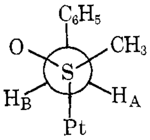
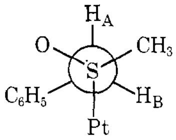
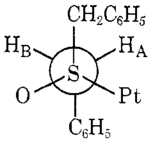
protons in both *dl* and *meso* forms satisfactorily reproduced the spectra. Compared with the diethyl sulfoxide complex, a significant reduction in the larger coupling has occurred. Two reasons may be involved. First, the substituent effect of benzyl at sulfur compared with ethyl may hinder the coupling mechanism, or, second, conformations about the S–CH_2 bond with *gauche* hydrogens may be more favored. The former seems unlikely since J_{Pt-CH_3} in the DMSO and $CH_3SOCH_2C_6H_5$ complexes are the same. Certainly, however, one conformation with *gauche* and *trans* hydrogens must be substantially populated to account for the observed difference. The conformations below appear favored, but the effective size of Pt makes their relative importance difficult to gauge. However H_A should have the larger coupling and, considering rotation about the Pt–S as before, is also predicted to lie at higher field, as observed.





For *cis*-$PtCl_2[CH_3SOCH(CH_3)_2]_2$ and *trans*-$PtCl_2[((CH_3)_2CH)_2SO]_2$ conformations with the methine proton *gauche* to Pt are definitely favored, in line with the very small coupling ($\not>$ 6–7 Hz). The preferred conformation about the Pt–S bond is one with one *CH_3*–CH further removed from the square plane than its geminal companion, thus accounting for the increased inequivalence compared with free sulfoxide.

In *cis*-$PtCl_2[(C_6H_5CH_2)_2SO]_2$, vicinal couplings of 27 and $\not>$5 Hz are observed, suggesting minor importance of that conformer with *gauche* hydrogens. Of the remainder, that shown would be predicted to be more heavily populated.



Although our data on the Pd(II) complexes are less extensive, similar lines of reasoning (both are d^8 complexes) account for the increase in methylene proton inequivalence on complexation. The general deshielding effect on coordination is associated simply with the σ-bond component between sulfur and the metal. A practical consequence is the increased acidity of such α hydrogens, and this could be useful for exchange purposes when groups facilitating exchange (*e.g.*, phenyl as in C_6H_5*CH_2*–$SOCH_2$) are absent. Some work along these lines has been reported.[29]

Acknowledgments.—The authors are grateful to the Department of Chemistry, Indiana University, for permitting this collaboration, and to Professor L. Montgomery for use of his dmr equipment. C. J. M. is grateful for the award of a Commonwealth postgraduate scholarship. This research was financed in part by grants (Grant No. ARGC-23) from the Australian Research Grants Committee, to whom we are grateful. Dr. N. S. Ham of CSIRO, Melbourne, Australia, has kindly provided us with data and views related to this work.

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CONTRIBUTION FROM CENTRO CHIMICA E TECNOLOGIA COMPOSTI METALLORGANICI
ELEMENTI TRANSIZIONE DEL CNR, FACOLTÀ DI CHIMICA INDUSTRIALE, 40136 BOLOGNA, ITALY

Formation of the Platinum–Olefin Bond Catalyzed by $SnCl_3^-$

BY R. PIETROPAOLO,[1] G. DOLCETTI, M. GIUSTINIANI, AND U. BELLUCO

Received September 12, 1969

The kinetics of the reactions between $PtCl_4^{2-}$ and various olefins have been studied in aqueous solutions 1.9 *M* in NaCl and 0.1 *M* in HCl, at 25°, in the presence of $SnCl_3^-$. The product is a π-olefinic complex of the Zeise's salt type. The rate law is a two-term expression of the type: $k_{obsd} = k'[ol] + k''[SnCl_3^-]^2$. The first term is interpreted as a bimolecular attack of the olefin on the $PtCl_4^{2-}$ complex and the second depends also on $[SnCl_3^-]^2$. As far as the first $SnCl_3^-$-uncatalyzed term is concerned, the reactivity changes in the order: allyl NH_3^+ > butyl NH_3^+ > allyl SO_3^- > allyl alcohol > pentenyl NH_3^+. The second $SnCl_3^-$-catalyzed term is interpreted as an easier attack of the olefin on a species of the type $Pt(SnCl_3)_2Cl_2^{2-}$, probably the *cis* isomer, formed in the rate-determining step. The accelerating effect of the group $SnCl_3^-$ is related to its high *trans* effect.

