Reactivity of [Pt₂(μ-S)₂(PPh₃)₄] towards activated aliphatic bromoacetyl electrophiles: Formation of mono-, homodi-, heterodi- and intramolecular-bridged alkylated products

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Abstract
Reactions of [Pt₂(μ-S)₂(PPh₃)₄] with activated aliphatic bromoacetyl alkylating agents BrCH₂C(O)C(CH₃)₃, BrCH₂C(O)CH₂CH₃ and BrCH₂C(O)C(O)CH₂Br, were investigated by electrospray ionization mass spectrometry (ESI-MS). The laboratory scale reactions gave the mono-, dicationic and bridged, μ-thiolate complexes [Pt₂(μ-S)(μ-SCH₂C(O)C(CH₃)₃)](PF₆)₄, [Pt₂(μ-SCH₂C(O)C(CH₃)₃)(μ-SCH₂C(O)CH₂CH₃)](PF₆)₄ and [Pt₂(μ-SCH₂C(O)C(O)CH₂S)(μ-SCH₂C(O)CH₂CH₃)](PF₆)₄. Sequential reactions of [Pt₂(μ-S)₂(PPh₃)₄] with BrCH₂C(O)C(CH₃)₃ and BrCH₂C(O)CH₂CH₃ yielded the heterodiallykylated complex [Pt₂(μ-SCH₂C(O)C(CH₃)₃)(μ-SCH₂C(O)CH₂CH₃)](PF₆)₄. The products were isolated as the [BPh₄]⁻ or [PF₆]⁻ salts and characterized by ESI-MS, IR, ¹H and ³¹P NMR spectroscopy and single-crystal X-ray crystallography.

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1. Introduction
The exceptional reactivities of the electron-rich bridging sulfide centers in the metalloligand, [Pt₂(μ-S)₂(PPh₃)₄], 1 toward metal fragments have been documented in the formation of multimetallic aggregates of main group elements [1–4], transition metals [1,4–9] and uranium [10]. Similar chemistry has been reported for selenium analogue [11,12] and closely related complexes with ¹,₄–9 and uranium [10]. Similar chemistry has been reported for selenium analogue [11,12] and closely related complexes with ¹,₄–9 and uranium [10].

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leaving group. Monoalkylated complex, \([\text{Pt}_2(\mu-\text{S})(\mu-\text{SR})(\text{PPh}_3)_3]^+\)
 can further react with a very strong electrophile, 3 or 5 to yield a heterodiaclylated complex of the type \([\text{Pt}_2(\mu-\text{SR})(\mu-\text{SR})(\text{PPh}_3)_4]^2+\)
\((R = \text{any electrophile and } R' = \text{CH}_3\text{C(O)}\text{O}\text{Ph or CH}_2\) [19,28]. However, heterodiaclylation of 1 that involve nucleophilic leaving group (e.g. Cl\(^-\), Br\(^-\) and I\(^-\)) may result in the displacement of the terminal PPH3 ligands to form complexes such as \([\text{Pt}_2(\mu-\text{SCH}_2\text{C(O)}\text{O})(\text{P})\text{SR}(\text{PPh}_3)_3]Br^+\) or \([\text{Pt}_2(\mu-\text{SCH}_2\text{C(O)(CH}_3\text{)}_2)(\text{PPh}_3)_4]\) [29] or expansion of the normally robust four-membered \([\text{Pt}_2(\mu-S)_2]\) core [30]. However, careful visualization of the reaction and modification of the conditions may eliminate formation of unwanted products. We recently reported the reverse of the PPH3 halide displacement [28] and the expansion of the \([\text{Pt}_2(\mu-S)_2]\) core from the rearrangement of a four-membered ring bridged derivative, \([\text{Pt}_2(\mu-\text{SCH}_2\text{C(O)(CH}_2\text{S})(\text{PPh}_3)_3]^+\) to a five-membered ring \([\text{Pt}_2(\mu-\text{SCH}_2\text{C(O)(CH}_3\text{)}_2)(\text{PPh}_3)_4]^+\) with no PPH3 displacement [30].

Manual injection of the reaction solution of 1 and an electrophile into ESI-MS from a reaction flask or vial involve mere screening of the species formed after longer interval of time and not monitoring of reaction progress and the formation of species in real time. Real time reaction visualization of chemical reaction [31] could be applied in characterisation of the formation of products and other species in the reaction of 1 with alkylation agents and help in eliminating undesired side reactions, improve isolation of target product, determine the reaction mechanism and allow for the acquisition of kinetic information on the reaction. To date, kinetic analysis has not previously been applied in the investigation of the synthetic complexities surrounding the double alkylation of 1. Consequently, the only reported electrophiles that are able to homodi- and heterodiaclylate 1 are BrCH\(_2\)C(O)Ph and Me\(_2\)SO\(_4\). Among the few electrophiles that are able to dialkylate 1, there is no clear similarities. In this contribution, we report on the micro-synthetic investigation of the reactivity of 1 towards the activated bromoacetyl aliphatic alkylation agents with closely related functionalities and the rates of formation of mono-, homodi- and bridging di-alkylated derivatives using the pressurized sample infusion electrospray ionization mass spectrometry (PSI-ESI-MS) technique. Importantly, this leads to further understanding of the conditions that encourage the double alkylation of 1 and these insights have been applied to allow rational modification of the laboratory scale synthesis of novel \(\mu\)-thiolate derivatizes of 1.

