Journal of Organometallic Chemistry, 254 (1983) 261–266
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATION AND REACTIONS OF *trans*-[$(PPh_3)_2Pt(CH_2SR)Cl$] (R = Me, Ph or C_6H_4Me-*p*)

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(Received April 18th, 1983)

Summary

Formation of *trans*-[$(PPh_3)_2Pt(CH_2SR)Cl$] (R = Me, Ph or C_6H_4Me-*p*) has been achieved by the oxidative addition of $ClCH_2SR$ to $(PPh_3)_4Pt$ in refluxing PhH. The reaction of $ClCH_2SMe$ with $(PMe_2Ph)_4Pt$ led to *cis*-[$(PMe_2Ph)_2PtCl_2$]. The reaction of *trans*-[$(PPh_3)_2Pt(CH_2SR)Cl$] with halogens ($X_2 = Br_2$ or I_2) led to the formation of $ClCH_2SR$ and XCH_2SR. 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 [$(PPh_3)_2$-$Pt(CH_2SMe)Cl$] at sulphur.

Introduction

Palladium and platinum complexes containing organothioalkyl groups ($RSCH_2$) 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 $MeSCH_2$ group, as in [$(PPh_2R)_2Pt(CH_2SMe)Cl$] (R = Ph or Me) and [$(PPh_2R)_2Pt(CH_2SMe)]PF_6$, as well as that with a bridging $MeSCH_2$ group, as in [$(PPh_3)Pt(CH_2SMe)Cl]_2$ [2] have been reported. Metathetic reactions with alkali metal halides have been studied. We wish now to report our findings of reactions of *trans*-[$(PPh_3)_2Pt(CH_2SR)Cl$] (R = Me, Ph or C_6H_4Me-*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.

0022-328X/83/$03.00

Preparation of chloromethyl p-tolyl sulphide, $ClCH_2SC_6H_4Me$-p

A stirred mixture of $MeS(O)C_6H_4Me$-*p* (3.2 g, 2.0×10^{-2} mol) (prepared from $MeSC_6H_4Me$-*p* and $NaIO_4$ [7]) and 3A molecular sieves (5 g) in CH_2Cl_2 was treated with a saturated solution of HCl in Et_2O (50 ml) for 2 h. The solution was decanted from the molecular sieves and the solvent removed. Distillation of the yellow residue yielded colourless $ClCH_2SC_6H_4Me$-*p*, b.p. 120–122°C/12 Torr (lit. [8] 126–129°C/15 Torr). Yield 2.0 g, 58%. ^1H NMR (60 MHz, $CDCl_3$): 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. C_8H_9ClS calcd.: C, 55.7; H, 5.2; S, 18.6; Cl, 20.6%.

Preparation of chloromethyl phenyl sulphide, $ClCH_2SPh$

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 Et_2O, 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, $CDCl_3$): δ 4.91 (2H, s,), 7.42 ppm (5H, m). Analysis. Found: C, 52.8; H, 4.3; S, 20.4; Cl, 22.1. C_7H_7ClS calcd.: C, 53.0; H, 4.4; S, 20.2; Cl, 22.4%.

Preparation of trans-chloro(thiomethoxymethyl)bis(triphenylphosphine)platinum-(II) · CH_2Cl_2, trans-[$(PPh_3)_2Pt(CH_2SMe)Cl$] · CH_2Cl_2

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 C_6H_{14} added to precipitate a white solid, which was recrystallised from CH_2Cl_2/C_6H_{14}. The product contained one mole of CH_2Cl_2 as solvate, m.p. 208–210°C (lit. [2] 209°C dec.) Yield 1.97 g, 91%. ^1H NMR (60 MHz, CD_2Cl_2): 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. $C_{39}H_{37}Cl_3P_2PtS$ calcd.: C, 51.9; H, 4.0; Cl, 11.8%.