Introduction

We have recently reported a study on the catalytic effect of the $SnCl_3^-$ ion on the formation of the metal–olefin bond in the attack of ethylene on $PtCl_4^{2-}$. The species which are catalytically active are the isomers *cis*- and *trans*-$Pt(SnCl_3)_2Cl_2^{2-}$, the *cis* isomer being more active than the *trans* one.[2] The research has been now extended to the reactions of $PtCl_4^{2-}$ with a series of α-olefins such as $CH_2{=}CHCH_2NH_3^+$, $CH_2{=}CHCH_2OH$, $CH_2{=}CHCH_2SO_3^-$, $CH_2{=}CHCH_2CH_2NH_3^+$, and

(1) On leave from Messina University, Messina, Italy.

(2) R. Pietropaolo, M. Graziani, and U. Belluco, *Inorg. Chem.*, **8**, 1506 (1969).

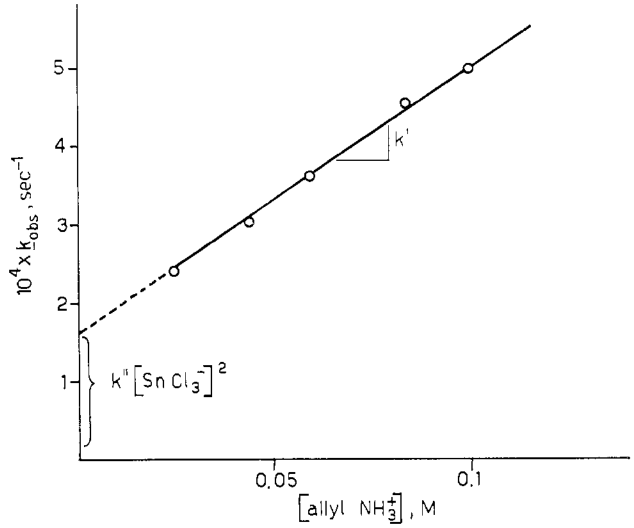

Figure 1.—Plot of the pseudo-first-order rate constants for reaction 1, at 25°, against the allyl NH_3^+ concentration; $[SnCl_3^-] = 5 \times 10^{-5}\ M$.

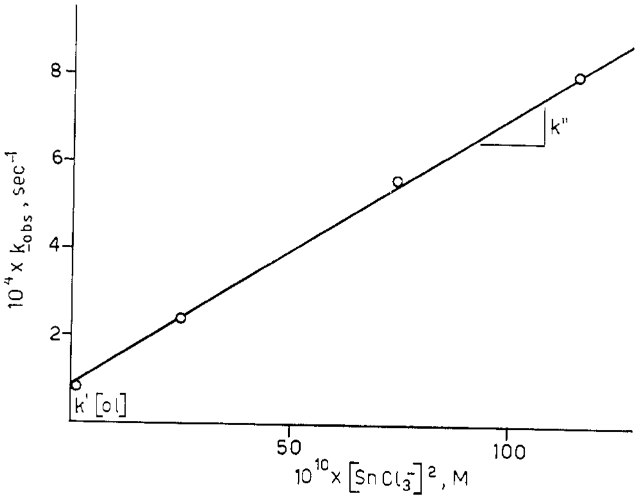

Figure 2.—Plot of the pseudo-first-order rate constants for reaction 1, at 25°, against $[SnCl_3^-]^2$; [allyl NH_3^+] = $3.25 \times 10^{-2}\ M$.

$CH_2{=}CHCH_2CH_2CH_2NH_3^+$ in order to investigate the mechanism of the $SnCl_3^-$-catalyzed path of the reaction.

Results and Discussion

The reactions examined are represented by the scheme

$$PtCl_4^{2-} + ol \xrightarrow{SnCl_3^-} Pt(ol)Cl_3^- + Cl^- \qquad (1)$$

(ol = olefin; its charge is omitted).

