

LIGAND REACTIVITY AND RESULTING CARBENE FORMATION IN THE COMPLEX $\text{Pt}(\pi\text{-CS}_2)(\text{Ph}_3\text{P})_2$

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Summary

Electrophilic attack at both sulphur atoms in the complex $\text{Pt}(\pi\text{-CS}_2)(\text{Ph}_3\text{P})_2$ by methyl or ethyl iodide results initially in the formation of a cationic carbene complex $[\text{PtI}(\text{Ph}_3\text{P})_2\{\text{C}(\text{SR})_2\}]\text{I}$ at 25°C. Subsequent reaction under reflux gives a neutral carbene complex with resultant loss of phosphine ligand

Introduction

Recent studies on the reactivity of coordinated carbon disulphide have indicated that complexes of the second and third row transition metals may react differently. The reaction of the complex $\text{Ru}(\pi\text{-CS}_2)(\text{CO})_2(\text{Ph}_3\text{P})_2$ with alkylating agents such as methyl iodide involves electrophilic attack at only the bound sulphur atom [1]. The analogous osmium complex, whilst showing a similar reaction with stoichiometric amounts of alkylating agent, reacts with an excess by means of electrophilic attack at both sulphur atoms [1]. The product of this reaction is the cationic carbene complex $[\text{OsI}(\text{CO})_2(\text{Ph}_3\text{P})_2\{\text{C}(\text{SMe})_2\}]\text{I}$.

The stabilities of the rhodium and iridium carbon disulphide complexes are too low to permit alkylation studies, but preliminary studies [2] on the palladium complex also indicate alkylation at only one sulphur atom by methyl iodide. This paper presents the results of an examination of the alkylation reactions of the platinum complex $\text{Pt}(\pi\text{-CS}_2)(\text{Ph}_3\text{P})_2$ with methyl and ethyl iodides.

Results and discussion

(1) Cationic carbenes

When the complex $\text{Pt}(\pi\text{-CS}_2)(\text{Ph}_3\text{P})_2$ is dissolved in either neat methyl or ethyl iodide at 25°C, a yellow solid precipitates within the first minute of reaction.

TABLE 1
 IR AND PMR DATA FOR CATIONIC CARBENE COMPLEXES

Compound	$\nu(\text{CS})$ (cm^{-1})	$\delta(\text{SR})$ (ppm)	$J(\text{PtCSCH})$ (Hz)
$[\text{PtI}(\text{Ph}_3\text{P})_2\{\text{C}(\text{SMe})_2\}]\text{I}$	998s, 941w 840w	3 23t 2 00t	7 20 6 00
$[\text{PtI}(\text{Ph}_3\text{P})_2\{\text{C}(\text{SEt})_2\}]\text{I}$	998s, 950w 850m	3 30m 0 83t 2 00m 1 28t	

The products isolated at this stage are cationic monodentate dithiocarbene complexes of general formula $[\text{PtI}(\text{Ph}_3\text{P})_2\{\text{C}(\text{SR})_2\}]\text{I}$ where R = ethyl or methyl. The ethyl complex, but containing a coordinated chloride and a tetrafluoroborate counterion, has been prepared recently by Angelici [3] by a quite different route, which does not involve the reactivity of a coordinated carbon disulfide group. These complexes can be metathesized with perchlorate anion and can be recrystallized from dichloromethane with 1.5 moles of solvent. They are monomeric and behave as 1 : 1 electrolytes in acetonitrile. IR $\nu(\text{CS})$, and PMR data are presented in Table 1 with elemental analysis, melting point, molecular weights and molar conductivities given in Table 2.

The $\nu(\text{C}=\text{S})$ frequencies at 1160 and 1141 cm^{-1} present in the starting $\pi\text{-CS}_2$ complex are lost and replaced by a strong band at 998 cm^{-1} together with very weak bands in the ranges 950–940 cm^{-1} and 850–840 cm^{-1} . In addition, the low $\nu(\text{C}-\text{S})$ ring frequency [4] at 651 cm^{-1} in the starting complex is also lost. These data are consistent with the fact that the ligand is a monodentate carbene containing two equivalent CS bonds.

