

PREPARATION AND REACTIONS OF *trans*-[(PPh₃)₂Pt(CH₂SR)Cl] (R = Me, Ph or C₆H₄Me-*p*)

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Summary

Formation of *trans*-[(PPh₃)₂Pt(CH₂SR)Cl] (R = Me, Ph or C₆H₄Me-*p*) has been achieved by the oxidative addition of ClCH₂SR to (PPh₃)₄Pt in refluxing PhH. The reaction of ClCH₂SMe with (PMe₂Ph)₄Pt led to *cis*-[(PMe₂Ph)₂PtCl₂]. The reaction of *trans*-[(PPh₃)₂Pt(CH₂SR)Cl] with halogens (X₂ = Br₂ or I₂) led to the formation of ClCH₂SR and XCH₂SR. Halide exchange occurs on reaction with MeI, EtI or EtBr in chloroform solution at ambient temperature. Hydrogen chloride cleaved the C–Pt bond. Trifluoroacetic acid (1 equivalent) reversibly protonated [(PPh₃)₂Pt(CH₂SMe)Cl] at sulphur.

Introduction

Palladium and platinum complexes containing organothioalkyl groups (RSCH₂) have been reported in the past few years [1–5]. More work has been reported on palladium complexes, with structures, reactions with halogens, alkyl halides and proton acids being featured. For platinum compounds, the preparation of complexes containing a monodentate MeSCH₂ group, as in [(PPh₂R)₂Pt(CH₂SMe)Cl] (R = Ph or Me) and [(PPh₂R)₂Pt(CH₂SMe)]PF₆, as well as that with a bridging MeSCH₂ group, as in [(PPh₃)Pt(CH₂SMe)Cl]₂ [2] have been reported. Metathetic reactions with alkali metal halides have been studied. We wish now to report our findings of reactions of *trans*-[(PPh₃)₂Pt(CH₂SR)Cl] (R = Me, Ph or C₆H₄Me-*p*) with halogens, alkyl halides and proton acids. A preliminary communication was concerned with part of this work [6].

Experimental

Deoxygenated solvents and nitrogen atmospheres were used. Alkyl halides were treated with aqueous potassium hydroxide, washed with water and dried over calcium chloride. They were redistilled before use.

Preparation of chloromethyl p-tolyl sulphide, ClCH₂SC₆H₄Me-p

A stirred mixture of MeS(O)C₆H₄Me-p (3.2 g, 2.0×10^{-2} mol) (prepared from MeSC₆H₄Me-p and NaIO₄ [7]) and 3A molecular sieves (5 g) in CH₂Cl₂ was treated with a saturated solution of HCl in Et₂O (50 ml) for 2 h. The solution was decanted from the molecular sieves and the solvent removed. Distillation of the yellow residue yielded colourless ClCH₂SC₆H₄Me-p, b.p. 120–122°C/12 Torr (lit. [8] 126–129°C/15 Torr). Yield 2.0 g, 58%. ¹H NMR (60 MHz, CDCl₃): δ 2.36 (3H, s) 4.89 (2H, s), 7.29 ppm (4H, q, *J* 8 Hz). Analysis. Found C, 55.5; H, 5.2; S, 18.9; Cl, 20.3. C₈H₉ClS calcd.: C, 55.7; H, 5.2; S, 18.6; Cl, 20.6%.

Preparation of chloromethyl phenyl sulphide, ClCH₂SPh

This was prepared, by a similar method as used for chloromethyl *p*-tolyl sulphide, from MeS(O)Ph (5.1 g, 3.6×10^{-2} mol) and HCl in Et₂O, b.p. 55–70°C/0.1 Torr (lit. [8] 58–61°C/0.15 Torr). Yield 3.5 g, 60%. ¹H NMR (60 MHz, CDCl₃): δ 4.91 (2H, s), 7.42 ppm (5H, m). Analysis. Found: C, 52.8; H, 4.3; S, 20.4; Cl, 22.1. C₇H₇ClS calcd.: C, 53.0; H, 4.4; S, 20.2; Cl, 22.4%.

