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Facile reductive excision of sulfur from a {Pt_2S_2} core in [$Pt_2(PPh_3)_4(\mu$-$S)_2$] to a {Pt_2S} triangle by carbon monoxide

Choon Hong Chin, T.S. Andy Hor *

Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge 0511, Singapore

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Abstract

A synthetic path is established in which [$Pt_2(CO)_x(PPh_3)_{4-x}(\mu$-S)] ($x = 0$–2) can be prepared from [$Pt_2(PPh_3)_4(\mu$-$S)_2$] under CO at low pressure whereby reductive desulfurization of a {$Pt^{II}_2S_2$} core gives way to a Pt–Pt bonded {Pt^{I}_2S} triangle with extrusion of COS gas.

Keywords: Platinum; Sulfide; Carbon monoxide; Reductive carbonylation; Carbonyl sulfide; Desulfurization

[$Pt_2(PPh_3)_4(\mu$-$S)_2$] (**1**) (Scheme 1) is among the best-studied dinuclear complexes with a four-membered {M_2S_2} chromophore [1]. It is air stable and reacts rapidly with a variety of electrophiles [2], Lewis bases [3] and halogenated solvents [4]. Its homologue, [$Pt_2(PPh_3)_4(\mu$-S)] (**8**) with a three-membered M_2S core and Pt–Pt bond, was first prepared 25 years ago [5] but, surprisingly, little is known of its chemistry. No carbonyl analogue of **1** is known whereas the monocarbonyl derivative [$Pt_2(CO)(PPh_3)_3(\mu$-S)] (**7**) of **8**, was synthesized in a two-step process from [$Pt(PPh_3)_3$] and carbonyl sulfide (COS) [6]. The dicarbonyl derivative [$Pt_2(CO)_2(PPh_3)_2(\mu$-S)] (**6**) was recently reported by Mingos and coworkers [7] in a cluster degradation of [$Pt_3(PPh_3)_4(\mu$-$CO)_3$] by COS [7]. Complex **1** is easily prepared from the metathesis of [$PtCl_2(PPh_3)_2$] [1a] whereas, in our hands, a pure sample of **8** could not be obtained for further characterization. Preparation of the carbonyl derivatives of **8** involves either the use of dangerous COS gas [6], which is also not easily accessible, or an impractical route via a cluster. We are therefore interested in exploring a simple method to prepare **8** from **1** with an aim that such a route is also applicable to other M_2S_2 and M_2S complexes. The success of this conversion would also allow us to develop the chemistry of **8** and its derivatives. The substitution and nucleophilic chemistry of **6** and **7** are the only reactivities known [6c,6d,7]. Although reductive carbonylation in metal salts and complexes is established [8], the action of CO on sulfide complexes is poorly developed. The merit of using CO as a reductant lies in its ready availability, easy application and removal, high selectivity and, very importantly, easy removal and inertness of its byproduct COS from the reaction mixture. The common choice of phosphine as a sulfur scavenger is not appropriate as **1** is not soluble in common organic solvents and shows no activity towards phosphines as a suspension. In this paper, we report the reductive action of CO on **1** and the relationship of **1** with its monosulfide and carbonyl derivatives under a CO atmosphere.

Under a CO pressure of 1 atm, a tetrahydrofuran (THF) suspension of **1** gradually clarifies and after 2 h gives a clear solution from which an orange–yellow solid of [$Pt_2(CO)(PPh_3)_3(\mu$-$S)_2$] (**2**) can be isolated [9]. Similar to **1**, **2** undergoes nucleophilic ring opening by $CDCl_3$ to give [$PtCl_2(PPh_3)_2$] and a complex tentatively assigned as [$Pt(SCDCl_2)_2(CO)(PPh_3)$] [10]. Under a mild CO pressure and upon heating, a toluene suspension of **1** gives way to a clear solution from which was isolated [$Pt_2(CO)_2(PPh_3)_2(\mu$-S)] (**6**) [11]. This species is also formed as the major product under milder conditions (30 psi, lbf in^{-2}, 80°C in THF for more than 24 h). There is no evidence of higher carbonyl substitution products at more vigorous conditions (100 lbf in^{-2},

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* Corresponding author.

