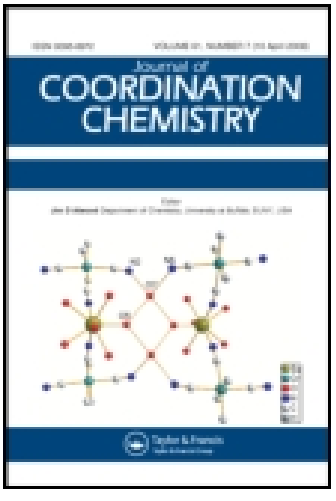

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E/Z isomerism in monoalkylated derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ containing 2,4-dinitrophenylhydrazone substituents

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E/*Z* isomerism in monoalkylated derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ containing 2,4-dinitrophenylhydrazone substituents

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Alkylation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with 2,4-dinitrophenylhydrazone-functionalized alkylating agents $XC_6H_4C\{=NNHC_6H_3(NO_2)_2\}CH_2Br$ (X = H, Ph) gives monoalkylated cations $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}C_6H_4X\}(PPh_3)_4]^+$. An X-ray diffraction study on $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}Ph\}(PPh_3)_4]BPh_4$ shows the crystal to be the *Z* isomer, with the phenyl ring and $NHC_6H_3(NO_2)_2$ groups mutually *trans*. ^{1}H- and $^{31}P\{^1H\}$ NMR spectroscopic methods indicate a mixture of *Z* (major) and *E* (minor) isomers in solution, which slowly convert mainly to the *E* isomer. Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the dinitrophenylhydrazone of chloroacetone $[ClCH_2C\{=NNH(C_6H_3(NO_2)_2\}Me]$ and $NaBPh_4$ gives $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}Me\}(PPh_3)_4]BPh_4$, which exists as a single (*E*) isomer.

Keywords: Platinum complexes; Alkylation reactions; Electrospray ionization mass spectrometry; X-ray crystal structure; Dinitrophenylhydrazones

1. Introduction

Alkylation and arylation reactions of the platinum(II) sulfide complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (1) [1, 2] are a versatile means of generating thiolate ligands on dinuclear platinum cores [3, 4]. Using this methodology, a wide range of functionality can be introduced. Recently, we reported the synthesis and characterization of a range of monoalkylated complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ from alkyl halides RX, where R contained a wide variety of C=O and C=N containing moieties, such as semicarbazones and oximes [5]. The alkylation chemistry has also been further extended to an investigation of the factors that promote dialkylation of the $\{Pt_2S_2\}$ core using activated alkylating agents of the type $RC(O)CH_2X$ (X = Cl, Br) [6].

In this contribution, we report a detailed study of the monoalkylation chemistry of some analogous alkylating agents that contain the 2,4-dinitrophenylhydrazone group. The formation of 2,4-dinitrophenylhydrazone derivatives of aldehydes and ketones is a

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classical derivatization strategy for their qualitative and quantitative determination, despite the fact that the outcome is usually quantitatively complicated by the formation of *E* and *Z* isomers [7, 8]. We previously reported a scoping study of alkylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ monitored using the technique of electrospray ionization mass spectrometry (ESI–MS) [9], which included a very preliminary study of some of the dinitrophenylhydrazones investigated herein [10]. However, these complexes were not isolated and characterized, and their initial identification was based solely on MS evidence; this article now reports the detailed synthesis and characterization of these new dinitrophenylhydrazone derivatives together with an investigation of isomerization.