2. Results and discussion

2.1. Kinetic profile, synthesis and characterizations

In the development of the chemistry of 1, electrospray ionization mass spectrometry (ESI-MS) has been a valuable tool. It is a robust, fast, highly sensitive technique, able to detect molecular masses at a wide range of minute concentrations, and achieve great accuracy due to its dynamic range. It is well-suited to the analysis of organometallics and coordination compounds because it is a “soft” ionization method, the molecular ion is easily discerned and fragmentation is minimal [32]. Pressurized sample infusion (PSI) is a real-time sample infusion technique for ESI-MS that was employed in this project which allows for the immediate visualization of the formation of products and for the kinetic information regarding their formation to be obtained [31,33,34]. This technique is analogous to a cannula transfer, in which the reacting solution is transferred through PEEK tubing directly into the ionizing source of the ESI-MS, through overpressure of the Schlenk flask with inert gas. ESI-MS has the advantage over other techniques for the efficient separation of complex reaction mixtures and continues monitoring of each charged species over time intervals of seconds, minutes to hours. The acquisition of each spectrum can take less than a second and each spectrum is then combined into a series of abundance traces. The shape of each trace provides a detailed kinetic profile for each species.

The kinetic profiles of the reactions of minuscule amounts of \([\text{Pt}_2(\mu-\text{S})_2(\text{PPh}_3)_4]\) or 1 towards the electrophiles BrCH\(_2\)C(O)C(CH\(_3\))\(_3\), a, BrCH\(_3\)C(O)CH\(_2\)CH\(_3\), b, and BrCH\(_2\)C(O)C(CH\(_2\))Br, c, in methanol were monitored by PSI-ESI-MS to determine the species formed, rate of reaction and completion time. A methanolic solution of 1 was transferred by PSI into ESI-MS. As soon as the signal for the mass of \([\text{M}+\text{H}]^+\) appeared at \(m/z = 1503.5\), BrCH\(_2\)C(O)C(CH\(_3\))\(_3\), a, was added to the reaction solution through a syringe. There was a fast but steady decrease in the intensity of the \(m/z = 1503.5\) peak and steady increase in the peak at \(m/z = 1603.9\) for the monomethylated product, \([\text{Pt}_2(\mu-\text{S})(\mu-\text{SCH}_2\text{C(O)(CH}_3\text{)(CH}_2\text{)}_3)(\text{PPh}_3)_4]^+\). No double alkylation of 1 by a was observed under ESI-MS conditions, presumably due to the deactivating effect of the electron donating methyl groups of the pinacolone moiety on the alkylation carbon of \(-\text{CH}_2\text{Br}\) group. Fig. 1 shows the ESI-MS plot of the reaction progress. Formation of the monomethylated product, 1a, was complete after 2 min as indicated by the disappearance of the \(m/z = 1503.5\) peak. The monomethylated complex was isolated from the laboratory scale reaction as the \([\text{BrCH}_2\text{C(O)C(CH}_3\text{)}_3]^+\) salt, \([\text{Pt}_2(\mu-\text{S})(\mu-\text{SCH}_2\text{C(O)C(CH}_3\text{)}_3)(\text{PPh}_3)_4]^+\] (BPh\(_4\)) to a yellow precipitate following filtration and the addition of excess NaBPh\(_4\) and shown by positive ion mode ESI-MS as pure 1a. Further stirring of the laboratory scale reaction for 24 h at 50 °C did not give any dialkylated product. 1aBPh\(_4\) contains two nonequivalent phosphorus centers (thiolate and sulfide). The \(3^1\text{H}]\)NMR spectrum shows two different resonances at \(\delta = 23.39\) and \(\delta = 23.90\) and well-separated satellite peaks due to \(^{195}\text{Pt}\) coupling. \(^{1}\text{H}\) [\(\text{PPh}_3\)] 3376 Hz and \(^{1}\text{H}\) [\(\text{Pt}(\text{PPh}_3)\)] 2653 Hz respectively, consistent with unsymmetrical monomethylated 1. The coupling constants are due to the differing trans influence [35] of the thiolate versus sulfide ligand, with phosphines trans to the higher trans-influence sulfide showing a coupling constant of 2653 Hz while those trans to thiolate show 3376 Hz. The \(^1\text{H}\) NMR spectrum shows resonances at \(\delta = 3.46\) and 0.66 which were assigned to CH\(_3\) and CH\(_2\) groups respectively and complicated signals in the phenyl region due to the terminal PPh\(_3\) groups. The IR spectra of 1aBPh\(_4\) showed absorption peaks at 1708 cm\(^{-1}\), characteristic of the carbonyl (C=O) group of the incorporated electrophile.