The pseudo-first-order rate constants, k_{obsd} (sec^{-1}), of these reactions obtained at different olefin concentrations, [HCl] = 0.1 *M*, and [NaCl] = 1.9 *M* are summarized in Table I. These constants depend on the nature and concentration of the entering olefin.

Rate data reported in Table II refer to kinetic runs carried out at a constant olefin concentration, [HCl] = 0.1 *M*, and [NaCl] = 1.9 *M*, while systematically changing the concentrations of $SnCl_2$ and $SnCl_3^-$. The concentration of $SnCl_3^-$ has been calculated from the values of the equilibrium constants for the $SnCl_2$–Cl^- system.[3]

TABLE I

VALUES OF k_{obsd} (SEC^{-1}) FOR THE REACTIONS AT 25°

$$PtCl_4^{2-} + ol \xrightarrow{SnCl_3^-} Pt(ol)Cl_3^- + Cl^-$$

IN AQUEOUS SOLUTIONS OF 1.9 *M* NaCl AND 0.1 *M* HCl; $[PtCl_4^{2-}] = 10^{-3}\ M$

10^2[olefin], *M*	$10^4[SnCl_2]$, *M* (initial)	$10^5[SnCl_3^-]$, *M*	10^4k_{obsd}, sec^{-1}
a. Olefin, $CH_2{=}CHCH_2NH_3^+$ (ClO_4^-)			
2.5	1.0	5.0	2.4
4.4	1.0	5.0	2.95
6.0	1.0	5.0	3.65
8.3	1.0	5.0	4.70
10.0	1.0	5.0	5.0
b. Olefin, $CH_2{=}CHCH_2SO_3^-$ (K^+)			
1.2	1.0	5.0	2.3
3.1	1.0	5.0	2.45
5.6	1.0	5.0	2.68
c. Olefin, $CH_2{=}CHCH_2OH$			
2.94	1.05	5.25	2.5
5.88	1.05	5.25	2.9
14.5	1.05	5.25	3.4
5.88	8.0	4.0	1.77
14.5	8.0	4.0	2.32
25.0	8.0	4.0	4.2
d. Olefin, $CH_2{=}CHCH_2CH_2NH_3^+$ (Cl^-)			
1.4	1.05	5.25	2.5
5.75	1.05	5.25	2.9
8.35	1.05	5.25	3.26
9.8	1.05	5.25	3.20
e. Olefin, $CH_2{=}CHCH_2CH_2CH_2NH_3^+$ (Cl^-)			
0.8	1.05	5.25	2.5
2.0	1.05	5.25	2.7
4.0	1.05	5.25	2.8

An example of the dependence of the rate constant k_{obsd} (sec^{-1}) upon the olefin concentration, at constant $[SnCl_2]$ and $[SnCl_3^-]$, is reported in Figure 1. Figure 2 shows the linear dependence of k_{obsd} (sec^{-1}) on the term $[SnCl_3^-]^2$, with a nonzero intercept. The kinetic law is

$$k_{obsd} = k'[ol] + k''[SnCl_3^-]^2 \qquad (2)$$

The intercept in Figure 2 corresponds to the first term k'[ol] of the above equation, whereas the slope corresponds to the value of k''. The slope in Figure 1 is k' and the intercept corresponds to the term $k''[SnCl_3^-]^2$. The values of k' (M^{-1} sec^{-1}) and k'' (M^{-2} sec^{-1}) are reported in Table III.

The validity of the general rate law (2) is confirmed by the following correlations, which have been experimentally determined. Data in Table IV show a reasonably good agreement between the extrapolated values of $k''[SnCl_3^-]^2$ as obtained from diagrams as in Figure 1 and those calculated from the k'' values determined independently (Figure 2). The nonzero intercept in Figure 2, *i.e.*, k'[olefin], is also in reasonably good agreement with the values calculated from the k', independently determined.[4] The first term of rate law (k', M^{-1} sec^{-1}) represents the bimolecular attack of the olefin on the $PtCl_4^{2-}$ anion.

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(3) G. Charlot, "L'Analyse Qualitative et ses Reactions en Solution," Masson Cie, Editeurs, Paris, 1957, p 246.

