

rate constant for nickel complex formation due to the influence of the ICB effect. This, in turn, implies that the stability constant of the nickel-EDTA complex may be larger than would otherwise be anticipated.

Although mechanism II has been postulated previously for EDTA reactions, the evidence was largely circumstantial and the preference for this mechanism was primarily attributed to the favorable charge on the carboxylic oxygen atoms. It is now seen that reaction *via* mechanism I is sterically hindered to the extent that mechanism II represents the more favorable reaction path. This conclusion has far-reaching implications for all branched multidentate ligands and suggests that the substitution of selected donor atoms at ex-

terior sites on branched ligands might be utilized to improve kinetic selectivity.

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Reaction of Tetrachloroplatinate(II) with Ethylene in the Presence of Chlorostannate(II) Ion

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Kinetic data are reported for the reaction of either tetrachloroplatinate(II) ion or Zeise's salt with SnCl_3^- . Data support a bimolecular attack of SnCl_3^- upon the substrate. Data for the reaction of tetrachloroplatinate(II) with ethylene in the presence of chlorostannate(II) ion (at various Pt:Sn ratios) in acidic aqueous solution are also reported. The ethylene absorption by the metal complex affording $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$ appears to involve both the *cis* and *trans* isomers, the *cis*- $\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2^{2-}$ being the more active absorbing intermediate. No ethylene absorption is detectable at high Sn:Pt ratios, at which the predominant species is the five-coordinated $\text{Pt}(\text{SnCl}_3)_3^{3-}$. Results are discussed in terms of the high *trans* effect and of the pronounced π -acceptor character of SnCl_3^- bonded to platinum(II).

Introduction

In recent years the chemistry of the tin-metal bond has attracted much interest because of its theoretical and practical implications exemplified by the investigations on the nature of the bond²⁻⁸ and by the homogeneous hydrogenation, carbonylation, and double-bond migration on unsaturated compounds catalyzed by platinum-tin chloride systems.⁹⁻¹³

In the case of hydrogenation reactions, since the formation of a platinum-olefin complex is a necessary step

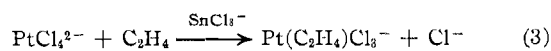
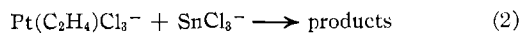
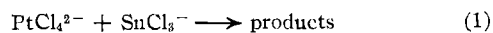
of the over-all process, the study of the factors governing the ease and occurrence of olefin coordination to transition metal ions appears most important.^{2a,14,15} The maximum rate of homogeneous hydrogenation of olefins and acetylenes catalyzed by Pt-Sn complexes has been found for molar Sn:Pt ratios higher than 5.^{16,17}

Among other chemical properties of tin-metal systems of d^8 transition metal ions, our attention has been drawn by the relevant observation of Cramer that whereas the formation of Zeise's salt from PtCl_4^{2-} and ethylene is rather slow, it is markedly accelerated by stannous chloride.^{18,19}

We have first examined the kinetic behavior of PtCl_4^{2-} with SnCl_3^- and then its role in the reaction of the ethylene absorption on tetrachloroplatinate(II) ion. The reactions studied are

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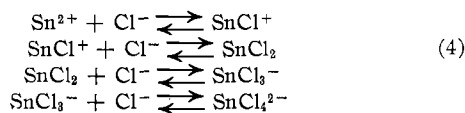


Experimental Section

Materials.—*trans*-($\text{N}(\text{CH}_3)_4$)₂[Pt(SnCl₃)₂Cl₂] was obtained as a red precipitate by adding $\text{N}(\text{CH}_3)_4\text{Cl}$ to a mixture of Na_2 [PtCl₄] and SnCl_2 (Pt:Sn ratio = 1:2) in an ethanol solution immediately after mixing. *cis*-($\text{N}(\text{CH}_3)_4$)₂[Pt(SnCl₃)₂Cl₂] was obtained as a yellow precipitate by adding $\text{N}(\text{CH}_3)_4\text{Cl}$ to an aged (*i.e.*, after about 20 min has elapsed since mixing of reactants) ethanol solution of Na_2 [PtCl₄] and SnCl_2 in the same ratio as above.²⁰ $(\text{N}(\text{CH}_3)_4)_2$ [Pt(SnCl₃)₆] was obtained as a red precipitate by adding $\text{N}(\text{CH}_3)_4\text{Cl}$ to a solution of K_2 [PtCl₄] and SnCl_2 (Sn:Pt ratio = 5) in 3 *M* hydrochloric acid.²⁶ These preparations were carried out under a nitrogen atmosphere. All of the other materials were of reagent grade and were used without further purification.