2. Results and discussion

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) reacts smoothly in methanol with the 2,4-dinitrophenylhydrazone derivative of $BrCH_2C(O)Ph$ [i.e. $BrCH_2C\{{=}NNHC_6H_3(NO_2)_2\}Ph$] in an analogous manner to reactions with other related monofunctional alkylating agents [5]. The progress of the reaction was indicated by the dissolution of the sparingly soluble **1** and replacement of the $[\mathbf{1}+H]^+$ ion by the molecular cation of the product in the ESI mass spectrum. From the resulting solution, the product was isolated as its tetraphenylborate salt $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{{=}NNHC_6H_3(NO_2)_2\}Ph\}(PPh_3)_4]BPh_4$ (**2a**·BPh_4), by the addition of excess $NaBPh_4$ to the reaction mixture. Similarly, the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the dinitrophenylhydrazone of $BrCH_2C(O)C_6H_4Ph$-4 gave $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{{=}NNHC_6H_3(NO_2)_2\}C_6H_4Ph\}(PPh_3)_4]PF_6$ (**2b**·PF_6), by precipitation with excess NH_4PF_6.

Crystals of **2a**·BPh_4 suitable for a single-crystal X-ray diffraction study were obtained by recrystallization from dichloromethane–diethyl ether, and a structure determination was carried out to fully characterize the compound. The molecular structure of the cation is given in figure 1 together with the atom numbering scheme, while selected bond lengths and angles are summarized in table 1. The structure determination confirms the product as a monoalkylated derivative of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with structural features very similar to those of the corresponding phenacyl compound $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_4]^+$ [5]. The complex has the typically folded butterfly $\{Pt_2S_2\}$ core showing a dihedral angle between the two PtS_2 coordination planes of 129.22°, which compares well with 133.8° in $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_2]^+$. As normal in complexes of this type, the Pt(1)–P(4) and Pt(2)–P(2) bonds are longer than Pt(1)–P(3) and Pt(2)–P(1), due to P(2) and P(4) being *trans* to the higher *trans*-influence [11] sulfide. Pt-S(sulfide) bond distances are notably shorter [Pt(1)–S(1) 2.3319(7), Pt(2)–S(1) 2.3379(7) Å] compared to Pt–S(thiolate) bond distances [Pt(1)–S(2) 2.3843(7), Pt(2)–S(2) 2.3541(7) Å].

The alkyl substituent on S(2) adopts the typical axial position, analogous to $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_2]^+$ [5]. The hydrazone has the $NHC_6H_3(NO_2)_2$ group and phenyl substituents mutually *trans*, formally making it the *Z* isomer on the basis of the Cahn–Ingold–Prelog priority rules [12]. The hydrazone N–N bond is positioned directly above Pt(2). The phenyl ring on C(2) is directed away from the $\{Pt_2S_2\}$ core, while the $NNHC_6H_3(NO_2)_2$ group is positioned to one side of the core.

