Thermal behaviour of bis(diphenyltrifluoromethylphosphine)dichloroplatinum(II)

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Abstract

The thermal behaviour of the ligand diphenyltrifluoromethylphosphine(I) and its complex bis(diphenyltrifluoromethylphosphine)dichloroplatinum(II) [Pt(CF$_3$Ph$_2$P)$_2$Cl$_2$] is described. The kinetic parameters and thermodynamic data for activation of the reaction, obtained by five different methods from the non-isothermal TG/DTG curve, are presented. The thermal reactions of the ligand in two steps and its complex in four steps are discussed.

INTRODUCTION

Diphenyltrifluoromethylphosphine(I), with its strongly electronegative trifluoromethyl group, has been reported to form stable complexes with platinum(II) chloride [1]. The stability of the complexes with various reactants, e.g. halogens, was also reported earlier [1]. A deeper insight into the stability can, however, be obtained by thermal analysis, which can yield information with regard to the mode of fragmentation of the groups attached to the phosphorus atom in the phosphine as well as in the platinum complex. The technique has therefore been extended to this phosphine because it offers a unique opportunity to study the fragmentation pattern of a complex system having the highly electronegative (3.3 [2]) and electron withdrawing (Taft polar substituent constant $\sigma^* = 2.81$ [3]) trifluoromethyl (CF$_3$) group, the phenyl group with its π electron cloud overlapping the d_π orbitals of phosphorus, the platinum–phosphine complex involving d_π–p_π bonding, and the platinum atom itself forming an electrovalent bond with chloride ions. It has been shown earlier [4] that the CF$_3$ group plays an important role in reducing the donor property of the phosphine, and therefore there is considerable modification in the

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overall electronic environment of the said phosphine as well as that of its complex with platinum. It is also interesting to note that the CF_3 group is responsible for steric interaction, and hence diphenyltrifluoromethylphosphine, on reaction with platinum chloride, forms the trans isomer in larger proportion than the cis isomer.

The thermochemistry of organometallic compounds containing the trifluoromethyl (CF_3) group has not received enough attention, although a number of such compounds have long been known. This paper is concerned with thermal studies of the ligand diphenyltrifluoromethylphosphine(I) and its complex bis(diphenyltrifluoromethylphosphine)dichloroplatinum(II) $[Pt(CF_3Ph_2P)_2Cl_2]$ as well as the kinetic and thermodynamic parameters obtained from their decomposition patterns.

EXPERIMENTAL

Preparation of compounds

Bis(diphenyltrifluoromethylphosphine)dichloroplatinum(II) $[Pt(CF_3Ph_2-P)_2Cl_2]$ was prepared by the reported method [1]. Diphenyltrifluoromethylphosphine (0.254 g) in acetone was added to an aqueous solution of potassium chloroplatinite (0.21 g) and the mixture was heated for 30 minutes. Removal of the acetone gave a resinous mass which, after purification with animal charcoal and water, gave a pale yellow solid melting at 230°C. Analysis: found C 40.20%; H 2.65%; F 14.85; calc, for $Pt(CF_3Ph_2P)_2Cl_2$, C 40.33%; H 2.60%; F 14.72%.

Thermal studies

The thermal behaviour of the compound was studied on an MOM derivatograph in an air atmosphere using a ceramic crucible at heating rates of 2.5, 5, and 10°C min^{-1}.

RESULTS AND DISCUSSION

The kinetic data on the activation energy E_a, the order of reaction n and the frequency factor $\log A$ and the thermodynamic data entropy of activation S^*, enthalpy of activation H^* and free energy of activation G^* were determined using the computer program [5] for different relationships reported by Freeman and Carroll [6], Horowitz and Metzger [7], modified Horowitz and Metzger (Dharwadkar and Karkhanavala [8]), Coats and Redfern [9] and Zsakó–Zsakó [10].