The same technique employed in the reaction of a and 1 above was used to profile the reaction of 1 with BrCH\(_2\)C(O)CH\(_2\)CH\(_3\), b. Fig. 2 shows the reaction profile. The monomethylated was fast and complete formation of \([\text{Pt}_2(\mu-\text{S})(\mu-\text{SCH}_2\text{C(O)C(CH}_3\text{)}_3)(\text{PPh}_3)_4]^+\). 1b occurred in 6 min followed by slower dialkylation to give \([\text{Pt}_2(\mu-\text{SCH}_2\text{C(O)(CH}_3\text{)}_2)(\text{PPh}_3)_4]^+\). 1c. The reaction completed in 100 min with the total consumption of the monomethylated species. The rate of alkylation of the free sulfide in the monomethylated complex, 1a, was slower than the monomethylated of 1 as expected, due to the positive charge on the monomethylated complex and steric shielding of the residual sulfide ligand by the incorporated group. The dialkylation product was isolated in the laboratory synthesis after stirring for 2 h to complete the reaction as the hexafluorophosphate salt, 1c[\(\text{Pt}(\text{PPh}_3)_2\)] by addition of excess NH\(_4\)PF\(_6\). Scheme 1 summarizes the reaction of 1 with these reactive electrophiles. The \(3^1\text{H}]\) NMR spectrum of 1c[\(\text{Pt}(\text{PPh}_3)_2\)] showed a single resonance at \(\delta = 19.17\), well-separated satellite peaks due to \(^{195}\text{Pt}\) coupling and \(^{1}\text{H}\) [\(\text{PPh}_3\)] 3059 Hz, which is in agreement with the symmetrical nature of the complex. The \(^1\text{H}\) NMR shows complicated signals around the phenyl region but also indicated distinct broad resonances at \(\delta = 2.58\), \(\delta = 1.88\) and \(\delta = 0.72\) assigned to protons of the two \(-\text{SCH}_3\), –CH\(_3\) and –CH\(_2\) groups respectively. The X-ray structure of 1c was determined and the molecular structure of the core shown in Fig. 4. The selected bond
lengths and angles are given in Table 1. The \( \text{Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_2 \) core of \( 1c \) has a dihedral angle, \( \theta \), of 159.82° between the two \( \text{PtS}_2 \) planes, which is considerably flatter when compared with the corresponding angles in \( \text{[Pt}_2(\mu\text{-SCH}_3\text{)}_2(\text{PPh}_3)_4]^+ \) (156.87°) [19], \( \text{[Pt}_2(\mu\text{-SCH}_2\text{C(O)Ph})_2(\text{PPh}_3)_4]^+ \) (156.36°) [28]. The IR spectra of \( 1c \) showed absorption peaks at 1712 cm\(^{-1} \) attributable to the incorporated carbonyl (>C@O) groups of the electrophile.

Exceptionally strong alkylating agents like \((\text{Me})_2\text{SO}_4\) and \(\text{PhC(O)CH}_2\text{Br}\) are notably able to alkylate the free sulfide in monoalkylated derivatives of the type \( \text{[Pt}_2(\mu\text{-S})(\mu\text{-SR})(\text{PPh}_3)_4]^+ \) [19,28]. The ability of \( \text{BrCH}_2\text{C(O)CH}_2\text{CH}_3 \) to double alkylate \( 1a \) indicates it is a stronger electrophile than \( \text{BrCH}_2\text{C(O)C(CH}_3)_3 \) and suggested it could further alkylate the unsubstituted sulfide in \( 1a \). In order to investigate this, a combination of the ESI-MS predetermined reaction times and conditions of the reactions of the two alkylating agents, \( 1a \) and \( 1b \) with \( 1 \) were strictly employed because prolonged stirring or elevated temperatures encourage undesired side reactions like the displacement of the terminal triphenyl phosphine ligands by the \( \text{Br}^- \) leaving species [28]. First, monoalkylated complex \( \text{[Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C(O)}\text{C(CH}_3)_3)(\text{PPh}_3)_4]^+ \), \( 1a \) was generated in situ by reacting 1:1 mol equivalent of \( \text{BrCH}_2\text{C(O)}\text{C(CH}_3)_3 \) and \( \text{[Pt}_2(\mu\text{-S})(\text{PPh}_3)_4]^+ \) and as soon as the formation of the monoalkylated complex was completed, excess \( \text{BrCH}_2\text{C(O)}\text{CH}_2\text{CH}_3 \) was added to the reaction mixture. The reaction completed after an hour to give only the heterodialkylated complex \( \text{[Pt}_2(\mu\text{-SCH}_2\text{C(O)CH}_2\text{CH}_3})(\mu\text{-SCH}_2\text{C(O)C(CH}_3)_3)(\text{PPh}_3)_4]^+ \), \( 1d \) which was subsequently isolated as the \( \text{PF}_6^- \) salt, \( \text{[Pt}_2(\mu\text{-SCH}_2\text{C(O)CH}_2\text{CH}_3})(\mu\text{-SCH}_2\text{C(O)C(CH}_3)_3)(\text{PPh}_3)_4](\text{PF}_6)_2 \), \( 1d \). The \( ^3\text{P}^{(1)}\text{H} \) NMR of \( 1d \) showed two well-separated resonance signals at \( \delta 18.62 \) and \( \delta 19.28 \) with a corresponding \( \text{J}(\text{PtP}) \) of 3078 Hz and 3082 Hz, for \( \text{–SCH}_2\text{C(O)CH}_2\text{CH}_3 \) and \( \text{–SCH}_2\text{C(O)C(CH}_3)_3 \) thiolate groups respectively. The crystal structure of \( 1d \) is shown in Fig. 5, with selected bond lengths and angles in Table 2. The structure adopted a syn conformation, an arrangement which minimizes steric interactions between the thiolate ligands with the bulky terminal \( \text{PPh}_3 \) ligands. The dihedral angle between the two \( \text{PtS}_2 \) planes is 158.56°. The carbonyl groups are positioned above the two platinum atoms at a distance of \( \text{[Pt}(1)\text{-O(2)} 2.839 \text{Å and Pt(2)–O(1)} 2.877 \text{Å. The sum of the van der } \text{Waals radii for Pt and O is } 3.24 \text{ Å} \) [36], so they are close enough to indicate a weak donor interaction. The IR spectra of \( 1d \) showed absorption peaks at 1713 cm\(^{-1} \) assigned to the incorporated carbonyl groups.