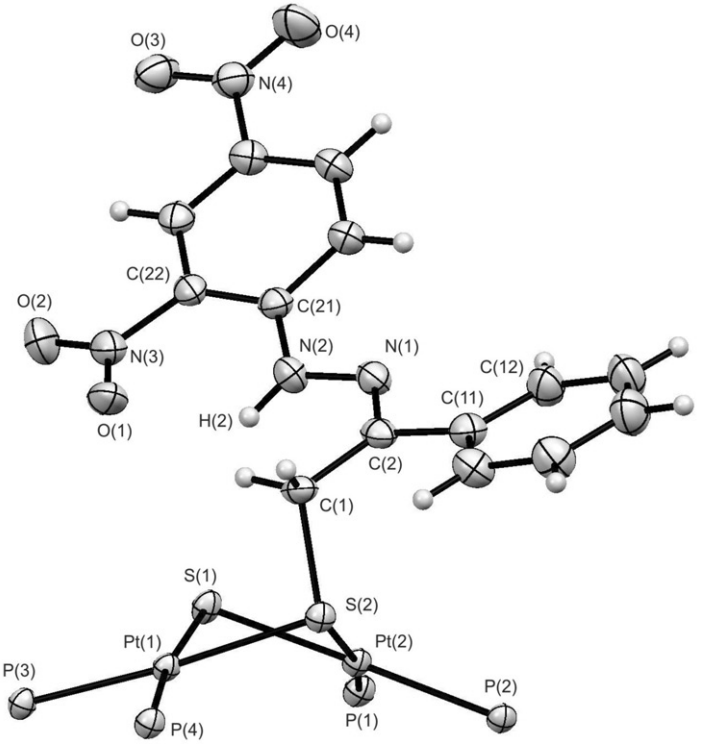


Figure 1. ORTEP diagram of the cation of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}Ph\}(PPh_3)_4]BPh_4$ (**2a**·BPh_4). Thermal ellipsoids are at the 50% probability level. Phenyl rings of the triphenylphosphine ligands and the BPh_4^- counterions have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}Ph\}(PPh_3)_4]BPh_4$ (**2a**·BPh_4); estimated standard deviations are in parentheses.

Pt(1)–S(1)	2.3319(7)	Pt(2)–S(1)	2.3379(7)
Pt(1)–S(2)	2.3843(7)	Pt(2)–S(2)	2.3541(7)
Pt(1)–P(3)	2.2657(7)	Pt(2)–P(1)	2.2880(7)
Pt(1)–P(4)	2.3060(7)	Pt(2)–P(2)	2.2940(7)
S(2)–C(1)	1.854(3)	C(1)–C(2)	1.502(4)
C(2)–N(1)	1.301(4)	N(1)–N(2)	1.379(4)
Pt(1)···Pt(2)	3.2162(2)	S(1)···S(2)	3.075(1)
S(1)–Pt(1)–S(2)	81.37(2)	S(1)–Pt(2)–S(2)	81.89(2)
P(3)–Pt(1)–S(1)	91.12(3)	P(1)–Pt(2)–S(1)	84.66(3)
P(3)–Pt(1)–P(4)	97.46(3)	P(2)–Pt(2)–S(2)	94.87(2)
P(4)–Pt(1)–S(2)	90.07(2)	Pt(1)–S(1)–Pt(2)	87.06(2)
P(1)–Pt(2)–P(2)	98.62(3)	Pt(1)–S(2)–Pt(2)	85.49(2)
C(1)–S(2)–Pt(1)	98.56(10)	C(1)–S(2)–Pt(2)	107.37(10)
C(2)–C(1)–S(2)	114.7(2)	N(1)–C(2)–C(1)	124.4(3)
N(1)–C(2)–C(11)	116.0(3)	C(2)–N(1)–N(2)	117.8(3)

The hydrazone NH interacts with an oxygen of the *ortho* nitro group forming a six-membered hydrogen-bonded ring. Such hydrogen–bond interactions in dinitrophenylhydrazones are well-known [13]. The H···O distance of 2.095(3) Å and the N···O separation of 2.672(4) Å fall well within the suggested ranges for N–H···O and N···O

distances of 1.60–2.40 Å [14] and 2.57–3.22 Å [15], respectively. The N–H bond also appears to be directed toward the free sulfide, S(1), raising the possibility of an N–H···S hydrogen bond [16, 17]. The sulfide centers of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ have been recently shown to form O–H···S hydrogen-bonded adducts with alcohols [18], while $[(Ph_3P)_4Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)NHC_6H_4NHC(O)CH_2S\}(\mu\text{-}S)Pt_2(PPh_3)_4]^{2+}$ (containing an *ortho*-phenylenediamide group) was also recently proposed to have an N–H···S interaction based on an N···S separation of 3.297 Å [19]. N···S distances in hydrogen-bonded systems are normally in the range 3.3–3.5 Å [20, 21]. However, the N···S separation in **2a**·BPh_4 is long [3.570(3) Å], and any N–H···S interaction will therefore be very weak.