The double resonances obtained for both the two methyl and the two ethyl groups in their PMR spectra are explained by the presence of *syn* and *anti* configurations with respect to the platinum caused by steric hindrance. The

 TABLE 2
 ANALYTICAL DATA FOR CARBENE COMPLEXES

Compound	M p ($^{\circ}\text{C}$)	Found (calcd) (%)	Molar conductivity ($\text{ohm}^{-1} \text{cm}^2$)
$[\text{PtI}(\text{PPh}_3)_2\{\text{C}(\text{SMe})_2\}]\text{I} \cdot 1.5 \text{CH}_2\text{Cl}_2$	123–124	C 39.9 (40.3) H 3.16 (3.26), S 5.54 (5.31) P 5.23 (5.14) I 22.2 (21.0) m w ^a 1040 (1207)	150 ($3.74 \times 10^{-5} \text{M}$) ^a
$[\text{PtI}(\text{PPh}_3)_2\{\text{C}(\text{SMe})_2\}]\text{ClO}_4 \cdot 1.5 \text{CH}_2\text{Cl}_2$	125–128	C 41.1 (41.2), H 3.43 (3.33) S 5.21 (5.43)	149 ($4.90 \times 10^{-5} \text{M}$) ^a
$[\text{PtI}(\text{PPh}_3)_2\{\text{C}(\text{SEt})_2\}]\text{I} \cdot 1.5 \text{CH}_2\text{Cl}_2$	127–129	C 41.2 (41.3), H 3.52 (3.51) S 4.67 (5.19) M w ^a 1100 (1235)	135 ($4.12 \times 10^{-5} \text{M}$) ^a
$\text{PtI}_2(\text{PPh}_3)_2\{\text{C}(\text{SMe})_2\} \cdot 0.5 \text{CH}_2\text{Cl}_2$	251–253	C 30.1 (30.0) H 2.64 (2.58) m w ^b 750 (859)	
$\text{PtI}_2(\text{PPh}_3)_2\{\text{C}(\text{SEt})_2\} \cdot 0.5 \text{CH}_2\text{Cl}_2$	241–242	C 31.8 (31.8); H 2.95 (2.95); S 6.95 (7.22) M.w. ^b 792 (887)	

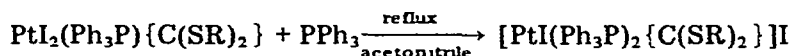
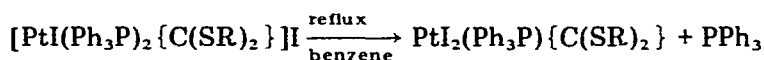
^a Determined in CH_3CN . ^b Determined in CHCl_3 .

details of this argument were recently advanced by Angelici [3] to explain similar double resonances in the complex $[\text{PtCl}(\text{Ph}_3\text{P})_2\{\text{C}(\text{SEt})_2\}]\text{BF}_4$. The PMR spectra show clearly that no alkylation on the metal has occurred but are consistent with attack at both sulphur atoms. X ray studies of these complexes are currently in progress.

(2) Neutral carbenes

When solutions of $\text{Pt}(\pi\text{-CS}_2)(\text{Ph}_3\text{P})_2$ in methyl or ethyl iodide are allowed to react under conditions of mild reflux for a longer period of time, yellow, sparingly soluble solids are eventually precipitated as well as formation of $[\text{Ph}_3(\text{R})\text{P}]\text{I}$ where R = methyl or ethyl.

These products are both non-electrolytes in acetonitrile and can be recrystallized from dichloromethane with 0.5 mol of solvent. They both analyse for complexes with empirical formula $\text{PtI}_2(\text{Ph}_3\text{P})\{\text{C}(\text{SR})_2\} \cdot 0.5\text{CH}_2\text{Cl}_2$ where R = methyl or ethyl, and molecular weights obtained in chloroform (Table 2) indicate clearly that both complexes are monomeric. While their low solubilities unfortunately preclude PMR measurements, the following reactions have been established.

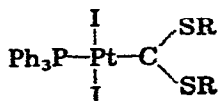


The IR spectra of the two complexes vary only slightly in frequency, but are distinct in their intensities, from the cationic carbene complexes and are as follows: R = methyl 990s, 933s, 845m; R = ethyl 992s, 954s, 863 (cm^{-1}).

These spectra are again consistent with the presence of a monodentate carbene ligand containing two equivalent CS bonds.

Analytically the methyl complex is identical to the product originally reported by Wilkinson [5] for this reaction, but it is clear that the structure suggested by him is incorrect. Since no alkylation on the metal occurs in the cationic carbene complexes it seems highly unlikely that any platinum-alkyl bonds exist in these neutral complexes as suggested by Wilkinson. It seems far more likely that the phosphine ligand is simply replaced by iodide in the appropriate solvent as indicated above and that in neat methyl iodide it is easily removed as $[\text{Ph}_3(\text{R})\text{P}]\text{I}$.