Spectra.—Infrared spectra in the 400–200-cm⁻¹ region were taken on a Perkin-Elmer 621 spectrophotometer using CsI cells and corresponded to the literature data where available.

Reactions of PtCl₄²⁻ and Pt(C₂H₄)Cl₃⁻ with SnCl₃⁻.—The reactions between PtCl₄²⁻ or Pt(C₂H₄)Cl₃⁻ and SnCl₃⁻ in acidic aqueous solution under a nitrogen atmosphere leading to Pt(SnCl₃)₆³⁻ were studied by spectrophotometric methods on a Beckman DK-2A recording spectrophotometer equipped with a thermostated cell compartment. The changes of absorbance at 310 mμ with time of the reaction solution were monitored. The reactions were carried out under pseudo-first-order conditions by using an excess of SnCl₂. The concentration of the reactive species SnCl₃⁻ in each run was calculated from the known values of the constants of the equilibria²¹



The rate constants, k_{obsd} (sec⁻¹), were obtained from the linear plots of $\log(A_\infty - A_t)$ vs. time. Values were reproducible within 5–10%.

Ethylene Absorption on PtCl₄²⁻ in the Presence of SnCl₃⁻.—Experiments of ethylene absorption under constant pressure were followed by using the device employed by Bolland²² and modified by Chalk and Smith.²³ The freshly prepared reaction solution was placed in a 5-ml round-bottomed flask immersed in a thermostatically controlled water bath and connected with the gas buret device, which also was similarly thermostated. The flask was vigorously agitated with a stirring frequency of 1000 min⁻¹. Under such conditions reactions were free from diffusion limitation. In fact, experiments performed using different agitation frequency gave about the same values of rate constants. That diffusion of ethylene into the solution was not the rate-controlling step was confirmed by the instantaneous consumption of ethylene by a diluted aqueous solution of bromine, stirred in the reaction flask. In a typical run, after filling the reaction flask under nitrogen atmosphere with the reaction mixture, through which nitrogen had previously been swept, stirring was commenced. The system was then evacuated and ethylene was introduced at 1 atm. The reaction was followed by measuring the volume of ethylene absorbed under constant pressure over a period of time. The ethylene constant-pressure conditions were assured by proper changes of volume in the gas buret automatically produced by an electrolytic cell containing a diluted aqueous solution of sulfuric acid fitted to the manometric system.

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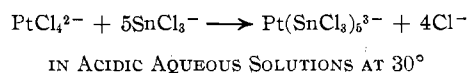
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Results

Rate data for reactions 1 and 2 are reported in Tables I and II. Absorption data for the reaction of ethylene with the Pt-Sn system are reported in Table III. All of these data refer to reactions obtained by using freshly prepared solutions, where for Sn:Pt ratios smaller than 5 the *trans*-Pt(SnCl₃)₂Cl₂²⁻ isomer is at first present in equilibrium with the *cis* isomer. For Sn:Pt ratios >5 Pt(SnCl₃)₆³⁻ becomes predominant.

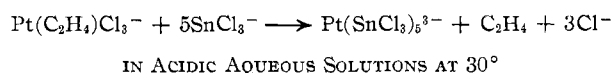
TABLE I
RATE DATA FOR THE REACTION^a



10 ³ [SnCl ₂], <i>M</i>	10 ³ [SnCl ₃ ⁻], <i>M</i>	10 ³ <i>k</i> _{obsd} , sec ⁻¹
2.1	1.05	8.9
4.2	2.1	21.8
8.4	4.2	43.1
21.0	10.5	115.0

$${}^a k_2 = 11 \text{ M}^{-1} \text{ sec}^{-1}. \quad [\text{PtCl}_4^{2-}] = 2 \times 10^{-5} \text{ M}; \quad [\text{HCl}] = 2 \text{ M}.$$