The thermal degradation of diphenyltrifluoromethylphosphine(I) (Ph_2CF_3P) was studied at a heating rate of 2.5°C min^{-1}. The limit of thermal stability was found to be 60°C, with a rapid total loss exhibiting a
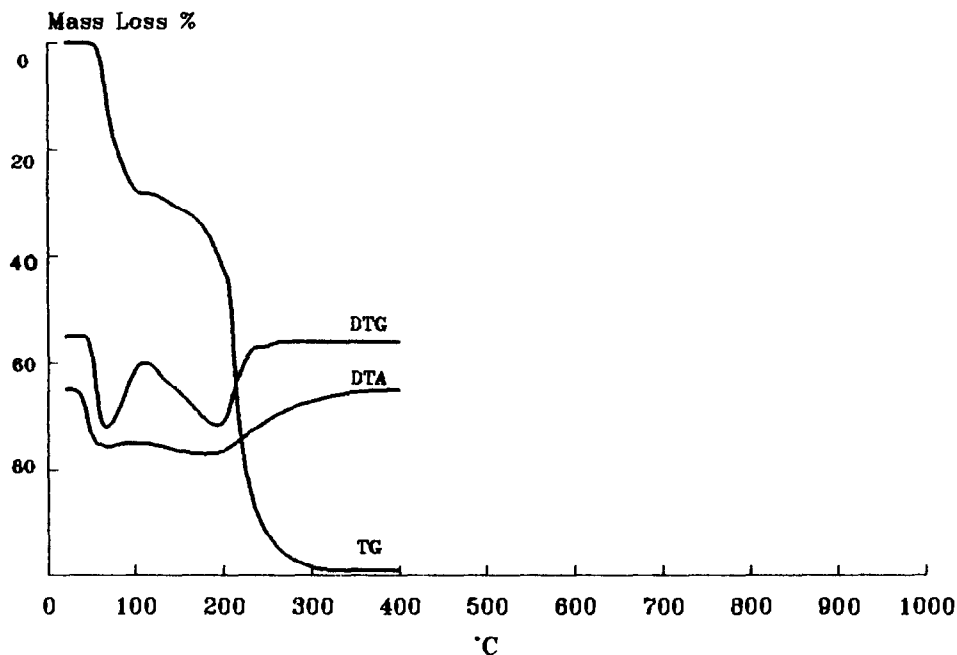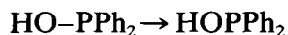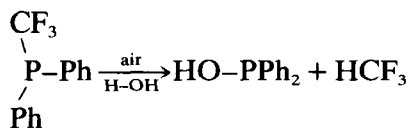
Fig. 1. Thermoanalytical curves of diphenyltrifluoromethylphosphine(I).

very slight kink on the TG and corresponding DTG curves from 60 to 90°C. However, when a mixture of 20 mg of Ph_2CF_3P on Al_2O_3 was subjected to heating at the same rate, a clear picture was observed on the TG and parallel DTG curves presented in Fig. 1. The loss is rapid but in two steps. The first loss (26.80%) in the range 60–110°C conforms with CF_3 (calc. 27.14%) and the second loss (71.20%) which continues up to 290°C is due to the oxidation of PPh_2 (calc. 72.86%). The total loss of phosphine is perhaps also accompanied by decomposition, which in the presence of alumina, acting as an activator, is differentiated from the removal of the CF_3 group. The corresponding DTG curve shows two peaks at about 80 and 180°C without corresponding the peaks in the DTA curve.

$$\begin{array}{c} CF_3 \\ \backslash \\ P\text{–}Ph \xrightarrow[\text{H–OH}]{\text{air}} HO\text{–}PPh_2 + HCF_3 \\ / \\ Ph \end{array}$$

$$HO\text{–}PPh_2 \rightarrow HOPPh_2$$

The dynamic thermogravimetric analysis (TG) presented in Table 1 and the TG curve depicted in Fig. 2 reveal that the decomposition of $Pt(CF_3Ph_2P)_2Cl_2$ occurs in four steps. In the first step (260–350°C) two

TABLE 1

Analysis of TG curve of bis(diphenyltrifluoromethylphosphine)dichloroplatinum(II)

Stage	Temp. (°C)	T_p [a]	Loss (%)		Moiety lost
			Found	Calc.	
1	215–225	220	No loss	Trans → cis	
2	270–350	320	26.50	26.98	$(CF_3Cl)_2$
3	360–410	385	14.00	13.67	PPh
4	415–480	430	19.00	19.50	Ph_2
5	500–650	600	14.00	13.67	PPh
6	residue	>650	27.00	27.26	PtO

[a] Peak temperature.

