Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REACTIVITY OF *trans*-$PtHX(PR_3)_2$ WITH CARBON DISULPHIDE

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(Received February 1st, 1971)

SUMMARY

Carbon disulphide inserts into the Pt–H bond in complexes of the type *trans*-$PtHX(PR_3)_2$ ($X = Cl, Br, I, CN$; $R = C_6H_5, C_2H_5$) to give $PtX(S_2CH)(PR_3)_2$ derivatives. From the reactions of these derivatives it is postulated that the (S_2CH) moiety is linked to the central metal through the sulfur atom (Pt–S–C(S)–H). The kinetics of the CS_2 insertion reaction have been studied and show that the reaction occurs in two stages. The first, which produces a labile intermediate, is first-order with respect to the metal complex and to CS_2. The second stage involves an intramolecular rearrangement of the intermediate to give the final product.

INTRODUCTION

It has recently been reported that carbon disulphide reacts with compounds containing metal–nitrogen bonds ($M{-}N<$, $M = Sn, Si, P$) to give the dithiocarbamate insertion products, $M{-}S{-}C(S){-}N<$[1,2]. A similar insertion reaction occurs when the pentacyanocobaltate(II) ion reacts with CS_2, the $(CN)_5Co{-}S{-}C(S){-}Co(CN)_5$ ion being formed[3]. Complexes of the type $Ni(NHR_2)_4^{2+}$ react with CS_2 to give nickel(II) dithiocarbamate complexes, $Ni(S_2CNR_2)_2$[4]. Insertion of CS_2 into hydrido and alkyl complexes of Rh^I, Ir^I and Pt^{II} [5], and pentacarbonyl alkyl derivatives of manganese and rhenium[6] have been reported very recently. For example $IrH(CO)[P(C_6H_5)_3]_3$ reacts with carbon disulphide by oxidative addition to form the insertion product: $Ir(CO)(S_2CH)[P(C_6H_5)_3]_2$:

$$IrH(CO)[P(C_6H_5)_3]_3 + CS_2 \rightarrow IrH(CO)(\pi\text{-}CS_2)[P(C_6H_5)_3]_2 + P(C_6H_5)_3 \xrightarrow[\text{transfer}]{H^-} \rightarrow Ir(CO)(S_2CH)[P(C_6H_5)_3]_2 \quad (1)$$

In the same paper it is reported that CS_2 reacts with the hydrido platinum complex $PtHCl[P(C_6H_5)_3]_2$ to give a product with two new bands at 990 and 930 cm^{-1} and no Pt–H bands.

We have now found that CS_2 reacts analogously with complexes of the type *trans*-$PtHX[P(C_6H_5)_3]_2$ to give insertion products:

$$trans\text{-}PtHX[P(C_6H_5)_3]_2 + CS_2 \rightarrow PtX(S_2CH)[P(C_6H_5)_3]_2 \quad (2)$$
$$X^- = Cl^-, Br^-, I^-, CN^-$$

We describe the synthesis and characterization of the products of reaction (2) and report kinetic studies of this insertion reaction.

EXPERIMENTAL SECTION

Materials

All the starting complexes were prepared by previously described methods[7,8]. Carbon disulphide and other solvents were reagent-grade and used without further purification. The absolute methanol for kinetic measurements was dried by refluxing over $Mg(OCH_3)_2$ and then distilled.

Reaction with carbon disulphide

(*a*). *trans*-$PtCl(S_2CH)[P(C_6H_5)_3]_2$. A solution of *trans*-$PtHCl[P(C_6H_5)_3]_2$ in carbon disulphide was refluxed for 3 days. Addition of hexane to the resulting deep-red solution gave the yellow crystalline complex *trans*-$PtCl(S_2CH)[P(C_6H_5)_3]_2$ in almost quantitative yield. The complex was recrystallized from dichloromethane/ether (m.p. 155–159°, with decomposition). (Found: C, 52.85; H, 3.72; Cl, 4.08; S, 7.26. $C_{37}H_{31}ClP_2PtS_2$ calcd.: C, 53.39; H, 3.75; Cl, 4.26; S, 7.70%.)

(*b*). *trans*-$PtX(S_2CH)[P(C_6H_5)_3]_2$ ($X^- = CN^-$, Br^-, I^-). These complexes were prepared analogously from the corresponding *trans*-$PtHX[P(C_6H_5)_3]_2$ complexes, and were identified from their IR spectra in Nujol mulls. The reactions were slower than that of the *trans*-$PtHCl[P(C_6H_5)_3]_2$, and took 5–10 days to go to completion.