(4) (a) R. M. Milburn and L. M. Venanzi, *Inorg. Chim. Acta*, **2**, 97 (1968); (b) G. Dolcetti and L. M. Venanzi, unpublished data.

SCHEME I

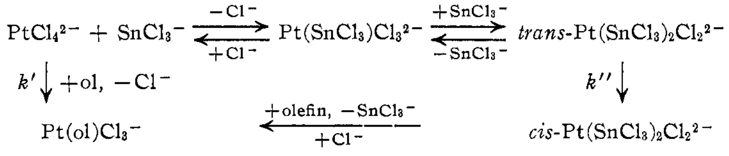

TABLE II

VALUES OF k_{obsd} (SEC^{-1}) FOR THE REACTIONS AT 25°

$$PtCl_4^{2-} + ol \xrightarrow{SnCl_3^-} Pt(ol)Cl_3^- + Cl^-$$

IN AQUEOUS SOLUTIONS OF 1.9 M NaCl AND 0.1 N HCl; $[PtCl_4^{2-}] = 10^{-3}$ M

10^2[olefin], M	$10^4[SnCl_2]$, M (initial)	$10^5[SnCl_3^-]$, M	$10^{10}[SnCl_3^-]^2$, M	10^4k_{obsd}, sec^{-1}
a. Olefin, $CH_2{=}CHCH_2NH_3^+$ (ClO_4^-)				
3.25	0.0	0.0		0.605[a]
3.25	0.22	1.1	1.2	0.71
3.25	1.0	5.0	25	2.4
3.25	1.72	8.6	73.9	5.7
3.25	2.20	11.0	121	8.0
b. Olefin, $CH_2{=}CHCH_2SO_3^-$ (K^+)				
3.1	0.0	0.0		0.26[a]
3.1	0.277	1.38	1.92	0.39
3.1	1.0	5.0	25	2.45
3.1	2.08	10.4	108	7.78
c. Olefin, $CH_2{=}CHCH_2OH$				
5.8	0.0	0.0		0.58[a]
5.8	0.165	0.825	0.68	0.63
5.8	0.8	4.0	16	1.77
5.8	1.05	5.25	27.5	2.9
5.8	1.4	7.0	49	5.0
d. Olefin, $CH_2{=}CHCH_2CH_2NH_3^+$ (Cl^-)				
3.6	0.0	0.0		0.295[b]
3.6	0.315	1.57	2.46	0.395
3.6	1.05	5.25	27.5	2.5
3.6	1.64	8.2	67.5	5.8
3.6	2.05	10.25	106	8.0
e. Olefin, $CH_2{=}CHCH_2CH_2CH_2NH_3^+$ (Cl^-)				
2.1	0.00	0.00	3.44	0.122[b]
2.1	0.37	1.85	3.44	0.150
2.1	1.05	5.25	27.5	2.7
2.1	1.80	9.00	81.0	6.0

[a] Data from ref 4a. [b] G. Dolcetti and L. M. Venanzi, unpublished data.

TABLE III

VALUES OF RATE CONSTANTS k' (M^{-1} SEC^{-1}) AND k'' (M^{-2} SEC^{-1}) FOR REACTION 1

Olefin	$10^3k'$, M^{-1} sec^{-1}	$10^{-4}k''$, M^{-2} sec^{-1}
$CH_2{=}CHCH_2NH_3^+$	3.43	6.55
$CH_2{=}CHCH_2NH_3^+$	3.43[a]	27.00[a]
$CH_2{=}CHCH_2SO_3^-$	0.82	7.5
$CH_2{=}CHCH_2OH$	0.74	8.08
$CH_2{=}CHCH_2CH_2NH_3^+$	1.08	8.0
$CH_2{=}CHCH_2CH_2CH_2NH_3^+$	0.57	7.3

[a] Values calculated at [NaCl] = 0.9 M, [HCl] = 0.1 M, and $[NaClO_4]$ = 1 M.

The catalytic effect of chlorostannate(II) ion on the formation of the platinum–olefin bond in these systems is therefore expressed by the second term of the kinetic equation (2). The second-order dependence on the concentration of $SnCl_3^-$ suggests a mechanism *via* formation of an intermediate, having two Pt–Sn bonds, in equilibrium with the species having the Pt–Cl bonds (Scheme I). The values of k'' include the constants of the involved preequilibria.