TABLE II
RATE DATA FOR THE REACTION^a



10 ³ [SnCl ₂], <i>M</i>	10 ³ [SnCl ₃ ⁻], <i>M</i>	<i>k</i> _{obsd} , sec ⁻¹
3	1.5	0.405
4.83	2.41	0.713
7.7	3.85	1.23

$${}^a k_2 = 297 \text{ M}^{-1} \text{ sec}^{-1}. \quad [\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-] = 2 \times 10^{-5} \text{ M}; \quad [\text{HCl}] = 3 \text{ M}.$$

Unfortunately we could not determine the rate constants of ethylene absorption for the various Pt-Sn species present in the reaction mixture for the following reasons. The equilibrium constant for the *cis* ⇌ *trans* isomerization of Pt(SnCl₃)₂Cl₂²⁻ is unknown and the attainment of the equilibrium is not immediate. Moreover during the course of each absorption run, whatever the Sn:Pt ratio, such ratio changes continuously as Zeise's salt is being formed. Consequently, other Pt-Sn species become important (*e.g.*, Pt(SnCl₃)₆³⁻) each one possessing its own reactivity toward ethylene absorption. Therefore, owing to the complexity of the system investigated, we prefer to express the experimental results in qualitative terms of half-time of ethylene absorption ($t_{1/2, \text{C}_2\text{H}_4}$, minutes) rather than in terms of rate constants. [Interestingly, plots of $\log(V_t - V_\infty)$ vs. time are roughly linear for an extent of reaction ranging from ca. 30 to 70%. V_t is the volume of ethylene absorbed at time t and V_∞ is the ethylene volume theoretically required (Pt:C₂H₄ = 1).] Such half-time is meant to be the time taken for absorption of half of the theoretically required amount of ethylene at completion (Pt:C₂H₄ = 1). Of course, comparison of such values must be done cautiously, without attributing too much meaning to the single values.

The value of $t_{1/2, \text{C}_2\text{H}_4}$ for the ethylene absorption by

TABLE III
ETHYLENE ABSORPTION FROM ACIDIC AQUEOUS
SOLUTIONS OF PtCl_4^{2-} ($5 \times 10^{-2} M$) IN THE PRESENCE
OF SnCl_2 AT 30°

[HCl], M	$10^3[\text{SnCl}_2]$, M	$10^3[\text{PtCl}_4^{2-}]/$ $[\text{SnCl}_2]$	$10^3[\text{SnCl}_3^-]$, M	$10^3[\text{SnCl}_4^{2-}]$, M	$t_{1/2}^{\text{C}_2\text{H}_4}$, min
3	5	10	2.55	0.089	18
3	10	5	5.1	0.18	18
3	25	2	12.7	0.44	13
3	50	1	25.5	0.89	12 ^b
3	100	0.5	51.0	1.8	15
3	100	0.5	51.0	1.8	3 ^a
3	250	0.2
1.5	5	10	2.38	0.34	25
1.5	10	5	4.8	0.67	39
1.5	25	2	12	1.69	27
1.5	50	1	23.8	3.4	68
1.5	100	0.5	48	6.7	47
1.0	5	10	1.98	0.63	73
1.0	10	5	3.98	1.27	42
1.0	25	2	9.9	3.18	172
1.0	50	1	19.8	6.3	130
1.0	100	0.5	39	12.7	225
1.0 ^c	50	1	25.5	0.89	12 ^b

^a Value of $t_{1/2}^{\text{C}_2\text{H}_4}$ (minutes) obtained by using an aged mixture solution of PtCl_4^{2-} and SnCl_3^- in acidic aqueous solution. ^b These experiments indicate that the ethylene absorption is not acidity sensitive. ^c $[\text{NaCl}] = 2.0 M$.