The IR spectra of the *trans*-$PtX(S_2CH)[P(C_6H_5)_3]_2$ complexes are the same as those of the complexes obtained by treating the chloro derivatives *trans*-$PtCl(S_2CH)[P(C_6H_5)_3]_2$ in acetone with LiBr, LiI, or NaCN.

(*c*). *trans*-$PtCl(S_2CH)[P(C_2H_5)_3]_2$. This was prepared by the procedure described above for *trans*-$PtCl(S_2CH)[P(C_6H_5)_3]_2$. From the deep red solution obtained by refluxing *trans*-$PtHCl[P(C_2H_5)_3]_2$ in carbon disulphide an oily compound was isolated which analyzed as $PtCl(S_2CH)[P(C_2H_5)_3]_2$. Its IR spectrum shows two new bands due to the (CSH) group at 1050 and 930 cm^{-1} and the Pt–H band is absent.

Reaction of trans-$PtCl(S_2CH)[P(C_6H_5)_3]_2$ with KCN

To a solution of *trans*-$PtCl(S_2CH)[P(C_6H_5)_3]_2$, (200 mg) in 50 ml of dichloromethane was added an excess of KCN dissolved in the minimum amount of methanol. The mixture was stirred for 24 h and the solvent evaporated to dryness under reduced pressure. The residue was extracted with water and the filtered solution was acidified with dilute HCl. Dithioformic acid, HCS_2H, was extracted with ether and precipitated as $Pb(S_2CH)_2$, $Ag(S_2CH)$ and $Co(S_2CH)_2$ by adding aqueous solutions of $Pb(O_2CCH_3)_2$, $AgNO_3$, and $Co(O_2CCH_3)_2$, respectively.

Kinetic measurements

The reaction was followed spectrophotometrically with a Unicam S.P.800 double-beam spectrophotometer equipped with a thermostatted cell compartment, and the rate of disappearance of *trans*-$PtHCl[P(C_2H_5)_3]_2$ was measured. The initial concentration of the complex was usually in the range 10^{-4}–3×10^{-4} *M*, and the concentration of CS_2 was at least 1000 times greater (0.1–2 *M*). Measured volumes of thermostatted solutions of the complex and the reagents were mixed in a 1-cm quartz cell placed in the thermostatted cell compartment of the instrument. The change in optical density (A) with time was recorded at a suitable wave-length, chosen by examination of the spectra of the initial and final complexes. The pseudo-first-order rate constants, k_{obsd}, were calculated from the slopes of the linear plots of log $(A_\infty - A_t)$ *vs.* time.

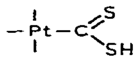
Instruments

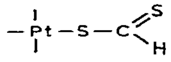
IR spectra were recorded on a Perkin–Elmer 621 spectrophotometer using a polystyrene standard and NMR spectra were recorded on a Varian DP60 spectrometer with TMS as internal standard.

Conductivity measurements were carried out with a LKB 5300 B conductivity bridge.

RESULTS AND DISCUSSION

The hydrido platinum(II) complex *trans*-$PtHCl[P(C_6H_5)_3]_2$ reacts readily with carbon disulphide to give the compound $PtCl(S_2CH)[P(C_6H_5)_3]_2$ in which the CS_2 moiety is S-bonded to the metal. The IR spectrum of the final product contains no Pt–H band, but has two new strong bands at 1050 and 930 cm^{-1}. On this basis two different structures (I) and (II) are possible:


(I)


(II)

The NMR spectrum shows a resonance at τ 7.95, but this does not enable structures to be distinguished, since the chemical shift of the SH proton is very variable and the signal could be due to either the $-CS_2H$ or the $-S_2CH$ group. However, we prefer structure (II) on the basis of the following evidence.

(*a*). The complex does not exhibit acidic properties; thus the molar conductivity in nitromethane is practically unchanged on adding pyridine in a conductometric titration.

(*b*). On treating the complex with an excess of KCN a water-soluble yellow solid, is formed which analyzes as KS_2CH. This in turn can be characterized as a salt of dithioformic acid[9] by addition of heavy metals ions (Ag^+, Pb^{2+}, Co^{2+}).

The chloride group in the $PtCl(S_2CH)[P(C_6H_5)_3]_2$ is easily replaced by other anions such as Br^-, I^-, CN^-, to give the corresponding bromo, iodo and cyano derivatives. These complexes were identical to those synthesized by treating the corresponding hydride derivatives with CS_2.