Preparation of trans-chloro(thiomethoxymethyl)bis(triphenylphosphine)platinum(II) · CH₂Cl₂, trans-[(PPh₃)₂Pt(CH₂SMe)Cl] · CH₂Cl₂

Tetrakis(triphenylphosphine)platinum (3 g, 2.4×10^{-3} mol) was suspended in deoxygenated benzene (35 ml). Chloromethyl methyl sulphide (a commercial sample) (0.93 g, 9.7×10^{-3} mol) was added and the mixture refluxed under nitrogen until the solution decolourised, (ca. 1.5 h). The volume of the solution was reduced to 5 ml and C₆H₁₄ added to precipitate a white solid, which was recrystallised from CH₂Cl₂/C₆H₁₄. The product contained one mole of CH₂Cl₂ as solvate, m.p. 208–210°C (lit. [2] 209°C dec.) Yield 1.97 g, 91%. ¹H NMR (60 MHz, CD₂Cl₂): δ 1.06 (3H, s), 1.36 (2H, t, *J*(PH) 8.0 Hz), 5.30 (2H, s), 7.40, 7.87 ppm (30H, 2m); IR: ν(Pt–Cl) 272s cm⁻¹. Analysis. Found: C, 51.2; H, 4.1; Cl, 11.8. C₃₉H₃₇Cl₃P₂PtS calcd.: C, 51.9; H, 4.0; Cl, 11.8%.

Preparation of trans-[chloro(phenylthiomethyl)bis(triphenyl)platinum(II)], [(PPh₃)₂Pt(CH₂SPh)Cl]

This was prepared from (PPh₃)₄Pt (2.8 g, 2.3×10^{-3} mol) and ClCH₂SPh (1.43 g, 9.2×10^{-3} mol) in benzene (35 ml). The white product was recrystallised from CH₂Cl₂/C₆H₁₄; m.p. 224–227°C dec. Yield 1.84 g, 93%. ¹H NMR (60 MHz, CD₂Cl₂) δ 1.87 (2H, t, *J*(PH) 8.0 Hz, *J*(Pt–H) 82.0 Hz), 6.70 (5H, m), 7.40, 7.89 ppm (30 H, 2m); IR ν(Pt–Cl) 284s cm⁻¹. Analysis. Found: C, 58.3; H, 4.2; Cl, 4.2. C₄₃H₃₇ClP₂PtS calcd.: C, 58.8; H, 4.0; Cl, 4.1%.

Preparation of trans-[chloro(p-tolylthiomethyl)bis(triphenylphosphine)platinum(II)], trans-[(PPh₃)₂Pt(CH₂SC₆H₄Me-p)Cl] · CH₂Cl₂

This was prepared from (Ph₃P)₄Pt (2.0 g, 1.6×10^{-3} mol) and *p*-MeC₆H₄SCH₂Cl (0.28 g, 6.0×10^{-3} mol) in benzene (35 ml). The pale yellow solid was recrystallised from CH₂Cl₂/C₆H₁₄. The yield of the CH₂Cl₂ mono-solvate, m.p. 200–203°C dec., was 1.26 g, 88%. ¹H NMR (60 MHz, CD₂Cl₂): δ 1.87 (2H, t, *J*(PH) 8.0 Hz, *J*(Pt–H) 82.0 Hz), 2.16 (3H, s), 5.30 (2H, s), 6.70 (4H, q *J* 9.3 Hz), 7.53, 8.02 ppm (30H, 2m), IR ν(Pt–Cl) 285 cm⁻¹. Analysis. Found: C, 54.7; H, 4.2; Cl, 10.4. C₄₅H₄₁Cl₃P₂PtS calcd.: C, 55.2; H, 4.2; Cl, 10.9%.

TABLE 1

REACTIONS OF *trans*-[(Ph₃P)₂Pt(CH₂SR)Cl] WITH HALOGENS IN CHLOROFORM AT AMBIENT TEMPERATURE

<i>trans</i> -[(Ph ₃ P) ₂ Pt(CH ₂ SR)Cl]		Relative amounts of products (%)	
R	X ₂	XCH ₂ SR(δ) ^a	ClCH ₂ SR(δ) ^a
Ph	Br ₂	80(4.82)	20(4.90)
Me	Br ₂	80(4.76)	20(4.82)
Ph	I ₂	40(4.56)	60(4.90)
Me	I ₂	40(4.50)	60(4.82)

^a δ = ¹H chemical shift of CH₂SR in ppm.*Interaction of chloromethyl methyl sulphide and tetrakis(dimethylphenylphosphine)platinum*