TABLE IV

VALUES (SEC^{-1}) OF THE INTERCEPTS OF FIGURES 1 AND 3 AS EXPERIMENTALLY FOUND AND AS CALCULATED[a]

	10^4 × intercept (Figure 1)		10^4 × intercept (Figure 3)	
Olefin	Found	$k''[SnCl_3^-]^2$	Found	k'[olefin]
$CH_2{=}CHCH_2NH_3^+$	1.57	1.64	0.65	1.13
$CH_2{=}CHCH_2SO_3$	2.18	1.88	0.26	0.254
	2.32	2.22		
$CH_2{=}CHCH_2OH$			0.55	0.43
	1.32	1.29		
$CH_2{=}CHCH_2CH_2NH_3^+$	2.36	2.20	0.30	0.38

[a] Values of $[SnCl_3^-]$ are from Table I; values of [olefin] are from Table II.

In fast preequilibria $trans$-$Pt(SnCl_3)_2Cl_2^{2-}$ is first formed and then it isomerizes to the *cis* form in the rate-determining step. This isomer should be the active species for the olefin absorption. This interpretation is in agreement with previous observations[5] that the *trans* → *cis* isomerization is retarded in the presence of $SnCl_3^-$. Furthermore it has been already qualitatively observed that a suspension containing the cis-$Pt(SnCl_3)_2Cl_2^{2-}$ isomer absorbs ethylene more rapidly than a fresh solution[2] containing mainly the *trans* isomer.

TABLE V

VALUES OF k_{obsd} (SEC^{-1}) FOR THE REACTIONS AT 25°

$$PtCl_4^{2-} + CH_2{=}CHCH_2NH_3^+ \xrightarrow{SnCl_3^-} Pt(CH_2{=}CHCH_2NH_3^+)Cl_3^- + Cl^-$$

IN AQUEOUS SOLUTIONS OF 0.9 M [NaCl] AND 0.1 M [HCl]; $[PtCl_4^{2-}] = 10^{-3}$ M

$10^2[CH_2{=}CH$-$CH_2NH_3^+]$, M	$10^4[SnCl_2]$, M	$10^5[SnCl_3^-]$, M	$10^{10}[SnCl_3^-]^2$, M	10^4k_{obsd}, sec^{-1}
2.95	0.45	1.77	3.10	0.6
2.95	0.80	3.11	9.67	2.4
2.95	1.00	3.93	15.40	4.0
2.95	1.05	4.13	17.00	5.0
2.95	1.26	4.96	24.6	6.7
2.95	1.54	6.06	36.7	10.2

Consistently a dependence of the k'' (sec^{-1}) on the $1/[Cl^-]^2$ term has been found. Table V reports the k_{obsd} (sec^{-1}) calculated at constant olefin concentration, [NaCl] = 0.9 M, [HCl] = 0.1 M, and $[NaClO_4]$ = 1 M, while changing systematically the concentrations of $SnCl_2$ and $SnCl_3^-$. In Figure 3 the dependence of k'' (sec^{-1}) on the term $1/[Cl^-]^2$ is reported for $[Cl^-]$ = 1 M and $[Cl^-]$ = 2 M.

A satisfactorily plotted linear dependence is obtained, supporting the proposed mechanism. The zero intercept is in good agreement with the equilibria of the $SnCl_2$–Cl^- system ($[SnCl_3^-] \rightarrow 0$ when $[Cl^-] \rightarrow \infty$).

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(5) J. F. Young, R. G. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 5176 (1964).

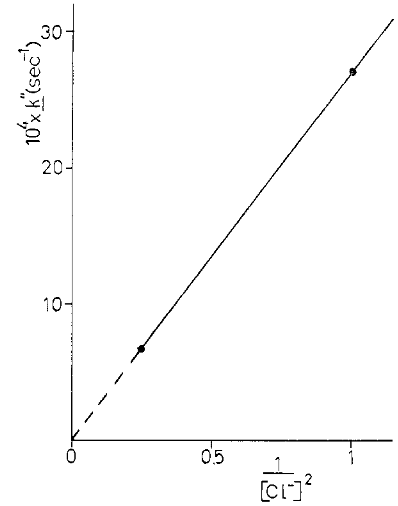

Figure 3.—Dependence of k'' on the term $1/[Cl^-]^2$.