molecules of chlorotrifluoromethane CF_3Cl are liberated, in the second step (360–410°C) one phenylphosphine (PPh) radical is lost by oxidation, in the third step (415–480°C) two phenyl Ph˙ radicals are lost by oxidation and, finally, in the fourth step (500–620°C) one phenylphosphine PPh radical is lost, leaving a residue of PtO. The corresponding DTA curve is also depicted in Fig. 2. The first one is a small exothermic peak at about 220°C without any loss evident in the TG curve, and is due to the
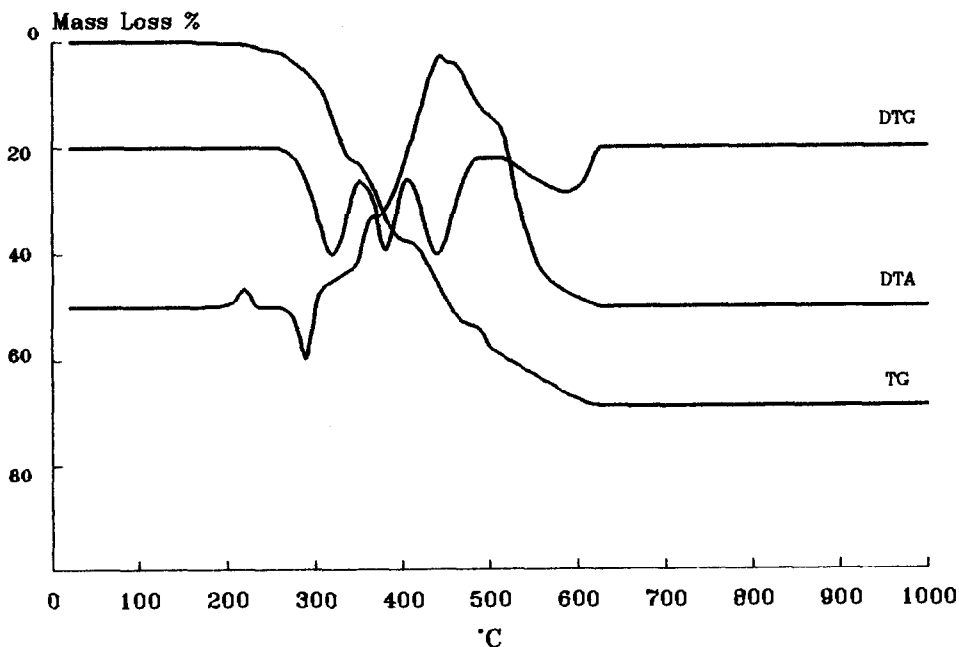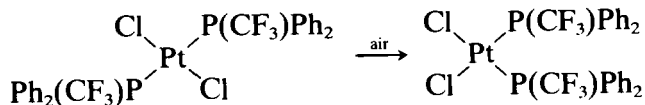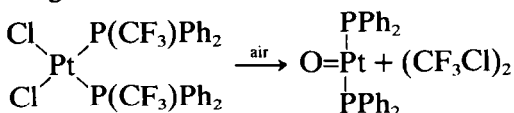

Fig. 2. Thermoanalytical curves of bis(diphenyltrifluoromethylphosphine)dichloro-platinum(II).

transformation of the complex from the trans to the cis isomer. The second sharp endothermic peak at about 300°C corresponds to the first loss in the TG curve of the complex, and subsequently a vigorous exothermic peak is observed in the range 320–600°C with humps at 320, 450 and 480°C. The following mechanism is inferred.
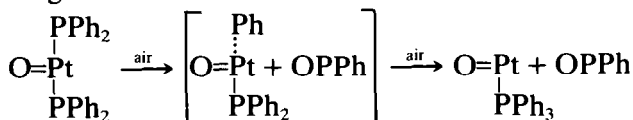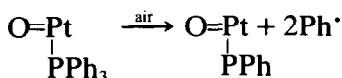
Stage 1

$$
\underset{Ph_2(CF_3)P}{\overset{Cl}{\diagdown}}\underset{Cl}{\overset{P(CF_3)Ph_2}{\diagup}}Pt \xrightarrow{air} \underset{Cl}{\overset{Cl}{\diagdown}}\underset{P(CF_3)Ph_2}{\overset{P(CF_3)Ph_2}{\diagup}}Pt
$$