Fig. 1 shows the ESI-MS profile of the reaction of \( \text{[Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]^+ \) (injected at 3 min) with \( \text{BrCH}_2\text{C(O)CMe}_3 \) (injected at 6 min) to form the monocation \( \text{[Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C(O)CMe}_3)(\text{PPh}_3)_4]^+ \), \( 1e \). The profile of the reaction of \( \text{[Pt}_2(\mu\text{-S})_2(\text{PPh}_3)_4]^+ \) with \( \text{BrCH}_2\text{C(O)CH}_2\text{Br} \) is shown in Fig. 2. The reaction was shown by PSI-ESI-MS to be very fast. The time between formation of the monoalkylated derivative \( \text{[Pt}_2(\mu\text{-S})(\mu\text{-SCH}_2\text{C(O)CH}_2\text{Br})(\text{PPh}_3)_4]^+ \), \( 1e \) and the expected bridging dialkylated derivative
Kinetic plots from the ESI-MS reaction profile data of the mono- and dialkylation reactions show they are both first order. The reaction profile shows two species, at m/z = 809.6 and 1436.8 compared with the expected mass m/z = 795(ca) of the product 1f. The ESI-MS of the isolated product from the bench top synthesis showed only a peak at m/z = 809.6. This species was tentatively assigned to the methanol adduct, \([\text{Pt} \{\mu-\text{SCH}_2\text{C(O)C(O)CH}_2\text{S}\} (\text{PPh}_3)_4 \cdot \text{OHCH}_3\}]^{2+}\), formed immediately upon formation of 1f.

A cation at m/z = 1436.8 is attributable to \([\text{Pt} \{\mu-\text{SCH}_2\text{C(O)C(O)CH}_2\text{S}\} (\text{PPh}_3)_3\text{Br} \cdot \text{OHCH}_3\}]^{+}\), which formed from the displacement of a PPh₃ by the Br⁻ leaving group. The masses were identified by comparing the high resolution mass spectral (HR-MS) isotope patterns with calculated isotope patterns [37]. Attempts at obtaining suitable single crystals of the products as the [PF₆]⁻ salt were unsuccessful.

[Pt₂(μ-SCH₂C(O)C(O)CH₂S) (PPh₃)₄]²⁺. 1f is less than two seconds. Formation of this type of methanol adduct has earlier been observed under ESI-MS conditions for the reaction of α,ω-monoketone electrophile, CICH₂C(O)CH₂Br with 1 [30]. The peak of a cation at m/z = 1436.8 is attributable to \([\text{Pt} \{\mu-\text{SCH}_2\text{C(O)C(O)CH}_2\text{S}\} (\text{PPh}_3)_2\text{Br} \cdot \text{OHCH}_3\}]^{+}\), in which Br⁻ had replaced a PPh₃ ligand also appeared.

Scheme 1. Alkylation reactions of \([\text{Pt}_2(\mu-S)\{(\text{PPh}_3)_4\}] \) (1) with reactive α-bromoketones alkylating agents, BrCH₂C(O)C(CH₃)₃ (a), BrCH₂C(O)CH₂CH₃ (b), and diketone, BrCH₂C(O)C(O)CH₂Br (c).
The corresponding tetraphenylborate complex 1f(BPh₄)₂ dried under vacuum overnight did however yield suitable crystals for X-ray structure determination. The structure of the dication is shown in Fig. 6 and the selected bond lengths and angles in Table 3.

The 3¹P{¹H} NMR spectrum of 1f( PF₆)₂ showed a single resonance at δ 19.62 showing ¹J(PtP) 3021 Hz, consistent with a highly symmetric structure of the complex. In the ¹H NMR spectrum, a broad resonance at δ 3.50 is assigned to the SCH₂ protons, and the complicated signals at the phenyl region indicated formation of 1f. The IR spectra showed absorption peaks that confirmed the formation of 1f( PF₆)₂ with a double peak at 1711 cm⁻¹ characteristic of the carbonyls of the diketone (–CH₂C(O)C(O)CH₂–) of the incorporated group.