The positive ion ESI mass spectra of the phenyl-substituted dinitrophenylhydrazones **2a**·BPh_4 and **2b**·PF_6 gave single ions at *m/z* 1802 and 1876, respectively, suggesting the formation of pure products. However, the $^{31}P\{^1H\}$ NMR spectra of freshly prepared solutions of the compounds in $CDCl_3$ gave almost identical spectra that showed the presence of two different isomers, as illustrated in figure 2(a) for **2b**·PF_6. These were subsequently shown (*vide infra*) to be the *E* and *Z* geometric isomers at the C=N bond (scheme 1). For **2b**, the major *Z* isomer shows two overlapping multiplets for two inequivalent PPh_3 ligands, showing $^1J(PtP)$ values of 3344 Hz (for PPh_3 *trans* to thiolate) and 2602 Hz (for PPh_3 *trans* to sulfide). The initially minor *E* isomer of **2b** gave better separated multiplets for the two PPh_3 environments with similar $^1J(PtP)$ coupling constants to the *Z* isomer [3411 and 2639 Hz]. The $^1J(PtP)$ coupling constants for **2a** and **2b** are similar to those previously reported for the ketone compound $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C(O)Ph\}(PPh_3)_2]BPh_4$ (3386 and 2630 Hz) [5].

The ^{1}H-NMR spectrum of the initially prepared solution of **2b**·PF_6 confirmed the presence of two isomers. In order to determine that the crystallographically characterized *Z* isomer was the major isomer in the initially prepared solution, further ^{1}H-NMR studies were carried out. The hydrazone NH protons are easily identified in the ^{1}H-NMR spectrum of the initial solution for the major and minor isomers at δ 10.68 and 11.19, by comparison with other dinitrophenylhydrazones, e.g. $CH_3C\{=NNHC_6H_3(NO_2)_2\}CH_3$ (δ NH 11.3) [22]. The spectrum also showed signals due to the SCH_2 protons at δ 4.40 and 3.65 for the major and minor isomers, respectively. Assignment of the NH and SCH_2 signals to the individual *E* and *Z* isomers was made on the basis of ROESY NMR data. Thus the SCH_2 resonance at δ 4.40 and the NH resonance at δ 10.68 (for the initial major isomer) exhibited mutual ROESY correlations, consistent with the close proximity of these protons in the *Z* isomer (scheme 1). However, the SCH_2 proton resonance in the initial minor isomer (at δ 3.65) showed a ROESY correlation to a nearby aromatic proton at δ 6.79 and not to the NH proton at δ 11.19. Similarly, this NH proton showed a ROESY correlation to an aromatic proton at δ 6.79 and not to the SCH_2 protons at δ 3.65. These correlations are consistent with the relationship between the NH and SCH_2 protons as given in the *E* isomer (scheme 1). Analysis of the starting alkylating agent $BrCH_2C\{=NNHC_6H_3(NO_2)_2\}C_6H_4Ph$ by ^{1}H-NMR indicated that the major component had the same spatial arrangement as observed in the initially major *Z* isomer of **2b**.

When the solution of **2b**·PF_6 used for NMR analysis was stored at -18°C for 6 months, there was reversal of the relative amounts of the two isomers in both the $^{31}P\{^1H\}$- and ^{1}H-NMR spectra, with the initially minor *E* isomer now being the major species (figure 2b). After a longer period (9 months) complete conversion had still not occurred. The conversion of the initial *Z* isomer to the *E* isomer in solution is