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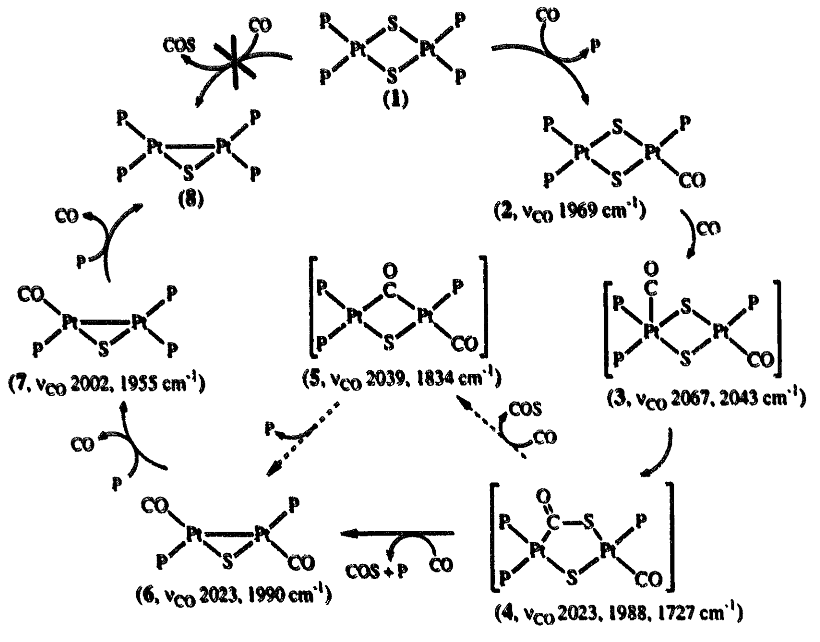
100°C, for 24 h) under which **6** is still isolated as the major product. Complex **6**, however, undergoes facile carbonyl replacement by PPh_3 at room temperature to give $[Pt_2(CO)(PPh_3)_3(\mu\text{-}S)]$ (**7**) [12]. The ^{31}P NMR spectra of **6** and **7** are in agreement with those reported by Balch and coworkers [6c] and Mingos and coworkers [6d,7] respectively. Addition of PPh_3 to **7** at room temperature leads to a loss of all carbonyl IR bands [13]. The responsible complex is tentatively identified as $[Pt_2(PPh_3)_4(\mu\text{-}S)]$ (**8**) [14].

From the IR spectra gathered for the reaction mixtures under different conditions, the reaction mechanism is complex as it involves many unstable intermediate species [15]. A proposed mechanism is given in Scheme 1 depicting the key intermediates. Isolation of **6** and **7** established a synthetic route for $[Pt_2(CO)_x(PPh_3)_{4-x}(\mu\text{-}S)]$ ($x = 0$–2) from **1** and proved that it is feasible to reduce Pt(II) to Pt(I), taking advantage of the facile formation of COS from CO and bridging sulfide [16]. The most likely mechanism involves (i) carbonyl coordination to give an 18-electron centre (**3**), (ii) CO insertion to the Pt–S bond reverting back to a 16-electron dimer (**4**) and (iii) displacement of the labile COS bridge by excess CO (resulting in **6**). The extrusion of COS could occur via a bridging carbonyl species **5** which is too unstable for isolation. This elimination of sulfide as COS represents a reverse pathway which demonstrates the use of COS as a sulfide source in the preparation of **7** [6,17] and other complexes [18]. This CO insertion mirrors a similarly remarkable intrusion of sulfur into the M–CO bond [19]. The removal of bridging sulfide by forming a COS bridge is an interesting contrast to the proposal of sulfide bridge formation by cleaving a CS_2 bridge in a reported synthesis of a PBu_2Ph derivative of **4** from $[Pt_3(PBu_2Ph)_3(\mu\text{-}CO)_3]$ [20]. The prelude of carbonyl coordination offers a proximity advantage for the insertion to occur. It also provides an electronic impetus as acidic ligands like CO (and PPh_3) are expected to strengthen the C–S bond formation [21] which leads to the subsequent extrusion of the labile COS. This form of sulfide extrusion from a doubly bridged sulfide moiety should not be confused with the well-known abstraction of sulfur by nucleophiles from a disulfide M–S_2–M [22] to a monosulfide M–S–M bridge. The former is a reductive process whereas the latter is effectively an extrusion of S^0. Under an applied pressure of CO, it is not surprising that **7** is not isolated as an intermediate in the formation of **6** from **1**.

It is significant that, after the removal of one sulfide bridge, the remaining sulfide is inert towards carbonyl attack under a higher pressure of CO. This illustrates the selectivity of CO towards sulfide excision and the inability of CO to reduce Pt(I) to Pt(0). This selectivity makes it practical to synthesize the Pt(I) sulfide species from the doubly bridged dimer **1**. This is an important consideration for future use of CO as a reductant and sulfur sponge.

We have no evidence that **8** can be formed directly from **1** by a simple mechanism involving CO insertion and COS liberation. A possible explanation is that **8** is unstable in a CO atmosphere, and that CO insertion into the Pt–S bond is facilitated and preceded by phosphine replacement by CO which favours the reduction.