Stage 2

$$
\underset{Cl}{\overset{Cl}{\diagdown}}\underset{P(CF_3)Ph_2}{\overset{P(CF_3)Ph_2}{\diagup}}Pt \xrightarrow{air} \underset{PPh_2}{\overset{PPh_2}{|}}O{=}Pt + (CF_3Cl)_2
$$

Stage 3

$$
\underset{PPh_2}{\overset{PPh_2}{|}}O{=}Pt \xrightarrow{air} \left[\underset{PPh_2}{\overset{Ph}{|}}O{=}Pt + OPPh \right] \xrightarrow{air} \underset{PPh_3}{\overset{}{|}}O{=}Pt + OPPh
$$

Stage 4

$$
\underset{PPh_3}{\overset{}{|}}O{=}Pt \xrightarrow{air} \underset{PPh}{\overset{}{|}}O{=}Pt + 2Ph^{\cdot}
$$

Stage 5

$$
\underset{PPh}{\overset{}{|}}O{=}Pt \xrightarrow{air} PtO + OPPh
$$
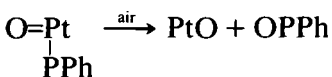
It is worth mentioning that the general aspect of the pyrolysis of the complex is not affected by different heating rates, but the DTA and DTG peaks and TG pattern are shifted to temperatures higher by 10°C with increasing heating rate.

The investigation indicates that the order of the decomposition reactions for the phosphine is 1, and the orders for the four steps observed for the complex are 1, 2, 0.5 and 1 respectively. This suggests that the mechanism of decomposition varies and occurs in different steps. The mechanisms followed in the first and the second steps for the phosphine

correspond with the second, third and last decomposition steps for the complex.

The proposed fragmentation pattern for the platinum complex receives strong support from the thermal analysis of the corresponding diphenyltrifluoromethylphosphine because, in both cases, the CF_3 group is the first to break off. This may be because of the strong electron withdrawing nature of the CF_3 group, which helps in the breaking of the $P-CF_3$ bond. The retention of the phenyl group by the phosphine in both cases must be attributed to the π-electron system of the phenyl group interacting with the d_π orbitals of phosphorus. This accounts for the second step, whereby the PPh group is fragmented and rearrangement of the phenyl group takes place to form a transitional complex with triphenylphosphine. Step three in the decomposition of the complex demonstrates the higher stability of the phenylphosphine PPh group and also of the Pt–PPh linkage. In both cases the $d_\pi-p_\pi$ bonding seems to be responsible for the higher dissociation energy required for the cleavage of the Ph group from P and PPh from Pt.

The experimental values in Tables 2–5 for the kinetic and thermodynamic parameters of the investigated reactions are averages of three measurements with uncertainties of ± 5.35 (FC), ± 6.73 (HM), ± 4.32

TABLE 2

Kinetic parameters of two steps of decomposition of the ligand diphenyltrifluoromethylphosphine(I) [a]

Method		Step 1	Step 2
FC	n	1	1
	E_a	47.34	62.23
	$\log A$	4.37	5.00
HM	n	1	1
	E_a	72.03	80.36
	$\log A$	5.59	6.16
DK	n	1	1
	E_a	45.61	60.42
	$\log A$	4.20	4.74
CR	n	1	1
	E_a	52.95	59.75
	$\log A$	4.44	4.70
ZZ	n	1	1
	E_a	54.39	62.76
	$\log A$	4.56	5.04

Abbreviations; FC = Freeman–Carroll [6]; HM = Horowitz–Metzger [7]; DK = Dharwadkar–Karkhanavala [8]; CR = Coats–Redfern [9]; ZZ = Zsakó–Zsakó [10]; T_p = peak temperature of DTG. Step 1, $T_p = 353$ K; step 2, $T_p = 453$ K. E_a in kJ mol^{-1}; $\log A$ in s^{-1}.

TABLE 3

Thermodynamic data of two steps of decomposition of the ligand diphenyltrifluoromethyl-phosphine(I) [a]

Method		Step 1	Step 2
FC	S^*	-162.64	-152.65
	G^*	101.82	127.82
	H^*	44.41	58.46
HM	S^*	-139.28	-130.44
	G^*	118.26	135.68
	H^*	69.10	76.59
DK	S^*	-165.90	-157.63
	G^*	101.24	128.06
	H^*	42.68	58.65
CR	S^*	-161.30	-158.40
	G^*	106.95	127.74
	H^*	50.02	55.98
ZZ	S^*	-159.00	-151.89
	G^*	107.58	127.80
	H^*	51.46	58.99

[a] The abbreviations have the same meaning as in Table 2. Step 1, $I_p = 353$ K; step 2, $T_p = 453$ K. S^* in J k^{-1} mol^{-1}; G^* and H^* in kJ mol^{-1}.