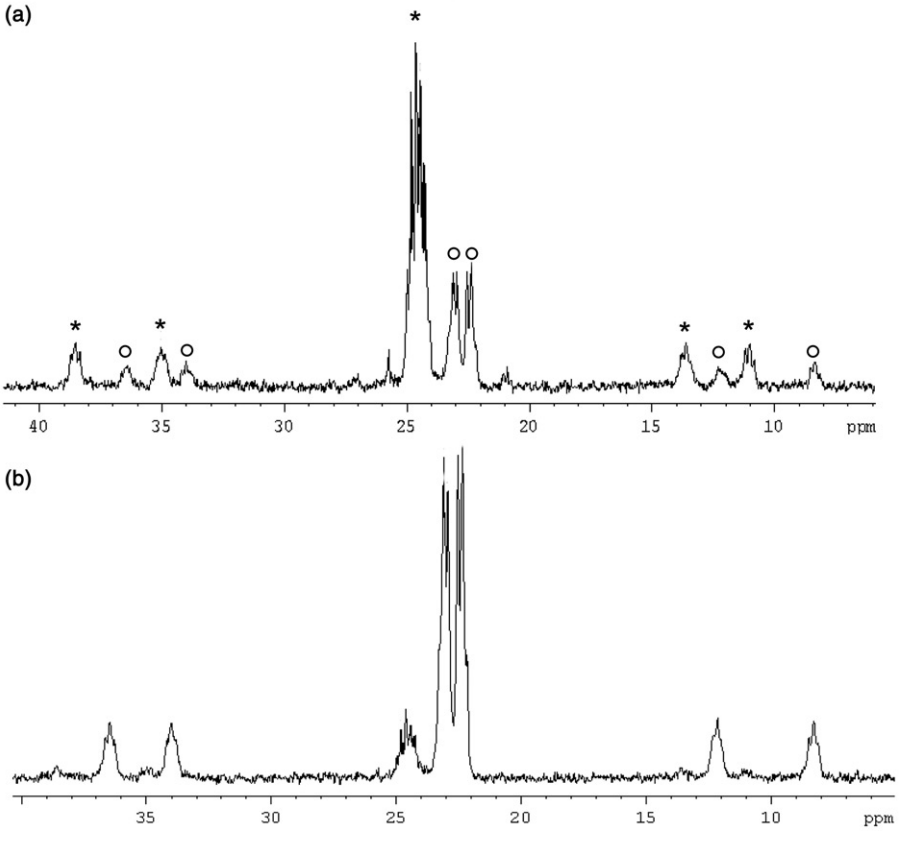
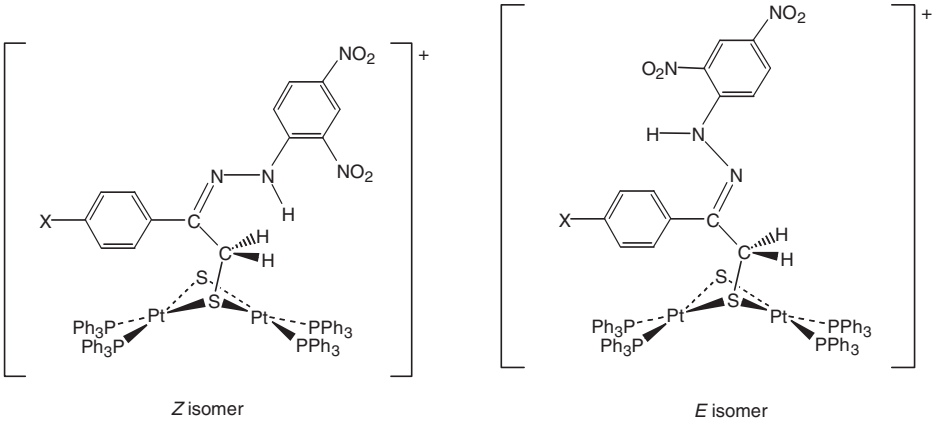


Figure 2. $^{31}P\{^{1}H\}$ NMR spectra of **2b**·PF_6 in $CDCl_3$: (a) freshly prepared solution; peaks due to the initially dominant *Z* isomer are indicated by stars, while those for the *E* isomer are indicated by circles; (b) after storage at −18°C for 6 months.