In the light of the latter results the general rate law (2) can be better expressed in the form

$$k_{obsd} = k'[ol] + k''\frac{[SnCl_3^-]^2}{[Cl^-]^2}$$

We recall here that the reaction rate for the formation of $Pt(SnCl_3)_5^{3-}$ starting from $PtCl_4^{2-}$ and a large excess of $SnCl_3^-$ (1:100–1000) has been found to depend linearly on the concentration of $SnCl_3^-$.[2] This suggests that in the latter experimental conditions the formation of $Pt(SnCl_3)_5^{3-}$ does not proceed through the *trans* → *cis* isomerization. Under our experimental conditions (*i.e.*, defect of $SnCl_3^-$ relative to $PtCl_4^{2-}$) the formation of $Pt(SnCl_3)_5^{3-}$ is prevented by formation of the *cis*-$Pt(SnCl_3)_2Cl_2^{2-}$ which reacts with the olefin to give in an undetermined pathway the π-olefinic platinum(II) complex.

The accelerating effect of the *cis*-$Pt(SnCl_3)_2Cl_2^{2-}$ can be related to the high *trans* effect of the $SnCl_3^-$ ligand[6] which allows an easier entry of the olefin molecule with a rate practically independent of its nature. The slight differences in the k'' (M^{-2} sec^{-1}) values (Table III) are under the limit of the experimental errors. The low discriminating power of the *cis*-$Pt(SnCl_3)_2Cl_2^{2-}$ complex toward the entering olefins is also consistent with the high *trans* effect of the $SnCl_3^-$ group.[6]

When reactions of the type (1) are carried out in the presence of boric acid or boron halides, there is no accelerating effect. It is already known that these species, interacting with the d_{z^2} filled orbital of Pt^{II}, can significantly modify the electronic density at the central metal, as can be detected from kinetic studies.[7] This is in accord with the idea that the attack of the olefin might occur on a substrate containing two $SnCl_3^-$ groups coordinated to the platinum atom. The question concerning the type of primary attack (nucleophilic or electrophilic) of the olefin on the platinum(II) atom still remains unanswered.

Experimental Section

Compounds.—The allylammonium perchlorate has been prepared from allylamine and perchloric acid and recrystallized from ether–ethanol. The potassium allylsulfonate has been prepared according to the method reported in the literature.[4a] The allylic alcohol was a commercial grade reagent and was used after fractional distillation. The butenylamine and the pentenylamine were prepared as reported in the literature.[8]

Potassium chloroplatinate(II) was a commercial grade reagent, recrystallized from 0.1 N HCl to eliminate possible traces of Pt^{IV}. The reaction products, $Pt(ol)Cl_3^-$, were prepared according to the methods reported in the literature[9] and characterized throughout by elemental analysis and uv spectra.

Kinetics.—The reactions have been carried out in water solution containing 0.1 M HCl and 0.9 or 1.9 M NaCl, to minimize the aquation of the $PtCl_4^{2-}$ anion.[10] The kinetics have been followed by using a Beckman DK 2A double-beam recording spectrophotometer with compartment for thermostated cells and measuring the optical density changes with time at the wavelength of 295 mμ. At this wavelength the absorption of the intermediate is negligible. The solutions of $SnCl_2$ were prepared under nitrogen atmosphere just before use. The reaction mixtures were prepared by adding to the Pt^{II} complex solutions a known volume of the solution of $SnCl_2$ containing the olefin at the desired concentration. The reactions were carried out under pseudo-first-order conditions, by keeping the olefin in large excess as compared to the platinum complex. The pseudo-first-order rate constants, k_{obsd} (sec^{-1}), were calculated from the linear plots of log $(A_\infty - A_t)$ *vs.* time, where A_t and A_∞ are the optical densities of the reaction mixture at 295 mμ at time t and at the end of the reaction, respectively. At the end of the reaction the noncatalytic $Pt(SnCl_3)_5^{3-}$ species is formed in a very low concentration.

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