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Preliminary Communication

Facile ligand transformation from bridging thio to terminal chloromethanethiolato. Bridge opening of $[Pt(\mu\text{-}S)(dppf)]_2$ by Dichloromethane to give $Pt(SCH_2Cl)_2(dppf)$ $[dppf = Fe(C_5H_4PPh_2)_2]$

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Abstract

Reaction of $PtCl_2$(dppf) or $[Pt(CH_3CN)_2(dppf)][BF_4]_2$ with Na_2S gives $[Pt(\mu\text{-}S)(dppf)]_2$. This bridging thio complex rapidly undergoes nucleophilic attack on CH_2Cl_2 to give $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Cl)(dppf)_2]Cl$, which cleanly converts into $[Pt(SCH_2Cl)_2(dppf)]$ with liberation of $[PtCl_2(dppf)]$. These reactions effectively complete a cycle which yields a chloromethanethiolato complex from Na_2S and CH_2Cl_2 via a thio complex.

Key words: Platinum; Sulfide; Diphosphine; Thiolate; Phosphine; Ferrocene

It is well known that the thio ligand, especially when in a μ_2-bridging mode, is susceptible to alkylation. Surprisingly however, not many thiolato complexes have been synthesized by this convenient means [1]. This alkylation is related to many hydrogenolytic, hydrodesulfurization, and C–X (X = chalcogen or halogen) activation processes [2]. When the nucleophilicity of the thio ligand is sufficiently high, chlorinated solvents such as $CHCl_3$ and CH_2Cl_2 are susceptible to attack. This is best exemplified in the preparations of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Cl)(PPh_3)_4]Cl$ (**1a**) [3] (from $[Pt(\mu\text{-}S)(PPh_3)_2]_2$ (**2a**) [4]) and of $[Mo_2(Cp^*)_2(\mu\text{-}SCH_2Cl)(\mu\text{-}S_2CH_2)]Cl$ (from $[Mo_2(Cp^*)_2(\mu\text{-}S)_2(\mu\text{-}S_2CH_2)]$) [5]. The former complex is prepared in near-quantitative yield at r.t., but, upon prolonged contact with CH_2Cl_2, it decomposes to Ph_3PS and other currently unknown products [3c]. We have identified these alkylation products and in this communication we report the synthetic significance of these decomposition steps.

In an attempt to suppress the dissociation and sulfurization of phosphine, a derivative of **2a** with chelating phosphine, $[Pt(\mu\text{-}S)(dppf)]_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) (**2b**) has been prepared. The chemistry of dppf as a ligand has attracted intense recent interest [6]. The preparation is effected either directly in a heterogeneous reaction between $PtCl_2$(dppf) [7,8*] and Na_2S or via $[Pt(CH_3CN)_2(dppf)][BF_4]_2$ [9,10*] (Scheme 1). Similar to the PPh_3 derivative **2a**, **2b** is only very sparingly soluble in common non-halogenated solvents. In CH_2Cl_2, it readily gives $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Cl)(dppf)_2]Cl$ (**1b**) [11*]. Upon standing in CH_2Cl_2, **1b** gradually gives way to $[Pt(SCH_2Cl)_2(dppf)]$ (**3b**) and $[PtCl_2(dppf)]$ (**4b**) [12*]. This conversion from **2b** to **3b** and **4b** via **1b** is illustrated in the ^{31}P-NMR spectral changes which show how an AA′BB′XX′ spin system (**1b**) gives way cleanly to the two characteristic 1 : 4 : 1 triplets expected for two $(A_2 + A_2X)$ systems (**3b** and **4b**) (Fig. 1). Unlike **3a** which has a deceptively simple spectral pattern because of the near equivalence of and strong coupling between the P_a and P_b nuclei, **3b** exhibits two segregated main resonances of P_a and P_b which differ by their different *trans* ligands. There is no spectroscopic evidence for the formation of $dppfS_2$.

Identification of **3b** and **4b** supports a decomposition pathway which involves the dication $[Pt_2(\mu\text{-}SCH_2Cl)_2(dppf)_2]Cl_2$ (**5b**) as the key intermediate. Bridge-opening of **5b** to give **3b** and **4b** is understood to be based on nucleophilic attack of chloride on one of the Pt^{II} centres (Fig. 2). The stability of the $\{Pt_2S_2\}$ 4-membered ring in **2** has been attributed to π-bonding effect [13], which also explains the structure being bent about the $S \cdots S$ hinge. Alkylation of the thio bridge, especially by an electron-withdrawing substituent, has been proposed to destroy this π effect, weaken the Pt–S bond and open up the hinged angle of the two Pt^{II} planes [14].

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* Reference number with asterisk indicates a note in the list of references.

