.32 [br, s, J(P-P₄) 2604], δ = 3224 [J(P-P₄) 2604]; ¹H NMR (300MHz, CDCl₃): δ = 7.35-6.70 (80H, m, 16Ph), 6.51 (1H, t, NH), 3.51 (2H, t, CH₂), 3.33 (4H, m, CH₂), 2.33 (4H, t, CH₂), 1.33 (2H, t, SCH₂); IR (KB): ν(C=O) 1645.33 cm⁻¹, ν(NH) 3418.94 cm⁻¹.
Synthesis of [Pt₂(µ-S)(µ-SCH₂CH₃NHC(O)N(CH₂CHO₂)₂NCH₃](PPh₃)₄](BrCH₃), 3b-BPh₄.

Excess CICH₂CH₃NHC(O)N(CH₂CHO₂)₂NCH₃ (8.2 mg, 0.040 mmol) was added to [Pt₂(µ-S)₄(PPh₃)₄] (50 mg, 0.033 mmol) in methanol (30 mL) in a 100 mL round bottom flask. The mixture was stirred at room temperature for 1 h to give a yellow solution. The solution was filtered to remove traces of solid matter and excess NaBPh₄ (14 mg) was added followed by distilled water (5 mL) to complete precipitation of the product from solution. The precipitate was washed with deionised water (40 mL) and diethyl ether (40 mL). M.p. 265-267 °C. Anal. Calc. for C₁₀H₈BN₂OP₄Pt₂; (Mw = 1992.90); C 65.55; H, 5.05; N, 2.35. Found: C, 64.99; H, 4.99; N. 2.10; ESI-MS m/z 1673.7. ([(M⁺) 100%); 3¹P{[¹H]} NMR: δp = 24.4 ppm [br, s, J(Pt-P₄) 2604]. J(Pt-P₄) 3245]; ¹H NMR (300 MHz, CDCl₃): δ = 7.37-6.71 (80H,m,16Ph), 6.89 (1H, t, NH), 3.97 (4H, m, CH₂), 2.96 (8H, m, 4CH₂), 2.75 (2H, t, SCH₂), 2.25 (3H, s, CH₃); IR (KBr): ν(C=O) 1661.73 cm⁻¹, ν(NH) 3438.23 cm⁻¹.

Preparation of [Pt₂(µ-S)(µ-SCH₂C(NH(CH(O)Py)N)(PPh₃)₄](PF₆)₄, 4b-PF₆

BrCH₂C(NH(CH(O)Py)N)(PPh₃)₄ (0.13 g, 0.040 mmol) was added to an orange suspension of [Pt₂(µ-S)₄(PPh₃)₄] (50 mg, 0.033 mmol) in methanol (20 mL) and the mixture stirred for 1 h. ESI-MS of the mixture indicated complete reaction. The solution was filtered to remove traces of solid matter and excess of NH₄PF₆ (80 mg, 0.49 mmol) was added, followed by distilled water (5 mL) to induce precipitation. A pale yellow powder of the product 4b-PF₆ (46 mg, 73%) was obtained after washing with deionised water (40 mL) and diethyl ether (40 mL) using vacuum suction filtration and drying in a vacuum. M.p.: 165-168 °C. Anal. calcld (%) for C₂₀H₁₆BN⁺OP₄PF₆; C 64.99; H, 4.99; N. 2.10; ESI-MS: m/z = 1740.6 ([(M⁺) 100%); 3¹P{[¹H]} NMR: δp = 23.7 [brs, J(Pt-P₄) 2668]. J(Pt-P₄) 3319]; ¹H NMR (300 MHz, CDCl₃): δ = 10.68 (1H, s, NH), 7.03-7.50 (69H, m, 14Ph), 3.65 (2H, br, SCH₂);IR (KBr): ν(C=O) 1698 cm⁻¹, ν(NH) 3455 cm⁻¹.

Results and Discussion

The complete conversion of the 1 to the alkylated derivation is indicated by the complete disappearance of the [1 + H]⁺ peak. The reactions of 1 with CICH₂CH₃NHC(O)N(CH₂CHO₂)₂O, 2 and CICH₂CH₃NHC(O)N(CH₂CHO₂)₂NCH₃, 3 synthesized according to Scheme 1 independently gave only an ESI-MS peak at m/z = 1660.6 and 1673.7 after stirring for 1 h, indicating complete formation of the products [Pt₂(µ-S)(µ-SCH₂CH₃NHC(O)N(CH₂CHO₂)₂O)(PPh₃)₄]⁺, 2b and [Pt₂(µ-S)(µ-SCH₂CH₃NHC(O)N(CH₂CHO₂)₂NCH₃](PPh₃)₄]⁺, 3b respectively (Scheme 2). The compounds were isolated as the [BPh₄] salts, 2b-BPh₄ and 3b-BPh₄.