Preparation of trans-[chloro(phenylthiomethyl)bis(triphenyl)platinum(II)], [$(PPh_3)_2Pt(CH_2SPh)Cl$]

This was prepared from $(PPh_3)_4Pt$ (2.8 g, 2.3×10^{-3} mol) and $ClCH_2SPh$ (1.43 g, 9.2×10^{-3} mol) in benzene (35 ml). The white product was recrystallised from CH_2Cl_2/C_6H_{14}; m.p. 224–227°C dec. Yield 1.84 g, 93%. ^1H NMR (60 MHz, CD_2Cl_2) 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. $C_{43}H_{37}ClP_2PtS$ calcd.: C, 58.8; H, 4.0; Cl, 4.1%.

Preparation of trans-[chloro(p-tolylthiomethyl)bis(triphenylphosphine)platinum(II)], trans-[$(PPh_3)_2Pt(CH_2SC_6H_4Me$-p$)Cl$] · CH_2Cl_2

This was prepared from $(Ph_3P)_4Pt$ (2.0 g, 1.6×10^{-3} mol) and *p*-$MeC_6H_4SCH_2Cl$ (0.28 g, 6.0×10^{-3} mol) in benzene (35 ml). The pale yellow solid was recrystallised from CH_2Cl_2/C_6H_{14}. The yield of the CH_2Cl_2 mono-solvate, m.p. 200–203°C dec., was 1.26 g, 88%. ^1H NMR (60 MHz, CD_2Cl_2): 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. $C_{45}H_{41}Cl_3P_2PtS$ calcd.: C, 55.2; H, 4.2; Cl, 10.9%.

TABLE 1

REACTIONS OF *trans*-[$(Ph_3P)_2Pt(CH_2SR)Cl$] WITH HALOGENS IN CHLOROFORM AT AMBIENT TEMPERATURE

trans-[$(Ph_3P)_2Pt(CH_2SR)Cl$]		Relative amounts of products (%)	
R	X_2	$XCH_2SR(\delta)$ [a]	$ClCH_2SR(\delta)$ [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 = ^{1}H chemical shift of CH_2SR in ppm.

Interaction of chloromethyl methyl sulphide and tetrakis(dimethylphenylphosphine)platinum

A solution of $(PPhMe_2)_4Pt$ (2.0 g, 2.7×10^{-3} mol) and $ClCH_2SCH_3$ (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*-[$(PPhMe_2)_2PtCl_2$]. This was recrystallised from CH_2Cl_2/C_6H_{14}, m.p. 196–198°C (lit. [9] 199–200°C). Yield 1.3 g, 90%. ^{1}H NMR (60 MHz, $CDCl_3$): 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*-[$PPhMe_2)_2PtCl_2$]. Analysis. Found: C, 35.1; H, 4.3; Cl, 13.4. $C_{16}H_{22}Cl_2P_2Pt$ calcd.: C, 35.4; H, 4.1; Cl, 13.1%.

Reactions with halogens

To a solution of [$(PPh_3)_2Pt(CH_2SR)Cl$] (0.12–0.15 *M*) in $CDCl_3$ was added the halogen. Yellow precipitates (dihalodiphosphineplatinum) formed in exothermic reactions. The relative amounts of organosulphur products were calculated from the ^{1}H NMR spectrum of the filtrate, see Table 1.

TABLE 2

REACTIONS OF *trans*-[$(PPh_3)_2Pt(CH_2SR)Cl$] WITH ALKYL HALIDES, R'X, IN CHLOROFORM AT AMBIENT TEMPERATURE

Reagents		Reaction time (h)	Product	M.p. (°C)	Analysis (Found (calcd.)(%))		
					C	H	X
[$(PPh_3)_2Pt(CH_2SMe)Cl$]	MeI	8	[$(PPh_3)_2Pt(CH_2SMe)I$]	206–209	50.3 (50.3)	3.6 (3.9)	13.7 [I] (14.0)
[$(PPh_3)_2Pt(CH_2SMe)Cl$]	EtI	12	[$(PPh_3)_2Pt(CH_2SMe)I$]	202–207	51.0 (50.3)	3.7 (3.9)	14.4 [I] (14.0)
[$(PPh_3)_2Pt(CH_2SMe)Cl$]	EtBr	60	[$(PPh_3)_2Pt(CH_2SMe)Br$]	194–198	52.6 (53.0)	4.2 (4.1)	9.1 [Br] (9.3)
[$(PPh_3)_2Pt(CH_2SPh)Cl$]	MeI	8	[$(PPh_3)_2Pt(CH_2SPh)I$]	218–223	53.9 (53.3)	4.0 (3.8)	13.8 [I] (13.1)
[$(PPh_3)_2Pt(CH_2SPh)Cl$]	EtBr	60	[$(PPh_3)_2Pt(CH_2SPh)Br$]	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$_3$)$_2$Pt(CH$_2$SMe)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°. ν(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$_3$)$_2$Pt(CH$_2$SPh)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 ν(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).