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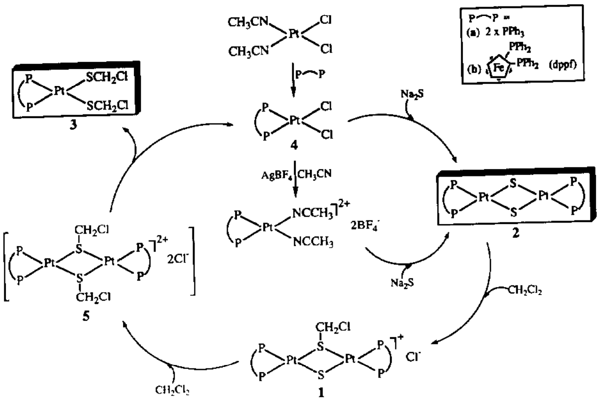

Scheme 1. Proposed mechanistic cycle showing the formation of $[Pt(SCH_2Cl)_2(P-P)]$ (**3**) from Na_2S and CH_2Cl_2 via $[Pt(\mu\text{-}S)(P-P)]_2$ (**2**) and $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Cl)(P-P)_2]Cl$ (**1**) and the regeneration of $[PtCl_2(P-P]$ (**4**).

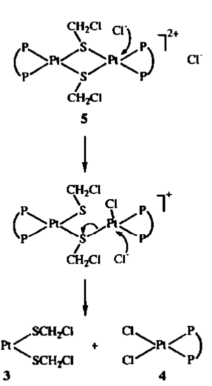

Fig. 2. Proposed mechanism for the formation of $[Pt(SCH_2Cl)_2(P-P)]$ (**3**) and $[PtCl_2(P-P)]$ (**4**) from $[Pt_2(\mu\text{-}SCH_2Cl)_2(P-P)_2]Cl_2$ (**5**) (P-P = $2 \times PPh_3$ (**a**), dppf (**b**)).

An interesting implication of this decomposition is the facile formation of a terminal thiolato complex from a bridging thio complex. This conversion when applied to a substituted thiolato group, such as chloromethanethiolato, is particularly useful because there has been to date no convenient alternative for such synthesis. Preparation of **3b** would usually require metathetic exchange of PtX_2(dppf) with chloromethanethio $ClCH_2SH$ [15] (or $[ClCH_2S]^-$) or oxidative addition of bis(chloromethyl)disulfide $ClCH_2S$-SCH_2Cl [16] on $Pt(dppf)_2$ [17]. Besides being obnoxious and unstable, these thio compounds are not readily available. The present route can in principle be applied generally to other substituted thiolato groups. Though thiolato ligands usually prefer a bridging mode [18], the preference for a terminal state in **3b** is prompted by the electronegative substituent on the alkyl group. As illustrated in Scheme 1, the final liberation of **4** completes a "catalytic" cycle which effectively generates a chloromethanethiolato complex from Na_2S and CH_2Cl_2. Further work will be carried out on the acid hydrolysis of **3** by HCl. If the reaction follows the expected course, it would liberate $HSCH_2Cl$ and an extra equivalent of **4**. This would complete a metal-mediated stoichiometric cycle which generates chloromethanethio from Na_2S and CH_2Cl_2.