A solution of (PPhMe₂)₄Pt (2.0 g, 2.7 × 10⁻³ mol) and ClCH₂SCH₃ (1.03 g, 1.08 × 10⁻² mol) in deoxygenated benzene (30 ml) was refluxed for 3 h. The solution was concentrated and hexane was added to precipitate *cis*-[(PPhMe₂)₂PtCl₂]. This was recrystallised from CH₂Cl₂/C₆H₁₄, m.p. 196–198°C (lit. [9] 199–200°C). Yield 1.3 g, 90%. ¹H NMR (60 MHz, CDCl₃): δ 1.78 (12H, 3d, *J*(PH) 10.7 Hz, *J*(Pt–H) 34.0 Hz), 7.40 ppm (10H, m); IR ν(Pt–Cl) 290, 310 cm⁻¹. *cis*-[(PPhMe₂)₂PtCl₂]. Analysis. Found: C, 35.1; H, 4.3; Cl, 13.4. C₁₆H₂₂Cl₂P₂Pt calcd.: C, 35.4; H, 4.1; Cl, 13.1%.

Reactions with halogens

To a solution of [(PPh₃)₂Pt(CH₂SR)Cl] (0.12–0.15 M) in CDCl₃ was added the halogen. Yellow precipitates (dihalodiphosphineplatinum) formed in exothermic reactions. The relative amounts of organosulphur products were calculated from the ¹H NMR spectrum of the filtrate, see Table 1.

TABLE 2

REACTIONS OF *trans*-[(PPh₃)₂Pt(CH₂SR)Cl] WITH ALKYL HALIDES, R'X, IN CHLOROFORM AT AMBIENT TEMPERATURE

Reagents	Reaction time (h)	Product	M.p. (°C)	Analysis (Found (calcd.)(%))		
				C	H	X
[(PPh ₃) ₂ Pt(CH ₂ SMe)Cl]	MeI 8	[(PPh ₃) ₂ Pt(CH ₂ SMe)I]	206–209	50.3 (50.3)	3.6 (3.9)	13.7 [I] (14.0)
[(PPh ₃) ₂ Pt(CH ₂ SMe)Cl]	EtI 12	[(PPh ₃) ₂ Pt(CH ₂ SMe)I]	202–207	51.0 (50.3)	3.7 (3.9)	14.4 [I] (14.0)
[(PPh ₃) ₂ Pt(CH ₂ SMe)Cl]	EtBr 60	[(PPh ₃) ₂ Pt(CH ₂ SMe)Br]	194–198	52.6 (53.0)	4.2 (4.1)	9.1 [Br] (9.3)
[(PPh ₃) ₂ Pt(CH ₂ SPh)Cl]	MeI 8	[(PPh ₃) ₂ Pt(CH ₂ SPh)I]	218–223	53.9 (53.3)	4.0 (3.8)	13.8 [I] (13.1)
[(PPh ₃) ₂ Pt(CH ₂ SPh)Cl]	EtBr 60	[(PPh ₃) ₂ Pt(CH ₂ SPh)Br]	213–216	55.2 (55.9)	4.3 (4.0)	9.1 [Br] (8.7)

Reactions with alkyl halides

To a solution of $[(PPh_3)_2Pt(CH_2SR)Cl]$ (0.12–0.15 M) in $CDCl_3$ (0.5 ml) was added equimolar alkyl halide, via a syringe. The course of the reaction was monitored by 1H NMR spectroscopy. When reaction was complete, as shown by loss of absorptions due to $[(PPh_3)_2Pt(CH_2SR)Cl]$, hexane was added to precipitate a yellow solid, which was recrystallised from dichloromethane/hexane, details are given in Table 2.

Reactions with proton acids

Reactions with $[(PPh_3)_2Pt(CH_2SMe)Cl]$. (a) Hydrogen chloride was bubbled through a solution of $[(PPh_3)_2Pt(CH_2SMe)Cl]$ (0.1 g) in $CDCl_3$. A yellow precipitate of *trans*- $[(PPh_3)_2PtCl_2]$ was obtained, m.p. 293–297°. $\nu(Pt-Cl)$ 335 cm^{-1} (lit. [10] 334 cm^{-1}). Yield 0.07 g, 68%. *trans*- $[(PPh_3)_2PtCl_2] \cdot CH_2Cl_2$. Analysis. Found: C, 49.6; H, 3.4; Cl, 18.1. $C_{37}H_{32}Cl_4P_2Pt$ calcd.: C, 48.8; H, 3.4; Cl, 19.5%.