3. Experimental

3.1. Materials and instrumentation

The alkylating agents BrCH₂C(O)C(CH₃)₃, BrCH₂C(O)CH₂CH₃ and BrCH₂C(O)C(O)CH₂Br were supplied by Alfa Aesar; CAUTION!: - highly toxic, potent lachrymator and vesicant and should be handled using appropriate safety precautions. cis-PtCl₂(PPh₃)₂, Na₂S_{9}H₂O, NH₄PF₆ and NaBPh₄ were supplied by Sigma–Aldrich. Reaction solvents: benzene (Sigma–Aldrich), methanol (Caledon Laboratories), dichloromethane (Sigma–Aldrich) and diethyl ether (EMD Chemicals) were reagent grade and used without further purification. [Pt₂(l-S)-SCH₂C(O)CH₂CH₃]²⁺ was synthesised according to a reported literature procedure by the metathesis reaction of cis-PtCl₂(PPh₃)₂ with Na₂S_{9}H₂O in benzene[17,38].

Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. NMR spectra were recorded in CDCl₃ solution, unless otherwise stated. ¹H and ³¹P{¹H} spectra referenced to TMS for ¹H and 85% phosphoric acid for ³¹P were recorded on a Bruker DRX 300 MHz spectrometer. IR spectra were obtained as KBr disks with a Perkin Elmer Spectrum FTIR spectrometer, version 10.4.3. Melting points of the compounds were determined with a Galenkamp melting point apparatus in air and uncorrected. ESI-MS of solid products were obtained by dissolving a small quantity of the material in 1–2 drops of dichloromethane, followed by dilution to
3.3. Syntheses of the alkylated complexes

3.3.1. Synthesis of \([\text{Pt}_2(\mu-S)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_3)_2)(\text{PPh}_3)_4](\text{BF}_4)_2, \text{1a}\)](\text{BF}_4)_2\)

To a suspension of \([\text{Pt}_2(\mu-S)(\text{PPh}_3)_4](\text{BF}_4)_2\) (50 mg, 0.033 mmol) in methanol (25 mL) was added large excess of \(\text{BrCH}_2\text{C}(\text{O})\text{C}(\text{O})\text{CH}_2\text{Br}\) (0.1 mL, 0.98 mmol, 32.4 mol equiv.) and solution stirred for 20 min at room temperature. Complete formation of the monoaalkylated product was confirmed by ESI-MS which showed \([\text{Pt}_2(\mu-S)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_3)_2)(\text{PPh}_3)_4]^+\) at \(m/z\) 1603.93. The solution was filtered and NaBPh\(_4\) (25.04 mg, 0.16 mmol) added to the clear filtrate. The resulting yellow precipitates were filtered, washed with water (4 × 10 mL) and diethyl ether (4 × 10 mL) and dried in air, giving \(\text{1a}(\text{BF}_4)_2\) (54 mg, 85%). M.p. 122–124 °C; Anal. Calc. for \(\text{C}_{176}\text{H}_{91}\text{BOP}_4\text{Pt}_2\text{S}_2\): C, 50.1; H, 3.2. Found: C, 48.7; H, 3.1.

3.3.2. Synthesis of \([\text{Pt}_2(\mu-S)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_2)\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3)(\text{PPh}_3)_4]^+\) \(\text{1c}\) (\text{PF}_6)_2\)

To a stirred suspension of \([\text{Pt}_2(\mu-S)(\text{PPh}_3)_4]\) (50 mg, 0.033 mmol) in methanol (25 mL) was added \(\text{BrCH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3\) (0.1 mL, 0.98 mmol, 32.4 mol equiv.). The solution was stirred for 2 h at room temperature. Complete formation of the product was confirmed by ESI-MS which showed \([\text{Pt}_2(\mu-S)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_2)\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{CH}_3)(\text{PPh}_3)_4]^+\) at \(m/z\) 821.58. The solution was filtered and NaH\(_2\text{BPh}_4\) (25.04 mg, 0.16 mmol) added to the clear, colorless filtrate. The resulting precipitate was filtered, washed with water (4 × 10 mL) and diethyl ether (4 × 10 mL) and dried, giving \(\text{1c}(\text{PF}_6)_2\) (44 mg, 68%) as a white solid. Crystals suitable for X-ray crystallography were isolated by vapour diffusion of diethyl ether into a dichloromethane solution of \(\text{1c}(\text{PF}_6)_2\).