aged solutions of PtCl_4^{2-} and SnCl_3^- (Sn:Pt = 2; that is, where the equilibrium between *trans*- and *cis*-Pt(SnCl_3)₂Cl₂²⁻ is reached) was about one-fifth that obtained from freshly prepared reactant solutions of PtCl_4^{2-} and SnCl_3^- , where the *trans* isomer is at first present (see Table III). The implication is clear here that *cis*-Pt(SnCl_3)₂Cl₂ is a more reactive substrate than the *trans* isomer for the ethylene absorption or alternatively the *cis* isomer is the only active species and the rate-determining step in fresh solutions is the *trans*-*cis* isomerization. However, in order to decide what portion of the activity of the Pt-Sn system is attributable to the *cis* isomer, the following experiment was carried out. We followed the progress of ethylene absorption by a saturated, acidic (3 M HCl), aqueous, 3-ml solution of *cis*-(N(CH₃)₄)₂[Pt(SnCl_3)₂Cl₂]. Under these conditions, the total amount of gas absorbed was 0.6 cm³, reflecting the low solubility of the *cis* compound. During the course of the reaction an orange-red precipitate formed slowly, which we believe to be the less soluble *trans*-(N(CH₃)₄)₂[Pt(SnCl_3)₂Cl₂] arisen from the interaction of the unreacted *cis* isomer with the SnCl_3^- set free upon coordination of ethylene to the *cis*-Pt(SnCl_3)₂Cl₂²⁻. The reaction was over in about 10 min; that is, it was faster than that involving the equilibrium mixture of *cis* and *trans* isomers.

The ethylene absorption by the Pt-Sn system does not apparently depend on the acidity of the medium. In fact, absorption experiments carried out at different hydrochloric acid concentrations but at the same chloride concentrations gave the same value of $t_{1/2}^{\text{C}_2\text{H}_4}$ (see experiments referred to by footnote *b* in Table III). On the other hand, increasing the chloride concentration renders the system more active toward ethylene absorp-

tion. An interpretation of this effect is attempted further in the Discussion.

Discussion

Pt^{II} reacts with SnX_3^- (X = Cl, Br) to form the one-, two-, or five-coordinated Sn compounds of $\text{PtL}_2\text{Cl}(\text{SnCl}_3)$, $\text{PtL}_2(\text{SnCl}_3)_2$, and $\text{Pt}(\text{SnCl}_3)_3^{3-}$ (L is an anionic or neutral ligand). Air-stable salts of the $\text{Pt}_3\text{Sn}_4\text{Cl}_{20}^{4-}$ anion, formulated as derivatives of a Pt_3Sn_2 metal cluster, have been also isolated.²⁴

Nmr, infrared studies, and chemical behavior of Pt-Sn compounds have shown that SnCl_3^- behaves as a weak σ donor but is a strong d_π - d_π metal-to-tin bond acceptor ligand (similar to the CN^- group^{6-8, 18, 25}) and probably this is responsible for its unusual ability to stabilize five-coordinate platinum(II) complexes. Strictly related to its electronic properties is believed to be the strong *trans* activation of SnCl_3^- expressed in the substitution reactions of tin-metal d⁸ complexes and the catalytic versatility of such systems, as displayed in numerous homogeneous catalytic reactions, among the most prominent ones being the hydrogenation of olefins.^{16, 26-29}

The catalytic effectiveness of complexes of the type ML_2X_2 (L = PR_3 or AsR_3 ; M = Pd or Pt; X = halide or pseudohalide) is enhanced by the presence of chlorides of group IVb elements (Si, Ge, Sn) which are believed to form metal-metal-bonded compounds: this would result in activation of molecular hydrogen and an easy hydrogen attack on the entering olefinic double bond. In addition, the coordinated electrophile may protect the central metal from reduction by H_2 .³⁰⁻³³

Ethylene adds on *trans*-Pt(P(C₂H₅)₃)₂HCl under very drastic conditions,³⁴ whereas catalytic amounts of SnCl_2 are markedly effective in speeding up the reaction under very mild conditions.¹⁹ The yield ratio of *cis*- to *trans*-2-olefin is also affected by SnCl_2 during the olefin isomerization.^{12, 35}

The nature of the catalytically active species which are present in the system Pt-Sn has yet to be ascertained. In fact, there are to date rather contrasting interpretations concerning the composition of compounds obtained by interaction of PtCl_4^{2-} with SnCl_3^- at various Pt:Sn ratios in solution. Thus, we have at first examined the reactions between $(\text{PtCl}_4)_2^{2-}$ and SnCl_3^- with the joint aim of determining which species are present and which are active in olefin absorption on the metal complex.