Scheme 1. Structures of the *Z* and *E* isomers of the cations $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{{=}NNHC_6H_3(NO_2)_2\}C_6H_4X\}(PPh_3)_4]^+$ (X = H **2a** or Ph **2b**), showing the spatial relationship between the NH and SCH_2 protons.

presumably driven by steric interactions, as found in previous studies of the *E–Z* isomerization of dinitrophenylhydrazones derived from substituted acetophenones [23]. In the *E* isomer, the steric bulk of the 2,4-dinitrophenyl group projects further away from the $\{Pt_2S_2\}$ core. The observation of this isomerization process suggests that any N–H $\cdots$ S hydrogen bond interaction (only possible in the *Z* isomer) must indeed be very weak.

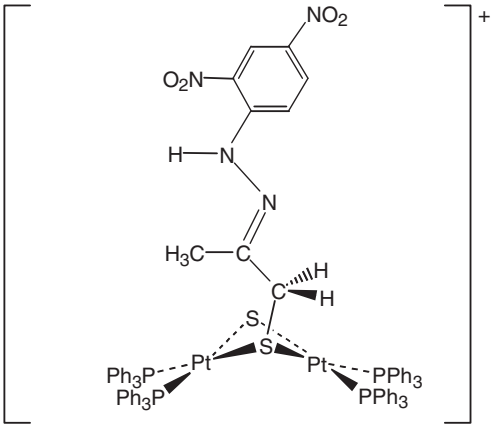
Finally, observation of both *E*/*Z* isomers appears to be confined to aryl ketone derivatives. Thus, reaction of **1** with dinitrophenylhydrazone of chloroacetone [$ClCH_2C\{=NNH(C_6H_3(NO_2)_2\}Me$] proceeded rapidly, giving a bright yellow-orange solution from which the salt $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}Me\}(PPh_3)_4]BPh_4$, **3**·$BPh_4$ was isolated by the addition of $NaBPh_4$. The product showed a single ion in its ESI mass spectrum, at *m*/*z* 1740, due to the product cation. The NMR spectra of this product also showed only a single isomer, in contrast to the aromatic-substituted dinitrophenylhydrazones described above. Thus, two ^{31}P resonances were observed for the two inequivalent types of PPh_3, showing coupling constants of 3342 and 2613 Hz. The ^1H-NMR spectrum showed a single NH resonance at δ 10.56, as well as single CH_2 and CH_3 resonances at δ 3.73 and 0.47, respectively. ^1H-ROESY NMR data showed enhancement of the CH_3 but not the NH proton on irradiation of the CH_2 protons, while irradiation of the NH proton produced an enhancement only in the methyl protons. This places the NH and CH_3 groups mutually *cis*, making the complex the *E* isomer (scheme 2).

In conclusion, this study has further extended the alkylation chemistry of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ to include alkylating agents containing 2,4-dinitrophenylhydrazone groups and demonstrated the occurrence of hydrazone *E–Z* isomerization in some derivatives.

3. Experimental

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (**1**) was prepared by the literature procedure [18, 24]. The dinitrophenylhydrazone alkylating agents $BrCH_2C\{=NNHC_6H_3(NO_2)_2\}C_6H_4Ph$, $BrCH_2C\{=NNHC_6H_3(NO_2)_2\}Ph$, and $ClCH_2C\{=NNHC_6H_3(NO_2)_2\}Me$ were prepared by the standard procedure for the conversion of ketones into their 2,4-dinitrophenylhydrazones [25], by the reaction of $BrCH_2C(O)C_6H_4Ph$ (2-bromo-4′-phenylacetophenone, Aldrich), $BrCH_2C(O)Ph$ (phenacyl bromide, BDH), or $ClCH_2C(O)CH_3$ (chloroacetone, BDH) with 2,4-dinitrophenylhydrazine (BDH) in acidified ethanol solution.