3.3.3. Synthesis of \([\text{Pt}_2(\mu-S)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_3)_2)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_3)_2)(\text{PPh}_3)_4]^+\) \(\text{1d}\) (\text{PF}_6)_2\)

To a stirred suspension of \([\text{Pt}_2(\mu-S)(\text{PPh}_3)_4]\) (50 mg, 0.033 mmol) in methanol (25 mL) was added \(\text{BrCH}_2\text{C}(\text{O})(\text{CH}_3)_2\) (0.1 mL, 0.98 mmol, 32.4 mol equiv.). The solution was stirred for 20 min at room temperature. Complete formation of the monoaalkylated product was confirmed by ESI-MS which showed \([\text{Pt}_2(\mu-S)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_3)_2)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_3)_2)(\text{PPh}_3)_4]^+\) at \(m/z\) 1601.93. Excess \(\text{BrCH}_2\text{C}(\text{O})(\text{CH}_3)_2\) (0.1 mL, 0.98 mmol) was added to the reaction mixture and stirred for 1 h. Complete formation of the heterodi-alkylated derivative \([\text{Pt}_2(\mu-S)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_3)_2)(\mu-\text{HC}_2\text{C}(\text{O})(\text{CH}_3)_2)(\text{PPh}_3)_4]^+\) was confirmed by ESI-MS which showed a \(m/z\) 836.79. The solution was gravity filtered and NaH\(_2\text{BPh}_4\) (25.04 mg, 0.16 mmol) added to the clear, colorless filtrate. The resulting precipitate was filtered, washed with water (4 × 10 mL) and diethyl ether (4 × 10 mL) and dried over vacuum, giving \(\text{1d}(\text{PF}_6)_2\) (44 mg, 68%) as white solids. Crystals suitable for X-ray crystallography were isolated by vapour diffusion of diethyl ether into a dichloromethane solution of \(\text{1d}(\text{PF}_6)_2\).

3.2. Pressurised Sample Infusion-Electrospray Ionization-Mass Spectrometry (PSI-ESI-MS) procedure

The kinetic profiles of the reactions were analyzed by PSI-ESI-MS. \([\text{Pt}_2(\mu-S)(\text{PPh}_3)_4]\) (1.60 mg) and excess amount of each of the electrophiles \(\text{BrCH}_2\text{C}(\text{O})(\text{CH}_3)_2\) (a, (ca 0.1 mL), \(\text{BrCH}_2\text{C}(\text{O})(\text{CH}_3)_2\) (b, (ca 0.1 mL) and \(\text{BrCH}_2\text{C}(\text{O})(\text{CH}_3)_2\)Br (c, (0.023 mg) were used in the experiments. The reaction solvent (methanol, 10 mL) was sparged with nitrogen on the Schlenk line to remove oxygen. 1 was added to the Schlenk flask. PEEK tubing was inserted through a septum into the reaction mixture solution, with the other end connected to the ESI-MS source. The methanolic solution of 1 was driven into ESI-MS using an overpressure using 2 psi argon. As soon as the signal for \([\text{1}^+\text{H}]^+\) at \(m/z\) 1503.5 reached a stable intensity, 1 mL methanol solution of the alkylating agent was injected by syringe through the septum into the reaction mixture to initiate the reaction. Spectra were recorded once per second to generate the abundance versus time data.
Crystallographic data for complexes 1c\((PF_6)_2\), 1d\((PF_6)_2\) and 1f\((BPh_3)_2\).