(b) Trifluoroacetic acid was added in portions via syringe to a solution of $[(PPh_3)_2Pt(CH_2SMe)Cl]$ (0.104 g, 1.28×10^{-4} mol) in $CDCl_3$. The reaction was monitored by 1H NMR spectroscopy. New absorptions appeared at δ 1.98 (t, J 16 Hz) and 2.78 ppm (t of d, J 16 Hz) with loss of original absorptions at δ 1.06(s) and 1.36(t) ppm of the reagent. Almost all the original organoplatinium had interacted with 1 equivalent of CF_3CO_2H . However addition of hexane and cooling to 0°C precipitated $[(PPh_3)_2Pt(CH_2SMe)Cl]$.

Reaction of $[(PPh_3)_2Pt(CH_2SPh)Cl]$. (a) Hydrogen chloride was bubbled through a solution of $[(PPh_3)_2Pt(CH_2SPh)Cl]$ (0.036 g, 4.1×10^{-5} mol) in $CDCl_3$. Addition of hexane resulted in the precipitation of $[(PPh_3)_2PtCl_2]$.

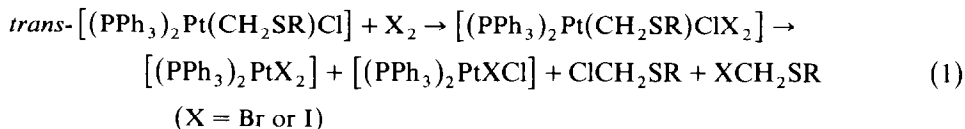
Results and discussion

The complex *trans*- $[(PPh_3)_2Pt(CH_2SMe)Cl]$ had been prepared by the oxidative addition of $ClCH_2SMe$ to $(PPh_3)_4Pt$ in refluxing benzene [2]. A similar route was used to obtain *trans*- $[(PPh_3)_2Pt(CH_2SR)Cl]$ (R = Ph and C_6H_4Me-p). However the attempted oxidative addition of chloromethyl methyl sulphate to tetrakis(dimethylphenylphosphine)platinum under the same conditions failed, *cis*- $[(PMe_2Ph)_2PtCl_2]$ being formed in 90% yield instead.

The complexes prepared were colourless crystalline materials, soluble in dichloromethane, chloroform and to a lesser extent, benzene. The complexes as solids are stable at ambient temperature for weeks and are stable in solution for days. They however decompose on melting. Crystallisation from CH_2Cl_2/C_6H_{14} led to the isolation of CH_2Cl_2 solvates for *trans*- $[(PPh_3)_2Pt(CH_2SR)Cl] \cdot CH_2Cl_2$ or R = Me and C_6H_4Me-p but not R = Ph.

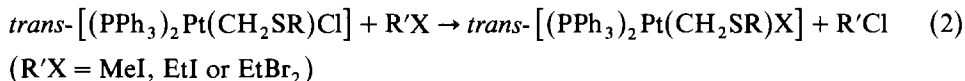
The 1H NMR spectra of $[(PPh_3)_2Pt(CH_2SR)Cl]$ in CD_2Cl_2 at 35°C revealed a triplet pattern for the methylene protons ($J(PH)$ 8 Hz, $J(Pt-H)$ 82.0 Hz); in the IR spectra $\nu(Pt-Cl)$ was in the region 270–285 cm^{-1} . These data suggest a *trans*-configuration [11].

The reactions between *trans*- $[(PPh_3)_2Pt(CH_2SR)Cl]$ (R = Me or Ph) with one equivalent of halogen ($X_2 = Br_2$ or I_2) resulted in C–Pt bond cleavage. Two organosulphides were however obtained (Table 1) (eq. 1).