TABLE 4

Kinetic parameters of different steps of decomposition of bis(diphenyltrifluoromethyl phosphine)dichloroplatinum(II) [a]

Method		Stage 2	Stage 3	Stage 4	Stage 5
FC	n	1	1.8	0.5	1.2
	E_a	77.82	255.59	275.61	131.46
	$\log A$	4.50	18.45	17.67	6.03
HM	n	1	2	0.5	1
	E_a	96.53	275.46	284.99	142.47
	$\log A$	6.24	20.14	19.24	6.55
DK	n	1	2	0.5	1
	E_a	75.90	245.94	273.62	136.87
	$\log A$	4.32	17.73	18.37	6.18
CR	n	1	2	0.5	1
	E_a	72.82	250.03	264.47	122.69
	$\log A$	3.25	17.77	16.82	4.80
ZZ	n	1	2	0.5	1
	E_a	79.50	251.04	262.91	125.52
	$\log A$	4.67	18.27	16.75	5.40

[a] The abbreviations have the same meaning as in Table 2. Stage 2, $T_p = 593$ K; stage 3, $T_p = 653$ K; stage 4, $T_p = 743$ K; stage 5, $T_p = 833$ K. E_a in kJ mol^{-1}; $\log A$ in s^{-1}.

TABLE 5

Thermodynamic data of different steps of decomposition of bis(diphenyltrifluoromethyl-phosphine)dichloroplatinum(II) [a]

Methods		Stage 2	Stage 3	Stage 4	Stage 5
FC	S^*	−164.46	101.84	86.29	−138.00
	G^*	170.42	183.66	209.10	239.48
	H^*	72.89	250.16	269.76	124.53
HM	S^*	−131.15	134.20	116.35	−128.04
	G^*	169.37	182.40	197.35	242.20
	H^*	91.60	270.03	279.14	135.54
DK	S^*	−167.91	88.05	99.69	−135.12
	G^*	170.54	183.01	197.69	242.50
	H^*	70.97	240.51	267.77	129.94
CR	S^*	−188.40	88.82	70.01	−161.55
	G^*	179.61	188.60	209.41	250.33
	H^*	67.89	244.60	258.62	115.76
ZZ	S^*	−161.21	98.39	68.67	−150.06
	G^*	170.17	181.36	208.79	243.59
	H^*	74.57	245.61	257.06	118.59

[a] The abbreviations have the same meaning as in Table 2. Stage 2, 593 K; stage 3, 653 K; stage 4, 703 K; stage 5, 833 K. S^* in $J\,K^{-1}\,mol^{-1}$; G^* and H^* in $kJ\,mol^{-1}$.

(DK), ±4.55 (CR) and ±3.63 (ZZ). The Horowitz–Metzger treatment of the experimental data gives higher values of E_a compared with those from the other methods.

The mean values of E_a for the phosphine are 54.46 and 65.10 kJ mol^{-1} and those for complex are 80.51, 255.61, 272.32 and 131.80 kJ mol^{-1} for the second, third, fourth and fifth stages respectively. It is interesting to note that the removal of the CF$_3$ radical from the phosphine occurred by picking up a proton from the air, whereas that from the complex involved abstraction of the chloride ion from the complex. In both the cases the E_a is relatively low, ranging from 54 to 80 kJ mol^{-1}. The rearrangement of the residue after formation of CF$_3$Cl from the complex is supported by the high values of E_a at stages 3 and 4. This may be attributed to the π electronic system of the phenyl group and the possible $d_\pi-p_\pi$ interaction with the triphenylphosphine system.

The entropy of activation S^* is calculated from the following relation

$$S^* = R \ln[(Ah)/(kT)] \tag{1}$$

where h and k are the Planck and the Boltzmann constant respectively.

The average values of S^* for the two step decomposition of the ligand are −157.62 and −150.20 J K^{-1} mol^{-1}. The mean values of G^* and H^* are 107.17 and 129.38 kJ mol^{-1} and 51.53 and 61.34 kJ mol^{-1} respectively.