<table>
<thead>
<tr>
<th>Identification code</th>
<th>1c((PF_6)_2) 3CH2Cl2</th>
<th>1d((PF_6)_2) 3CH2Cl2</th>
<th>1f((BPh_3)_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C24H56C12F12O12Pt2S2</td>
<td>C24H56C12F12O12Pt2S2</td>
<td>C128H114B2O3P4Pt2S2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>2390.29</td>
<td>2149.97</td>
<td>3687.31</td>
</tr>
<tr>
<td>T (K)</td>
<td>120(2)</td>
<td>120(2)</td>
<td>120(2)</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(\alpha)</td>
<td>C2/c</td>
<td>C2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 13.4440(15) Å,</td>
<td>a = 17.3992(10) Å,</td>
<td>a = 37.415(4) Å,</td>
</tr>
<tr>
<td></td>
<td>(\alpha = 86.265(2))°,</td>
<td>(\alpha = 90^\circ)</td>
<td>(\alpha = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>b = 17.5218(19) Å,</td>
<td>b = 23.2587(14) Å,</td>
<td>b = 14.6486(17)Å,</td>
</tr>
<tr>
<td></td>
<td>(\beta = 81.410(2))°,</td>
<td>(\beta = 92.3282(2))</td>
<td>(\beta = 115.810(4)^\circ)</td>
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<td></td>
<td>c = 18.331(2) Å,</td>
<td>c = 21.1180(13) Å,</td>
<td>c = 27.674(4) Å,</td>
</tr>
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<td></td>
<td>(\gamma = 87.858(2))°,</td>
<td>(\gamma = 90^\circ)</td>
<td>(\gamma = 90^\circ)</td>
</tr>
<tr>
<td>V (Å(^3))</td>
<td>4258.9(8)</td>
<td>8539.9(9)</td>
<td>11583(5)</td>
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<tr>
<td>Z</td>
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<td>4</td>
<td>4</td>
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<tr>
<td>Density (calculated) (g cm(^{-3}))</td>
<td>1.708</td>
<td>1.672</td>
<td>1.319</td>
</tr>
<tr>
<td>Absorption coefficient ((\mu)) (mm(^{-1}))</td>
<td>3.704</td>
<td>3.645</td>
<td>2.554</td>
</tr>
<tr>
<td>F(000)</td>
<td>2164</td>
<td>4257</td>
<td>4656</td>
</tr>
<tr>
<td>Crystal color, habit</td>
<td>Colorless, rod</td>
<td>Colorless, block</td>
<td>Colorless, block</td>
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<tr>
<td>Crystal size (mm(^3))</td>
<td>0.114 x 0.062 x 0.041</td>
<td>0.080 x 0.060 x 0.054</td>
<td>0.510 x 0.229 x 0.114</td>
</tr>
<tr>
<td>(\theta) range for data collection</td>
<td>1.165-27.337°</td>
<td>1.425-27.298°</td>
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</tr>
<tr>
<td>Index ranges</td>
<td>-17 &lt; k &lt; 17, -22 &lt; l &lt; 22, -23 &lt; l &lt; 23</td>
<td>-21 &lt; h &lt; 21, -29 &lt; k &lt; 20, -18 &lt; l &lt; 18, -26 &lt; l &lt; 26, -35 &lt; l &lt; 35</td>
<td></td>
</tr>
<tr>
<td>Reflections collected</td>
<td>88400</td>
<td>137757</td>
<td>119881</td>
</tr>
<tr>
<td>Independent reflections (\left(R_{int}\right))</td>
<td>19160 (0.0565)</td>
<td>17853 (0.1098)</td>
<td>13007 (0.0293)</td>
</tr>
<tr>
<td>Completeness to (\theta = 25.242^\circ)</td>
<td>100.0%</td>
<td>100.0%</td>
<td>99.9%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Numerical</td>
<td>Numerical</td>
<td>Numerical</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9314 and 0.7508</td>
<td>0.9901 and 0.8015</td>
<td>0.8156 and 0.4016</td>
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<tr>
<td>Refinement method</td>
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<td>Full-matrix least-squares on (F^2)</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>19160/10/20</td>
<td>17853/11/1018</td>
<td>13007/3/658</td>
</tr>
<tr>
<td>Goodness-of-fit (GOF) on (F^2)</td>
<td>1.444</td>
<td>1.023</td>
<td>1.062</td>
</tr>
<tr>
<td>Final R indices (&gt; \sigma(R))</td>
<td>R(_1) = 0.0617, wR(_2) = 0.1359</td>
<td>R(_1) = 0.0487, wR(_2) = 0.1063</td>
<td>R(_1) = 0.0252, wR(_2) = 0.0636</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R(_1) = 0.0802, wR(_2) = 0.1432</td>
<td>R(_1) = 0.0857, wR(_2) = 0.1215</td>
<td>R(_1) = 0.0304, wR(_2) = 0.0672</td>
</tr>
<tr>
<td>Extinction coefficient</td>
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<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Largest difference peak and hole (e Å(^{-1}))</td>
<td>4.670 and -2.895</td>
<td>2.983 and -1.561</td>
<td>2.642 and -0.730</td>
</tr>
</tbody>
</table>

3.3.4. Synthesis of \([Pt_2\{\mu-SCH_2C(O)(O)CH_2S\}(PPh_3)_4]\)(PF_6)_2, 1f\((BPh_3)_2\)

A suspension of \([Pt_2\{\mu-S\}2(PPh_3)_4]\) (50 mg, 0.033 mmol) and BrC\(_2\)H\(_2\)C\(_2\)H\(_2\)Br (0.0081 mg, 0.033 mmol) in methanol (25 mL) was stirred for 25 min at room temperature. Complete formation of a cyclized product was confirmed by ESI-MS which showed a single peak of the methanol adduct, \([Pt_2\{\mu-SCH_2C(O)(O)CH_2S\}(PPh_3)_4]OHCH\(_2\)\) at m/z = 809.6. The solution was filtered and NH\(_4\)PF\(_6\) (25.04 mg, 0.16 mmol) was added to the clear, colourless filtrate. The resulting white precipitate was filtered, washed and \(\text{NH}_4\text{PF}_6\) (25.04 mg, 0.16 mmol) was added to the clear, colourless filtrate. An arbitrary sphere of data was recorded, on a MiTeGen loop. The loop was transferred to a Bruker APEX-II diffractometer equipped with a CCD area detector under a cold gaseous nitrogen stream. An arbitrary sphere of data was recorded, using Mo K\(_\alpha\) radiation (\(\lambda = 0.71073\) Å) and combination of \(\omega\) and \(\phi\)-scans of 0.5° [39]. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by intrinsic phasing methods and expanded routinely [40]. The model was refined by full-matrix least-squares analysis of \(F^2\) against all reflections [41]. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 \(U_{eq}\)(C) for methyl, 1.2 \(U_{eq}\)(C) for all others). Crystallographic data are summarised in Table 4.