SnCl_2 reacts with $\text{Na}_2(\text{PtCl}_4)$ (Sn:Pt = 2) affording almost at once a red compound which is believed to be

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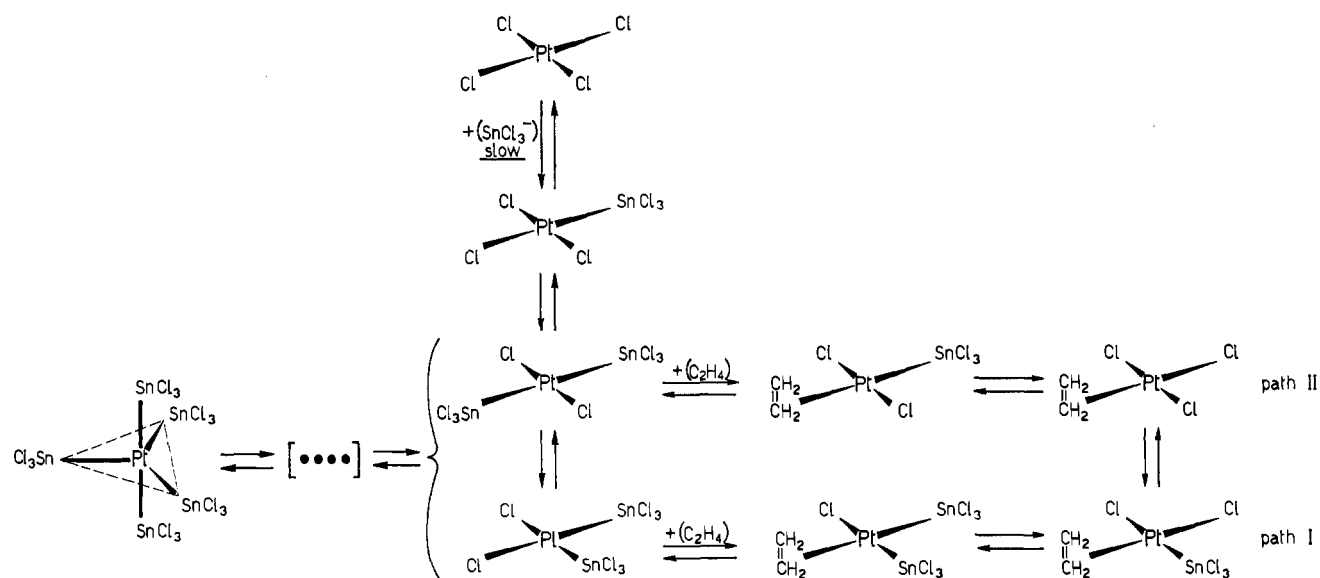


Figure 1.—Reaction scheme for the ethylene absorption on PtCl_4^{2-} in the presence of SnCl_3^- in hydrochloric acid aqueous solution. The charges of the complexes the entering and the leaving groups have been omitted.

the kinetically favored $\text{trans-Pt}(\text{SnCl}_3)_2\text{Cl}_2^{2-}$. On standing, the red solution turns yellow after about 0.5 hr. This is considered to be the thermodynamically stable *cis* isomer. At higher Sn:Pt ratios (>8) the five-coordinated $\text{Pt}(\text{SnCl}_3)_5^{3-}$ has been reported as becoming the predominant species. The conversion of the various species into one another can be brought about by properly changing the concentrations of SnCl_3^- and Cl^- , according to the establishment of solution equilibria.

Data reported in Tables I and II are related to the rate of formation of $\text{Pt}(\text{SnCl}_3)_5^{3-}$ from SnCl_2 and either PtCl_4^{2-} or $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3^-$ in acidic aqueous solution. As can be seen, both processes are second order. In the case of PtCl_4^{2-} this suggests a bimolecular slow replacement of Cl^- by SnCl_3^- as the first stage of the stepwise over-all reaction.