ESI mass spectra were recorded on a VG Platform II instrument. Solutions of approximate concentration *ca.* 0.1 mg mL^{-1} were prepared by dissolving a small quantity of sample in a few drops of either dichloromethane or acetonitrile, followed by dilution to *ca.* 1.5 mL with methanol. Confirmation of species was facilitated by comparison of observed and calculated isotope distribution patterns, the latter obtained from the *Isotope* program [26]. *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. NMR spectra were recorded in $CDCl_3$ solution on a Bruker Avance DRX300 spectrometer using XWIN-NMR software version 3.0. IR spectra were recorded as KBr discs using a



Scheme 2. Structure of the cation $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}CH_3\}(PPh_3)_4]^+$ **3** as the *E* isomer observed by ^{1}H-NMR studies.

Digilab FTS2000 Scimitar Series FT-IR with Digilab Merlin Version 3.4 software. Melting points were recorded on a Reichert Thermovar apparatus, and are uncorrected.

3.1. *Synthesis of* $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}Ph\}(PPh_3)_4]BPh_4$ *(2a·*BPh_4*)*

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (149 mg, 0.099 mmol) and $BrCH_2C\{=NNHC_6H_3(NO_2)_2\}Ph$ (76 mg, 0.201 mmol) in methanol (40 mL) were stirred for 1 h giving a cloudy yellow-orange solution. The solution was filtered and $NaBPh_4$ (73 mg, 0.214 mmol) added to the filtrate to give a yellow-orange precipitate. The product was filtered, washed successively with water (10 mL), methanol (10 mL), and diethyl ether (10 mL) and dried to give **2a**·BPh_4 (121 mg, 58%). Found: C, 61.4; H, 4.3; N, 2.6. $C_{110}H_{91}N_4BO_4P_4Pt_2S_2$ requires C, 62.2; H, 4.3; N, 2.6%. M.p. 168–172°C. IR ν(NH) 3285; ν(C=N) 1614; $\nu(NO_2)$ 1512, 1335 cm^{-1}. ESI–MS (cone voltage 20 V) *m*/*z* 1802 ($[M]^+$, 100%). $^{31}P\{^1H\}$ NMR: *Z* isomer, δ 24.4 [m, ^{1}J(PtP) 3341 and 2602]; *E* isomer, δ 23.3 [m, ^{1}J(PtP) 2648] and 22.6 [m, ^{1}J(PtP) 3424]. Selected ^{1}H-NMR data: *Z* isomer, δ 10.5 (s, NH), 4.45 (s, br, SCH_2); *E* isomer, δ 11.1 (s, NH), 3.60 (s, br, SCH_2).

3.2. *Synthesis of* $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}C_6H_4Ph\}(PPh_3)_4]PF_6$ *(2b·*PF_6*)*

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (100 mg, 0.067 mmol) and $BrCH_2C\{=NNHC_6H_3(NO_2)_2\}C_6H_4Ph$ (36.4 mg, 0.080 mmol) in methanol (25 mL) were stirred for 1 h giving a clear, deep yellow-orange solution. After filtration to remove a small amount of insoluble matter, NH_4PF_6 (80 mg, 0.491 mmol) was added to the filtrate. Water (10 mL) was added to assist precipitation, the product was filtered, washed with diethyl ether (40 mL), and dried to give **2b**·PF_6 (91.5 mg, 68%). The product was recrystallized by vapor diffusion of diethyl ether into a dichloromethane solution of the complex. Found: C, 54.2; H, 3.7; N, 2.7. $C_{92}H_{75}N_4F_6O_4P_5Pt_2S_2$ requires C, 54.6; H, 3.7; N, 2.8%. IR ν(C=N) 1613;

$\nu(NO_2)$ 1501, 1333 cm^{-1}. ESI–MS (cone voltage 20 V) m/z 1876 ($[M]^+$, 100%). $^{31}P\{^1H\}$ NMR: Z isomer, δ 24.5 [m, ^1J(PtP) 3344 and 2602]; E isomer, δ 23.1 [m, ^1J(PtP) 2639] and 22.5 [m, ^1J(PtP) 3411]. Selected ^1H-NMR data: Z isomer, δ 10.68 (s, NH), 4.40 (s, br, SCH_2); E isomer, δ 11.19 (s, NH), 3.65 (s, br, SCH_2).