Another surprising feature is the ease at which phosphine substitution can occur in a $\{Pt_2S_2\}$ molecular



Scheme 1. A schematic representation of the reaction mechanism for the reductive desulfurization of $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$ (**1**) by CO (P = PPh_3). (The reaction systems used for the steps from **6** to **8** are not under CO pressure.)

core. This reaction proceeds readily and completely in THF but not in a non-donor solvent such as toluene. The Lewis-base chemistry of **1** is well known [1–3]. However, as this complex is almost insoluble in common organic solvents [23], its solution behaviour, including its ligand dissociation or substitution, is entirely unknown. The isolation of **2**, being a derivative of **1** and completely soluble in many organic solvents, would allow us to develop the solution chemistry of this Pt_2 disulfide series.

The prospect of using CO in a dual role as a sulfur scavenger and reducing agent for sulfur-rich clusters and aggregates is promising. We are currently studying this strategy in an attempt to develop the sulfide A frames [24] and related dinuclear complexes of platinum [25].

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[9] Recrystallization from hexane yielded microcrystals analyzed as $Pt_2(CO)(PPh_3)_3(\mu\text{-}S)_2 \cdot C_6H_{14}$. Found: C, 54.1; H, 3.9; P, 6.5; Pt, 26.5; S, 4.7. $C_{61}H_{59}OP_3Pt_2S_2$ Calc.: C, 54.1; H, 4.4; P, 6.9; Pt, 28.8; S, 4.7%.

[10] Opening of the $\{Pt_2S_2\}$ ring by $CHCl_3$ and CH_2Cl_2 has been discussed in detail together with the identification of the products (see [4]).

[11] A suspension of $Pt_2(PPh_3)_4(\mu\text{-}S)_2$ (0.396 g, 0.26 mmol) in toluene (40 ml) was flushed with CO gas and stirred in a stainless steel bomb cylinder of an autoclave (Parr T316SS reactor with magnetic drive) for $3\frac{1}{2}$ h at 100°C under a CO pressure of 60 $lb \cdot in^{-2}$. The resultant clear light-yellow solution was added to hexane to induce precipitation. Recrystallization from toluene–hexane gave pure $[Pt_2(CO)_2(PPh_3)_2(\mu\text{-}S)] \cdot \frac{1}{2}C_6H_5CH_3$ with 50–60% yields. The identity of the complex was verified by IR and NMR spectroscopy (see [7]). Found: C, 47.4; H, 3.6; P, 5.9; Pt, 34.0; S, 2.5%. $C_{41.5}H_{34}O_2P_2Pt_2S$ Calc.: C, 47.5; H, 3.2; P, 5.9; Pt, 37.2%.

[12] Solid PPh_3 (0.078 g, 0.30 mmol) was added to a solution of $[Pt_2(CO)_2(PPh_3)_2(\mu\text{-}S)]$ (0.288 g, 0.29 mmol) in toluene (40 ml). The mixture was stirred in vacuo at room temperature for 45 min. Addition of hexane gave $[Pt_2(CO)(PPh_3)_3(\mu\text{-}S)] \cdot H_2O$ (0.205 g (58%)) which was verified by IR and ^{31}P NMR (see [6c,7]). Found: C, 51.9; H, 3.5; S, 2.5; Pt, 29.7. $C_{55}H_{47}O_2P_3Pt_2S$ Calc.: C, 52.6; H, 3.7; S, 2.6; Pt, 31.1%.

[13] The gaseous discharge of the reaction flask, which contains CO, decolourizes a dilute solution of acidified $KMnO_4$.

[14] A yield of 68% of $Pt_2(PPh_3)_4(\mu\text{-}S) \cdot 2H_2O$ was obtained from 0.045 g of **7**. Found: C, 56.9; H, 3.5; P, 7.2; Pt, 27.6; S, 2.4. $C_{72}H_{62}OP_4Pt_2S$ Calc.: C, 57.4; H, 4.2; P, 8.2; Pt, 25.9; S, 2.1%.

[15] Complexes **2** and **6–8** were isolated but **3–5** were detected as intermediates in the reaction mixtures. The IR spectra of these species were recorded under atmospheric pressure in CO (**2–5**) or argon (**6–8**) atmosphere. Solutions containing **2–5** were drained out from the autoclave liner (under CO) and their spectra recorded immediately. No strenuous effort was made to detect the transient species which exist only under high pressure conditions. Spectral assignments of the unisolable intermediates are tentative.

[16] Although no vigorous attempt was made to detect or trap the minute quantity of the liberated COS gas in the presence of a large excess of CO gas in the high pressure reactor, identification of the several key intermediates, especially **7**, left little doubt that elimination of sulfide occurs as COS. The absence of elemental sulfur, H_2S, $S{=}PPh_3$ or other sulfur compounds as byproducts further supported this claim.

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