3.4.1. \([Pt_2\{\mu-SCH_2C(O)(O)CH_2S\}(PPh_3)_4]\)(PF_6)_2, 1c\((PF_6)_2\) and 1f\((BPh_3)_2\) crystallized as colourless rod-like crystals. There are two molecules of the platinum-containing dication, four molecules of the associated \(PF_6^-\) anion and six molecules of dichloromethane of crystallization in the unit cell of the primitive, centrosymmetric, triclinic space group \(P1\). The structure of the cation is as expected. The complex consists of two Pt centers, each coordinated in a four-coordinate square planar fashion by two triphenyl phosphine ligands and two sulfurs of the bridging thiolate moieties. There is residual electron density near the Pt centers. Successive attempts to improve the data through re-integration and absorption correction could not improve these Fourier peaks. The fold angle formed by the two coordination planes about the Pt centers is: 26.82(6)°. The two mercaptopentanone chains are oriented in a sin fashion.

3.4.2. \([Pt_2\{\mu-SCH_2C(O)(O)CH_2S\}(PPh_3)_4]\)(PF_6)_2, 1d\((PF_6)_2\) 3CH2Cl2

The complex crystallized as colourless block-like crystals from a vapour diffusion of diethyl ether into the dichloromethane solution. There is one molecule of the di-platinum dication and two
molecules of [PF₆]⁻ anion in the asymmetric unit of the primitive, centrosymmetric, monoclinic space group P2₁/n. Also within the asymmetric unit are three disordered dichloromethane molecules.

The dication consists of two Pt centers, each coordinated in a slightly distorted four-coordinate, square planar fashion by two triphenylphosphine ligands and the two bridging sulfur atoms of the two thiolate ligands (Fig. 5 and Table 2). Bond distances about the Pt centers are unexceptional.

There is disorder of the thiolate ligands within the structure. The ratio was modeled as 0.6:0.4 at each site. Thus, 60% of the time the t-Bu and ethyl chain are in one position and the remaining 40% their positions are reversed (with respect to, for example, S1). The disorder was observed clearly in the major component where the terminal carbon of the ethyl chain was misoriented with respect to the t-Bu group that it overlays. The disorder for the minor component was readily observed for the t-Bu group (C10A–C12A), however, the ethyl group was found to overlap with C6 fairly closely. Only the slightly exaggerated atomic displacement ellipsoid of that atom indicated its likely position. Mild bond distance and angle restraints were applied to the model to retain a reasonable geometry to the disordered components. All of the disordered t-Bu/ethyl carbon atoms were refined with isotropic displacement parameters.

In addition to the salt, there are one full occupancy and two partial occupancy dichloromethane molecules of crystallization. All three are located within a channel within the lattice. Examination of residual electron density after modeling these solvent molecules indicates that there is likely considerable displacement of the solvent within this channel and the model here accounts for a reasonable estimate. Bond distance restraints were applied to sensibly model these disordered solvent molecules. The partially occupied solvent molecules were refined with independent site occupancy factors giving 0.75 and 0.45 at each site.

3.4.3. [Pt₂(μ-SCH₂C(O)CH₂S)(PPh₃)₄][BPh₄]₂, 1f

The complex crystallizes as colorless block-like crystals from dichloromethane/diethyl ether. There are four molecules of the di-platinum di-cation, eight molecules of [BPh₄]⁻ anion and four molecules of diethyl ether, disordered over two sites, in the unit cell of the C-centered, centrosymmetric, monoclinic space group C2/c. The di-platinum cation consists of two Pt centers, each coordinated in a square-planar fashion by two cis-triphenylphosphine ligands and bridged by the two sulfur atoms of a 2,3-dioxobutane-1,4-bis(thiolate) anion (Fig. 6 and Tables 3). The cation resides on the crystallographic twofold axis at [0.5, 0.25, 0.5], thus only half of the cation is represented in the asymmetric unit. The [BPh₄]⁻ anion resides in a general position.

The ether of crystallization was modeled with half occupancy atoms to yield reasonable atomic displacement parameters. Also present in the initial model was diffuse, disorganized electron density that could not be reliably modeled as any particular molecular species. Application of the SQUEEZE routine in PLATON [42] showed the presence of four void spaces within the unit cell, each having a void volume of 253 Å³ and accounting for 42 e⁻ each. The intensity information for this density was corrected. This solvent content has not been included in the chemical formula because its identity is unknown. Bond distances and angles within the molecules are otherwise as expected.

4. Conclusions

The investigation has demonstrated the successful synthesis of novel mono- and homoditi- and heteroditi- and bridgingdi-alkylated derivatives of [Pt₂(μ-S)₂(PPh₃)₄]. 1 through the reaction of bromaocyl alkylating agent with the high nucleophilicity of the μ-sulfido ligands. The inability of electrophile BrCH₂C(O)CH₂CH₃, a to double alkylate 1 but BrCH₂C(O)CH₂CH₃, b strongly suggest that apart from the leaving group, there is a threshold of residual positive charge on the alkylating carbon that encourages the dialkylation. We plan to explore the coordination chemistry of the incorporated ketone groups towards other metal fragments. The ability of using the functionalized derivatives to access multimetalic molecules may likely depend on moderating their reactivity towards metal centers. The use of PSI-ESI-MS for real time reaction visualization will be a productive technique in further investigation of the chemistry of this system.

Acknowledgments

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Appendix A. Supplementary material

CCDC 1431896, 1431897 and 1431898 contains the supplementary crystallographic data for 1c, 1d, and 1f. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.05.022.

References