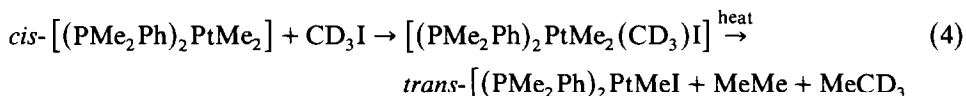
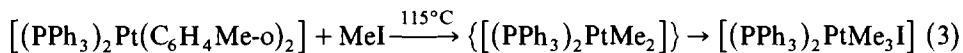
The cleavage of simple platinum-alkyl bonds by halogens is well-known [12]; the reaction is considered to take place via oxidative addition to give an octahedral Pt^{IV} complex which subsequently undergoes reductive elimination of an alkyl halide. Although in some cases the Pt^{IV} compound is sufficiently stable to be isolated, e.g. as in reaction of Cl₂ with *cis*-[(PEt₃)₂PtMe₂] [13], no Pt^{IV} complex was isolated from reactions of the *trans*-[(PPh₃)₂Pt(CH₂SR)Cl] in this study. The formation of the two halomethyl sulphides from [(PPh₃)₂Pt(CH₂SR)Cl] can be accounted for by the intermediacy of [(PPh₃)₂Pt(CH₂SR)ClX₂]. From the relative bond strengths Pt-I > Pt-Br > Pt-Cl it would be expected that ClCH₂SR would be preferentially formed. That this is not always the case, clearly points to the involvement of other factors, such as the configurations of the octahedral Pt^{IV} intermediates.

Reactions of alkyl bromides and iodides with *trans*-[(PPh₃)₂Pt(CH₂SR)Cl] led to halide exchanges even at ambient temperature in chloroform solution (eq. 2).

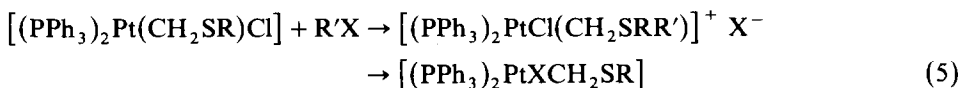


The analogous Pd complexes are slightly the more reactive [5]. The reactivity of the alkyl halides was in the sequence MeI > EtI > EtBr.

Other types of reaction of alkyl halides with σ bonded organoplatinum compounds to be previously reported are (i) replacement of one organic group by another, e.g. [14,15] (eq. 3) and (ii) formation of alkanes (eq. 4) [16,17]. These

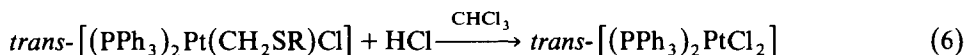


reactions proceed via oxidative addition/reductive elimination sequences [14]. Whether such a sequence or one involving attack on S operates for the RSCH₂Pt



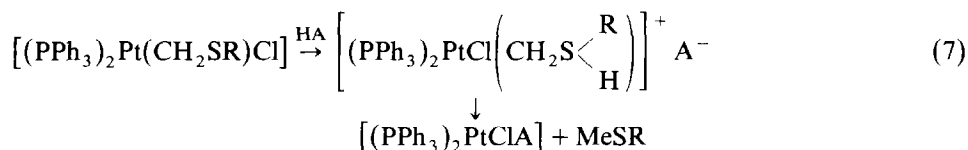
complexes is unclear. The greater reactivity of the palladium(II) than the platinum analogues argues for the direct attack on sulphur rather than the oxidative addition/reductive elimination sequence. In addition the direct attack on sulphur is supported by the isolation of [(PPh₃)₂PtCl(CH₂SMe₂)⁺ SO₃F⁻] from reaction of MeOSO₂F and *trans*-[(PPh₃)₂PtCl(CH₂SMe)] [2].

Hydrogen chloride cleaves the Pt-CH₂SR bonds in CHCl₃ solution (eq. 6).



Various examples of simple alkyl-platinum cleavage by proton acids have been reported [14]. Mechanisms for these reactions include S_E2 mechanisms, oxidative addition/reductive elimination sequences, and direct electrophilic attack by the electrophile on the C-Pt bond. In addition to these possibilities, there is for the RSCH₂Pt complexes one involving initial attack at sulphur by the proton source,

followed by cleavage (eq. 7)



A reversible protonation step was suggested by the following. Interaction of 1 equivalent of CF_3CO_2H with $[(PPh_3)_2Pt(CH_2SMe)Cl]$ led to a considerable change in the 1H chemical shifts of the CH_2SCH_3 protons (see Experimental section) yet $[(PPh_3)_2Pt(CH_2SMe)Cl]$ is recovered in high yield on addition of hexane. A reversible interaction of a proton acid was more clearly illustrated with the palladium analogue [4]. Use of CF_3CO_2H and longer reaction times led to C–Pt bond cleavage, as happens more readily with HCl.

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