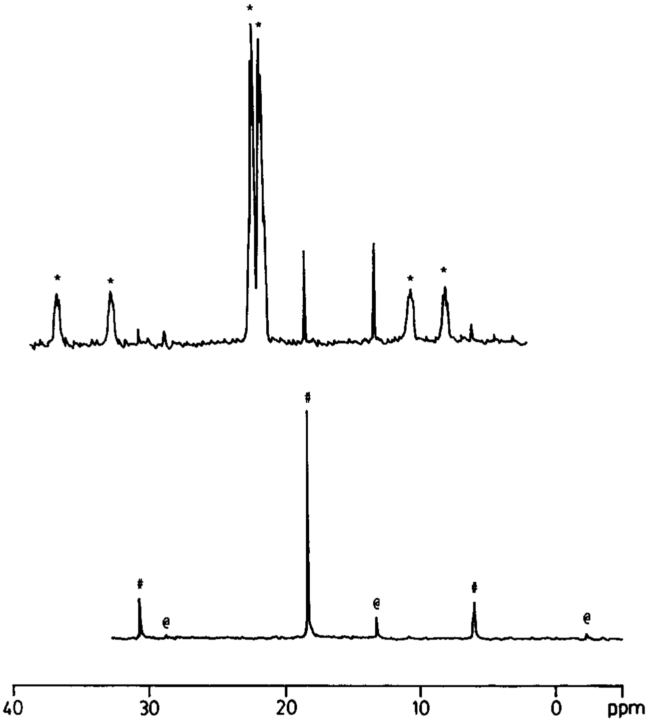

Fig. 1. ^{31}P-NMR spectra of $[Pt(\mu\text{-}S)(dppf)]_2$ and CH_2Cl_2 in $CDCl_3$ showing (a) the predominant formation of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Cl)(dppf)_2]Cl$ (**1b**) in a freshly prepared sample with minor quantities of $[Pt(SCH_2Cl)_2(dppf)]$ (**3b**) and $[PtCl_2(dppf)]$ (**4b**); (b) its complete conversion to **3b** and **4b** upon standing (the latter spectrum was taken on the product crystals with **4b** mostly removed) (* $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Cl)(dppf)_2]Cl$, **1b**; # $[Pt(SCH_2Cl)_2(dppf)]$, **3b**; @ $[PtCl_2(dppf)]$, **4b**).

In order to show that this ligand transformation is effective irrespective of the electronic effect imposed by the phosphine groups on the metal, we have also synthesized the analogous $[Pt(SCH_2Cl)_2(PPh_3)_2]$ (**3a**) from $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Cl)(PPh_3)_4]Cl$ (**1a**) [19*].

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8 *cis*-$PtCl_2$(dppf) (**4b**) (2.01 g, 90%) is prepared from $PtCl_2(CH_3CN)_2$ (0.896 g, 2.574 mmol) and dppf (1.432 g, 2.575 mmol) in CH_2Cl_2 at r.t. ^{31}P-NMR ($CDCl_3$): δ 13.15 ppm [J(P–Pt) 3768 Hz].

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10 $Na_2S \cdot 9H_2O$ (2.706 g, 11.27 mmol) was added to a suspension of **4b** (1.823 g, 2.22 mmol) in degassed benzene (50 ml) and the mixture stirred for 48 h. The resultant orange suspension was filtered and washed thoroughly with MeOH and H_2O to give **2b** (1.54 g, 88%). Anal. Calcd.: C, 52.25; H, 3.61; P, 7.93; S, 4.10; Fe, 7.15; Pt, 24.96. Found: C, 52.53; H, 3.49; P, 7.68; S, 4.85; Fe, 7.53; Pt, 22.59%. Alternatively, **4b** was stirred with $AgBF_4$ in CH_3CN to give $[Pt(CH_3CN)_2(dppf)][BF_4]_2$, which was isolated and stirred with excess Na_2S in CH_3CN to give **2b** (54%).

11 **2b** was dissolved in CH_2Cl_2, filtered and the fresh yellow filtrate was evaporated to dryness and crystallized to give **1b**. Molar conductivity Λ_m (10^{-3} M, CH_2Cl_2) 50.3 ohm^{-1} cm^2 $mole^{-1}$. ^1H-NMR ($CDCl_3$) δ ($-SCH_2Cl$) 4.25 ppm (m). ^{31}P-NMR ($CDCl_3$) (Brüker ACF 300 MHz) 22.14 [m, J(P–Pt) 3524], 21.53 [m, J(P–Pt) 2698].

12 Conversion of **1b**, to **3b** and **4b**, can be carried out in CH_2Cl_2 or monitored by ^{31}P-NMR in $CDCl_3$. Analytically pure crystals of **3b** can be obtained by slow diffusion of hexane into a CH_2Cl_2 solution **2b**. The resultant orange-red microcrystals can be physically separated from the co-deposited **4b** under the microscope. Anal. Calcd. for **3b**: C, 47.37; H, 3.51; P, 6.80; Fe, 6.14; Pt, 21.38. Found: C, 47.57; H, 3.25; P, 6.97; Fe, 6.05; Pt, 21.26%. Molar conductivity Λ_m (10^{-3} M, CH_2Cl_2) 1.5 ohm^{-1} cm^2 $mole^{-1}$. ^1H-NMR ($CDCl_3$) δ ($-SCH_2Cl$) 5.72 [t, J(H–Pt) 40 Hz]. ^{31}P-NMR ($CDCl_3$) δ 18.27 [t, J(P–Pt) 2994 Hz].

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19 The preparation of **3a** (bright yellow crystals) follows that of **3b** except that **3a** is always contaminated by a trace of **4a**. Anal. Calcd. for **3a**: C, 51.71; H, 3.86; Cl, 8.04; P, 7.26; S, 7.03; Pt, 22.11. Found: C, 54.44; H, 3.74; Cl, 9.79; P, 6.85; Pt, 22.05%. Molar conductivity Λ_m (10^{-3} M, CH_2Cl_2) 4.8 ohm^{-1} cm^2 $mole^{-1}$. ^1H-NMR ($CDCl_3$) δ ($-SCH_2Cl$) 5.67 [t, J(H–Pt) 43 Hz]. ^{31}P-NMR ($CDCl_3$) δ 21.51 [t, J(P–Pt) 2927 Hz).