The mean values of S^*, for the four step decomposition of the complex are -162.63, 102.26, 88.28 and $-142.55 \, \mathrm{J \, K^{-1} \, mol^{-1}}$. The average values of G^* and H^* are 172.02, 183.41, 204.47 and $243.62 \, \mathrm{kJ \, mol^{-1}}$ and 75.58, 250.18, 266.31 and $124.88 \, \mathrm{kJ \, mol^{-1}}$ respectively.

Analysis of the kinetic and thermodynamic data by using a computer program [5] has shown that the rate of thermal decomposition cannot be determined solely by the activation energy E_a, since the frequency factor varies over a considerable range. It is the free energy of activation G^* which determines the rate of reaction at a given temperature [11].

A comparison of the data indicates that the magnitude of the negative entropy of activation is high, which supports the observation that there is appreciable thermal decomposition. The entropy of activation of phosphine and its complex for decomposition step one involving removal of the CF_3 group is more positive in the complex than in the phosphine itself. In the light of the report that loosely bound complexes have higher entropy compared with tightly bound ones [12], this observation indicates that the CF_3 group is more loosely bound in the complex than in the phosphine. This is perhaps to be expected because the strong electron withdrawing nature of the CF_3 group imparts to it the tendency to pull itself off from the structural environment of the complex, while the $d_\pi - p_\pi$ interaction of the phosphorus and the phenyl group on the one hand and the $d_\pi - d_\pi$ interaction of the phosphine with the platinum ion on the other hand provide stabilization and thus a pushing force. The net effect is the ready splitting off of the CF_3 group and picking up of chloride ion from platinum in the complex.

The residual transitional complex without the CF_3 group has a higher, albeit only slightly, entropy of activation compared with the complex having this group, as well as the phosphine which has lost the CF_3 group. The lower entropy of activation of $HO-PPh_2$ as compared with the phosphine is again perhaps due to the $d_\pi - p_\pi$ interaction of the phosphorus and phenyl groups. The change from the phosphine, which has a lower entropy of activation and is hence more ordered, to the complex, which has a higher S^* value and hence is less ordered, is suggested by the data to be responsible for the higher entropy of activation observed for the complex at stage 3.

The low value of entropy of activation observed at stage 4 is indicative of a more organized structure compared with stage 3. It may be seen that the transitional complex formed at stage 3 is a rearrangement of the residue involving the transitional complex which, owing to the high entropy, is suggested as being loosely held. The suggested scheme of decomposition amply supports the loose structure.

The negative value of S^* for stage 5 is again indicative of a higher order or an organized structure. High energy is required for the decomposition, and oxidation yields the compound suggested by the scheme and duly supported by the thermal analysis.

The above set of arguments is supported by data obtained from the rate constant k calculated via the relation $k = A \exp(-E_a/R)$ at peak temperature T_p. For stage 2, k is $3.19 \times 10^{-3} \, \text{s}^{-1}$, which is quite low but is expected to be so because of the pull and push forces noted above. The next stage has a higher value of k, $1.07 \times 10^{-2} \, \text{s}^{-1}$, suggesting that the observed stability is due to the $d_\pi - p_\pi$ and $d_\pi - d_\pi$ bonding in the diphenylphosphine adduct with platinum as the central atom. The higher value of $5.87 \times 10^{-1} \, \text{s}^{-1}$ for k for stage 4 supports the transitional state formation of the triphenylphosphine complex. Finally, the low value of k ($1.93 \times 10^{-2} \, \text{s}^{-1}$) for stage 5 suggests that the oxidation of the platinum complex is an easy reaction because the phosphine is detached merely by oxidizing it.

In order of the decomposition reactions stated in the scheme from stages 2–5 provides important support for the mechanism because the information strongly suggests dependence on the concentration at each stage. It is worth noting that the order of reaction for stages 2 and 5 is 1, for stage 3 it is 2 and for stage 4 it is 0.5. The removal of the phenylphosphine group and the formation of the transitional complex of diphenylphosphine with platinum in stage 3 is a second order reaction, perhaps because the other product is formed along with the transitional complex in equimolar proportion and hence support is given to the scheme presented here. Additionally, the formation of the transitional complex in stage 4 through the transfer of a phenyl group appears to occur in two stages. This is also implied by its having an order of 0.5.

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