In an attempt to elucidate the mechanism of the insertion of CS_2 into the Pt–H bond, eqn. (2), some kinetic measurements were carried out. Scanning the spectrum in the UV region from time to time during the course of the reaction with carbon disulphide revealed that there were two distinct stages of spectrophotometric change. An isosbestic point was present at 358 nm after the completion of the first stage, and so in other runs the second stage of the reaction could be ignored by taking optical density measurements at this wavelength and the values of k^{I}_{obsd} were determined. The rate constants of the second stage, k^{II}_{obsd}, were obtained from observations at a wavelength at which the difference in optical density between the spectra of the products of the two stages of the over-all reaction was greatest. The usual treatment for consecutive reactions was applied in this case.

At relatively low concentrations of CS_2 the first stage of the reaction becomes slower than the second, and so the isosbestic point disappears. The observed rate constants for each stage are reported in Table 1.

TABLE 1

RATE CONSTANTS FOR REACTION (3) IN METHANOL AT 25°

$[CS_2]$ (M)	$10^4 \times k^{I}_{obsd}$ (sec^{-1})	$10^4 \times k^{II}_{obsd}$ (sec^{-1})
0.13	2.0	
0.55	5.7	
1.15	13.0	4.6
1.60	18.1	4.5
2.10	24.0	4.7

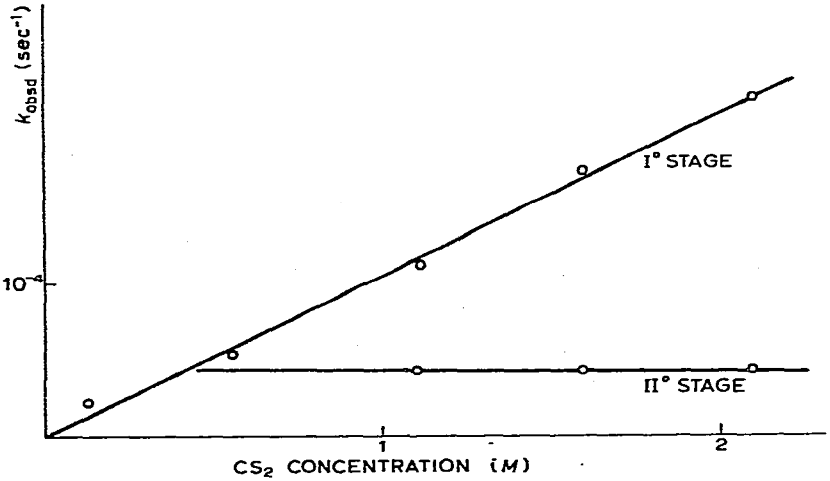
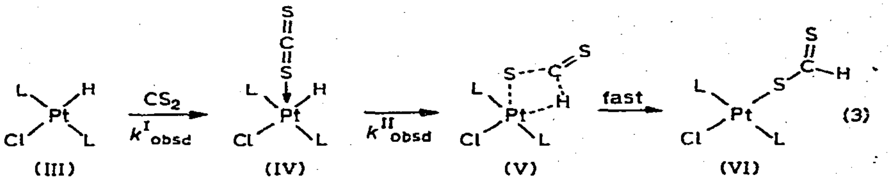


Fig. 1. Pseudo-first-order rate constants (k_{obsd}) *vs.* CS_2 concentration.

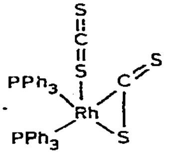
The results show that the rate of the first step depends on the concentration of CS_2, whereas the rate for the subsequent step (k^{II}_{obsd}) is unaffected by changes in the CS_2 concentration. By plotting the pseudo-first-order rate constants *vs.* the CS_2 concentration two straight lines are obtained, as shown in Fig. 1. For the first step of the reaction, the observed rate constants fit the relationship:

$$k^{I}_{obsd} = k^{I} \cdot [CS_2] \, .$$

On the basis of these kinetic results we propose the mechanism shown in eqn. (3).



The first step involves an interaction between the platinum atom and the carbon disulphide to give a labile five-coordinated intermediate, of type (IV); this could be detected in ether solution, but was too reactive to be isolated. In the IR spectrum of an ether solution a band assigned to ν(Pt–H) appears at a higher frequency (2255 cm^{-1}) than that of ν(Pt–H) (2220 cm^{-1}) in the starting hydrido complex, showing that there is an increase in the oxidative state of the central metal. Moreover donation via the sulphur atom has been proposed[10] for the somewhat unstable rhodium complex (VII).



(VII)

In the second step the insertion product is produced by an intramolecular migration of the hydride group, which probably involves a four-centre transition state.

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