Zeise's salt reacts with SnCl_3^- about 30 times faster than PtCl_4^{2-} . Owing to the high *trans* effect of ethylene compared to chloride ligand,³⁶ the substitution of chloride *trans* to ethylene should be fast. In the intermediate formed in this first stage, $\text{trans-Pt}(\text{C}_2\text{H}_4)(\text{SnCl}_3)_2\text{Cl}_2^-$, the ethylene moiety is labilized by the strong *trans*-active SnCl_3^- , so that its replacement by an additional SnCl_3^- is likely to be fast and reversible. From now on the reaction pathway becomes identical with that pertaining to PtCl_4^{2-} . However, any subsequent step leading to $\text{Pt}(\text{SnCl}_3)_5^{3-}$ may become the rate-controlling one for reactions starting from Zeise's salt.

As for the absorption of ethylene on PtCl_4^{2-} promoted by SnCl_3^- , data in Table III point out the following features. (i) The highest rate of absorption is obtained for Sn:Pt ratios lower than 5. Within such range of relative concentrations the predominant Pt-Sn species in solution are, as reported above, *cis*- and *trans*- $\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2^{2-}$. The *cis* isomer is more reactive toward ethylene than the *trans* complex. However, we cannot exclude that also this species is active. (ii) At Sn:Pt ratios higher than 5 (that is, when the predomi-

nant species becomes $\text{Pt}(\text{SnCl}_3)_5^{3-}$) no absorption of olefin is observed. This suggests that the five-coordinated species cannot be the catalytically active one. Accordingly, even for Sn:Pt ratios lower than 5, never was the absorption of ethylene found to be quantitative (Pt:C₂H₄ = 1) owing to the formation of an appreciable amount of the unreactive $\text{Pt}(\text{SnCl}_3)_5^{3-}$ species toward the end of the reaction.

On the basis of the above findings, one can surmise the reaction scheme of Figure 1. The much easier addition of ethylene to $\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2^{2-}$ compared to PtCl_4^{2-} is probably related (a) to the higher *trans* effect of SnCl_3^- compared to Cl^- and (b) to the more pronounced π -acceptor character of SnCl_3^- bonded to Pt^{II}. The first stage of the reaction involves a bimolecular attack leading to two labile intermediate isomers bearing Pt-Sn and Pt-olefin bonds: *cis*- $\text{Pt}(\text{C}_2\text{H}_4)(\text{SnCl}_3)_2\text{Cl}_2^-$ (path I) and *trans*- $\text{Pt}(\text{C}_2\text{H}_4)(\text{SnCl}_3)_2\text{Cl}_2^-$ (path II).

When such an intermediate is the *cis* isomer (path I), the presence of a molecule of olefin *trans* to SnCl_3^- is likely to labilize the latter ligand, since both groups can compete *via* π bonding for the same filled nonbonding d orbital of Pt^{II} of proper symmetry (*trans*-incompatible ligands). Thus replacement of the SnCl_3^- in the *trans* position is facilitated and leads to the penultimate intermediate *cis*- $\text{Pt}(\text{C}_2\text{H}_4)(\text{SnCl}_3)_2\text{Cl}_2^-$.

When the attack of ethylene occurs upon *trans*- $\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2$, the intermediate of the first stage is *trans*- $\text{Pt}(\text{C}_2\text{H}_4)(\text{SnCl}_3)_2\text{Cl}_2^-$ (path II). In such a case, the two strong π ligands SnCl_3^- probably labilize each other and replacement of either one of them by olefin will be feasible. Then from *trans*- $\text{Pt}(\text{C}_2\text{H}_4)(\text{SnCl}_3)_2\text{Cl}_2^-$, the SnCl_3^- group will be easily displaced by Cl^- in the subsequent equilibrium leading to Zeise's salt.