We therefore suggest the structure shown in Scheme 1 for these neutral complexes where R = methyl or ethyl, but the stereochemistry of the two iodides is not known for certain.



SCHEME 1 The suggested structure of the neutral complex $\text{PtI}_2(\text{Ph}_3\text{P})\{\text{C}(\text{SR})_2\}$

Analytical data, melting points and molecular weights for these complexes are given in Table 2

X ray structural determinations of these complexes are in progress.

Experimental section

The ^1H NMR spectra were obtained on a Varian T60 spectrometer, and IR measurements were made with a Beckman IR 12 spectrophotometer. Molecular weights were determined on a Mechrolab 302 osmometer, and conductivity measurements were carried out with a Beckman Model RC-18A conductivity Bridge. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany.

All reactions are carried out under a nitrogen atmosphere. $\text{Pt}(\pi\text{-CS}_2)(\text{PPh}_3)_2$ was prepared as described in the literature [5]

(a) $[\text{PtI}(\text{PPh}_3)_2\{\text{C}(\text{SMe})_2\}] \cdot 1.5\text{CH}_2\text{Cl}_2$

$\text{Pt}(\pi\text{-CS}_2)(\text{PPh}_3)_2$ (0.25 g) was dissolved in 5 ml methyl iodide and the reaction mixture stirred for 2 min at 25°C . The yellow product was filtered off and recrystallized from CH_2Cl_2 by the addition of n-hexane as bright yellow crystals. Yield 0.31 g (82%).

(b) $[\text{PtI}(\text{PPh}_3)_2\{\text{C}(\text{SMe})_2\}]\text{ClO}_4 \cdot 1.5\text{CH}_2\text{Cl}_2$

$\text{Pt}(\pi\text{-CS}_2)(\text{PPh}_3)_2$ (0.25 g) was dissolved in 5 ml methyl iodide at 25°C and the resulting yellow product was filtered off after 2 min. It was then dissolved in acetone and NaClO_4 (0.10 g) added. The solution was stirred for 5 min and a yellow solid was then precipitated with n-hexane. Recrystallization of the product from CH_2Cl_2 by the addition of n-hexane gave pale yellow crystals. Yield 0.23 g (62%).

(c) $[\text{PtI}(\text{PPh}_3)_2\{\text{C}(\text{SEt})_2\}] \cdot 1.5\text{CH}_2\text{Cl}_2$

$\text{Pt}(\pi\text{-CS}_2)(\text{PPh}_3)_2$ (0.25 g) was added to 5 ml ethyl iodide and the suspension was stirred for 25 min at 25°C . The yellow product was filtered off and recrystallized from CH_2Cl_2 by the addition of n-hexane as bright yellow crystals. Yield 0.24 g (62%).

(d) $\text{PtI}_2(\text{PPh}_3)_2\{\text{C}(\text{SMe})_2\} \cdot 0.5\text{CH}_2\text{Cl}_2$

$\text{Pt}(\pi\text{-CS}_2)(\text{PPh}_3)_2$ (0.4 g) was refluxed in 10 ml methyl iodide for 20 min. The resulting yellow solid was recrystallized from CH_2Cl_2 by the addition of n-hexane. Yield 0.246 g (58%).

(e) $\text{PtI}_2(\text{PPh}_3)_2\{\text{C}(\text{SEt})_2\} \cdot 0.5\text{CH}_2\text{Cl}_2$

$\text{Pt}(\pi\text{-CS}_2)(\text{PPh}_3)_2$ (0.4 g) was refluxed in 10 ml ethyl iodide for 30 min. The resulting yellow solid was recrystallized from CH_2Cl_2 by the addition of n-hexane. Yield 0.23 g (51%).

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References

- 1 K R Grundy, R O Harris and W R Roper, *J Organometal Chem*, **90** (1975) C34
- 2 D H Farrar and A Walker unpublished results.
- 3 E.D Dobrzynski and R J Angelici, *Inorg. Chem* **14** (1975) 1513
- 4 I S Butler and A E Fenster *J Organometal Chem*, **66** (1974) 161
- 5 M C Baird and G Wilkinson *J Chem Soc A*, (1967) 865