$$\textit{trans}\text{-}[(PPh_3)_2Pt(CH_2SR)Cl] + X_2 \rightarrow [(PPh_3)_2Pt(CH_2SR)ClX_2] \rightarrow [(PPh_3)_2PtX_2] + [(PPh_3)_2PtXCl] + ClCH_2SR + XCH_2SR \quad (1)$$

(X = Br or I)

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 Cl_2 with *cis*-$[(PEt_3)_2PtMe_2]$ [13], no Pt^{IV} complex was isolated from reactions of the *trans*-$[(PPh_3)_2Pt(CH_2SR)Cl]$ in this study. The formation of the two halomethyl sulphides from $[(PPh_3)_2Pt(CH_2SR)Cl]$ can be accounted for by the intermediacy of $[(PPh_3)_2Pt(CH_2SR)ClX_2]$. From the relative bond strengths Pt–I > Pt–Br > Pt–Cl it would be expected that $ClCH_2SR$ 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*-$[(PPh_3)_2Pt(CH_2SR)Cl]$ led to halide exchanges even at ambient temperature in chloroform solution (eq. 2).

$$\textit{trans}\text{-}\left[(PPh_3)_2Pt(CH_2SR)Cl\right] + R'X \rightarrow \textit{trans}\text{-}\left[(PPh_3)_2Pt(CH_2SR)X\right] + R'Cl \qquad (2)$$

$(R'X = MeI, EtI \text{ or } EtBr_2)$

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

$$\left[(PPh_3)_2Pt(C_6H_4Me\text{-}o)_2\right] + MeI \xrightarrow{115°C} \{\left[(PPh_3)_2PtMe_2\right]\} \rightarrow \left[(PPh_3)_2PtMe_3I\right] \quad (3)$$

$$\textit{cis}\text{-}\left[(PMe_2Ph)_2PtMe_2\right] + CD_3I \rightarrow \left[(PMe_2Ph)_2PtMe_2(CD_3)I\right] \xrightarrow{\text{heat}} \textit{trans}\text{-}\left[(PMe_2Ph)_2PtMeI + MeMe + MeCD_3 \right. \qquad (4)$$

reactions proceed via oxidative addition/reductive elimination sequences [14]. Whether such a sequence or one involving attack on S operates for the $RSCH_2Pt$

$$\left[(PPh_3)_2Pt(CH_2SR)Cl\right] + R'X \rightarrow \left[(PPh_3)_2PtCl(CH_2SRR')\right]^+ X^- \rightarrow \left[(PPh_3)_2PtXCH_2SR\right] \qquad (5)$$

complexes is unclear. The greater reactivity of the palladium(II) then 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 $[(PPh_3)_2PtCl(CH_2SMe_2)]^+ SO_3F^-$ from reaction of $MeOSO_2F$ and *trans*-$[(PPh_3)_2PtCl(CH_2SMe)]$ [2].

Hydrogen chloride cleaves the Pt–CH_2SR bonds in $CHCl_3$ solution (eq. 6).

$$\textit{trans}\text{-}\left[(PPh_3)_2Pt(CH_2SR)Cl\right] + HCl \xrightarrow{CHCl_3} \textit{trans}\text{-}\left[(PPh_3)_2PtCl_2\right] \qquad (6)$$

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 $RSCH_2Pt$ complexes one involving initial attack at sulphur by the proton source,

followed by cleavage (eq. 7)

$$[(PPh_3)_2Pt(CH_2SR)Cl] \xrightarrow{HA} \left[(PPh_3)_2PtCl\left(CH_2S\begin{matrix}R\\H\end{matrix}\right)\right]^+ A^- \quad (7)$$

$$\downarrow$$

$$[(PPh_3)_2PtClA] + MeSR$$

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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