Finally data in Table III clearly indicate that the half-time of ethylene absorption on the Pt-Sn system greatly decreases as the hydrochloric acid concentration increases. This may be due both to the effect of Cl^- on the equilibria outlined in Figure 1 and to the increased

concentration of SnCl^+ species (see eq 4) which can successfully compete as an electrophile with the ethylene for coordination sites on the metal complex through interaction with the filled, originally $5d_{z^2}$ platinum orbital. The increased concentration of SnCl_2 (see eq 4) may also be responsible for the observed effect since SnCl_2 can compete as nucleophile for the originally $6p_z$

platinum orbital. In fact there is considerable evidence that in some rhodium(I) four-coordinated complexes the attack of the olefin upon metal is mainly nucleophilic.³⁷

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Axial Ligation of Copper(II) Bis(*t*-butylacetoacetate) by Pyridine Donors. Thermodynamics and Solvent Effects

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Equilibrium constants and enthalpies for 1:1 adduct formation of copper(II) bis(*t*-butylacetoacetate), $\text{Cu}(t\text{-BuOac})_2$, with a series of pyridine donors have been measured in cyclohexane by calorimetric and spectrophotometric methods. Agreement between the two methods was found to be good. The equilibrium constants and enthalpies were found to correlate linearly with the corresponding shift in methanol OH stretching frequency, except for 2-methylpyridine, where a steric effect is proposed. Calorimetric studies in benzene, carbon tetrachloride, and chloroform have shown the thermodynamics of adduct formation with pyridine to be solvent dependent. Equilibrium constants and enthalpies decreased with change in solvent in the order $\text{C}_6\text{H}_{12} > \text{C}_6\text{H}_6 > \text{CCl}_4 > \text{CHCl}_3$. The epr parameters for $\text{Cu}(t\text{-BuOac})_2$ are solvent dependent. The $\langle a \rangle$ values increase in the order $\text{C}_6\text{H}_{12} < \text{CCl}_4 < \text{C}_6\text{H}_6 < \text{CHCl}_3$, which is contrasted with the large decrease in $\langle a \rangle$ observed in donor solvents. Infrared spectra of copper(II) bis(trifluoroacetylacetonate) and copper(II) bis(trifluoroacetylacetonate)-pyridine show that upon adduct formation the pyridine ring vibrational frequencies increase and that the metal-oxygen stretching frequency decreases.

Introduction

Neutral bis chelates of Cu(II) are Lewis acceptors which have the ability to coordinate further with donor molecules to form mono and bis adducts.²⁻⁷ Adduct formation is accompanied by large changes in electronic and magnetic properties.⁷⁻¹³ An understanding of these changes can provide a basis for understanding the electronic structures and chemical bonding in metal chelates as well as revealing general properties of donor-acceptor complexes. The interpretation of metal chelate behavior in solution must begin with the characterization of the nature of the species in solution which can in part be accomplished by studying the thermodynamics of adduct formation. Thermodynamic studies are also a valuable means for locating and

identifying regular changes in properties of the donor and acceptor fragments on adduct formation which are reflected by measurements such as the electronic spectra.

We recently reported a study of the formation and properties of five-coordinate adducts of copper(II) bis(*t*-butylacetoacetate) with a series of 4-alkylpyridines.⁷ Evidence was presented that the observed electronic spectral and magnetic changes varied regularly with the thermodynamics of adduct formation.

This paper reports on a more complete study of the thermodynamics of 1:1 adduct formation of copper(II) bis(*t*-butylacetoacetate), $\text{Cu}(t\text{-BuOac})_2$, with a series of alkyl-substituted pyridine donors in cyclohexane solvent. Thermodynamic data from both calorimetric and spectrophotometric studies are presented and compared. Thermodynamic studies of the $\text{Cu}(t\text{-BuOac})_2$ -py system in the series of solvents C_6H_{12} , CCl_4 , C_6H_6 , and HCCl_3 are reported and discussed in terms of the solvent interactions with pyridine, $\text{Cu}(t\text{-BuOac})_2$, and the adduct. Heats of solution of pyridine are used as a means of reflecting the pyridine-solvent interactions. Solvent effects on the $\text{Cu}(t\text{-BuOac})_2$ epr parameters $\langle a \rangle$ and $\langle g \rangle$ are taken as an indication of the solvent-Cu(*t*-BuOac)₂ interactions. Vibrational spectra for $\text{Cu}(\text{TFAcac})_2$ and $\text{Cu}(\text{TFAcac})_2 \cdot \text{py}$ and the regular change in d-d spectral intensity for $\text{Cu}(t\text{-BuOac})_2 \cdot \text{B}$ with the donor ability of B are used to

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