3.3. *Synthesis of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}Me\}(PPh_3)_4]BPh_4$ ($3\cdot BPh_4$)*

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (150 mg, 0.100 mmol) and $ClCH_2C\{=NNH(C_6H_3(NO_2)_2\}Me$ (54 mg, 0.198 mmol) in methanol (40 mL) were stirred at room temperature for 30 min giving a clear, bright yellow-orange solution. $NaBPh_4$ (70 mg, 0.205 mmol) was added to give a bright yellow precipitate. The product was filtered, washed successively with water (10 mL), methanol (10 mL), and petroleum spirits (10 mL), and dried to give **3**·BPh_4 as a bright yellow solid (139 mg, 68%). Found: C, 61.1; H, 4.4; N, 2.8. $C_{105}H_{89}N_4BO_4P_4Pt_2S_2$ requires C, 61.2; H, 4.4; N, 2.7%. M.p. decomposition >152°C. IR ν(NH) 3287; ν(C=N) 1616; $\nu(NO_2)$ 1509, 1335 cm^{-1}. ESI–MS (cone voltage 20 V) m/z 1740 ($[M]^+$, 100%). $^{31}P\{^1H\}$ NMR, δ 24.9 [m, ^1J(PtP) 3342] and 23.6 [m, ^1J(PtP) 2613]. Selected ^1H-NMR data, δ 10.56 (s, NH), 3.73 [s, br, 2H, SCH_2, ^3J(PtH) 33] and 0.47 (s, 3H, CH_3).

3.4. *X-ray crystal structure determination of $[Pt_2(\mu\text{-}S)\{\mu\text{-}SCH_2C\{=NNHC_6H_3(NO_2)_2\}Ph\}(PPh_3)_4]BPh_4$ ($2a\cdot BPh_4$)*

Crystals (orange blocks) were grown by vapor diffusion of diethyl ether into a dichloromethane solution of the complex at room temperature. Intensity data and unit cell dimensions were obtained on a Bruker SMART CCD diffractometer at the University of Auckland.

The structure was solved for the positions of the Pt atoms using the Patterson methods option of SHELXS-97 [27]. The structures of the cation and anion were developed routinely. Later difference maps showed significant electron density associated with disordered solvents in the lattice, possibly two CH_2Cl_2 and one ether molecules. These could not be sensibly modeled, so they were eliminated using the SQUEEZE procedure of PLATON [28] and were not included in the refinement.

Full-matrix least-squares refinement (SHELXL-97) [29] was based on F_o^2 with all non-hydrogen atoms anisotropic and hydrogen in calculated positions converged with $R_1 = 0.0247$ ($I \geq 2\sigma(I)$), $wR_2 = 0.0596$ (all data), goodness-of-fit = 1.068. A final difference map showed no feature greater than 1.039 and -0.932 e $Å^{-3}$. All calculations were carried out by the SHELX-97 suite of programs.

3.5. *Crystal data for $C_{110}H_{91}BN_4O_4P_4Pt_2S_2$*

$M_r = 2121.86$; triclinic; space group P-1; $a = 14.4408(2)$ Å; $b = 16.5455(3)$ Å; $c = 22.9006(2)$ Å; $\alpha = 89.355(1)°$, $\beta = 72.784(1)°$, $\gamma = 78.209(1)°$; $V = 5109.12(12)$ $Å^3$; $Z = 2$, $T = 83(2)$ K, λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 2.891 mm^{-1}; $d_{calcd} = 1.379$ g cm^{-3}; 48,989 reflections collected; 20,704 unique ($R_{int} = 0.0224$).

Supplementary material

CCDC no. 824691 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, *via* www.ccdc.cam.ac.uk/data_request/cif.

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