Scheme 1: Synthesis of morpholine and 1-methylpiperazine derivatives of 1-chloro-2-isocyanoethane

Scheme 2: The synthesis of monoalkylated complexes [Pt₂(µ-S)(µ-SR)(PPh₃)₄]⁺

The reactions of the hydrazone, BrCH₂C(=NHNHC(O)Py)N, 4 with 1 proceeded very quickly with the solubilisation and change of the orange colour of MeOH solution of 1 into a clear pale yellow solution. The formation of the corresponding monoalkylated derivative, [Pt₂(µ-S)(µ-SR)(NHC(O)Py)N(PPh₃)₄]⁺, 4b completed after 30 mins of stirring at room temperature and was isolated as the [PF₆] salt, 4b-PF₆.
Figure 1: $^1$H NMR (300 MHz) spectra of 4b·PF$_6$ showing -SCH$_2$ and complicated complicated signals in the aromatic region

The $^1$H NMR spectra of the alkylated derivatives gave complicated signals in the aromatic region due to the four terminal triphenylphosphine (PPh$_3$) groups which could not be easily assigned (see Figure 1). This is because of the large number of phenyl rings due to terminal PPh$_3$ ligands in the complexes. However, the signals attributable to non-phenyl hydrogen atoms of the attached group were identifiable. The signals due to SCH$_2$ protons in the monoalkylated complexes occurred between 1.33-3.65 ppm. The methylene SCH$_2$ protons were easily identified as a broad triplet signal with broad satellite peaks produced by coupling to the $^{31}$P and $^{195}$Pt atoms respectively [26]. This observation was a good indication that not only was the alkyl group present, but it was also bonded to one of the sulfur atoms of 1.

The $^{31}$P ($^1$H)NMR spectra of all the complexes show common features. In the complexes the signal due to the two different phosphorus environments appeared superimposed on one another. This is because the two sets of triphenylphosphine ligands, cis- or trans- to S$^2$- coincidentally have almost identical chemical shifts. The two signals were however, distinguished by their different $^1$J(Pt-P) coupling constants. The two different phosphorus groups have different coupling constants to $^{195}$Pt, with the phosphines cis to the SR ligand, P$_A$ and P$_B$ trans to the S$^2$. The two phosphorus atoms cis to SR gave rise to the smaller $^1$J(Pt-P) coupling constant. This is because of the higher trans influence [27] of S$^2$, relative to SR, lengths the Pt-P$_A$ bond, resulting in a smaller $^1$J(Pt-P) value. The $^{31}$P($^1$H) NMR spectra of the complexes show similar features as 2b·BPh$_4$ [Figure 2] showed that the signals for both P$_A$ and P$_B$ were flanked by two satellite peaks, one on each side gave rise to $^1$J (Pt-P$_A$) 2604, $^1$J(Pt-P$_B$) 3224. Similarly $^{31}$P($^1$H)NMR of complexes 3b·BPh$_4$ and 4b·PF$_6$ $^1$J (Pt-P$_A$) 2604, $^1$J(Pt-P$_B$) 3245 and $^1$J(Pt-P$_A$) 2668, $^1$J(Pt-P$_B$) 3319] coupling constants for the complexes respectively.

Figure 2: $^{31}$P($^1$H) NMR of 2b·BPh$_4$ showing the near equivalence of the chemical shifts of the two P$_A$ and P$_B$ environments and the satellite peaks

The infrared (IR) spectra of the electrophile and the complexes show peaks attributable to the characteristic functionalities of the attached groups. The IR peaks were assigned to confirm the presence of the functional groups of the electrophiles in the alkylated complexes. Absorptions bands attributable to the >C=O stretch of the electrophiles were same [1693.56 cm$^{-1}$; 2 and 3] and >NH absorption bands at 3430.30 and 3408.33 cm$^{-1}$, 2 and 3 respectively. Same groups were observed in the complexes at {1645.33 cm$^{-1}$; 2b·BPh$_4$}, {1661.73 cm$^{-1}$; 3b·BPh$_4$}, and {1698 cm$^{-1}$, 4b·PF$_6$} in the IR spectra of the complexes. The absorption due to >NH were also observed in all the complexes at {3418.94 cm$^{-1}$; 2b·BPh$_4$}, {3455 cm$^{-1}$, 3b·BPh$_4$}, and {3455 cm$^{-1}$, 4b·PF$_6$}

Conclusions
The nucleophicity of the sulfide centres in [Pt$_2$(μ-S)$_2$(PPh$_3$)$_3$] has been exploited in the synthesis of novel multifunctional monoalkylated di-platinum complexes. The reaction products further illustrate the potential of grafting different organic moieties through sulfide alkylation of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_3$]. Potentially, the isolated compounds can serve as a synthetic precursor to multinuclear metal aggregates but utilizing the unalkylated derivative.

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References