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Role of Cationic Trans Intermediates in Promoting the Insertion of Unsaturated Hydrocarbons into Platinum-Hydrogen and Platinum-Carbon Bonds.

A Study of the Insertion Reaction Involving Compounds of the

Type $\text{trans-}[\text{PtMe}(\eta^2\text{-C}_3\text{H}_4)(\text{PMe}_2\text{Ph})_2]^+\text{Z}^-$

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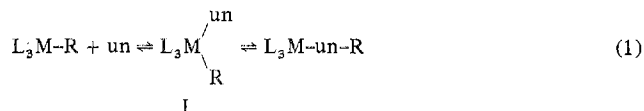
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The insertion reaction of methylplatinum complexes $\text{trans-}[\text{PtMe}(\pi\text{-allene})(\text{PMe}_2\text{Ph})_2]^+\text{Z}^-$, to $\text{cis-}[\text{Pt}(\pi\text{-2-methylallyl})(\text{PMe}_2\text{Ph})_2]^+\text{Z}^-$, where $\text{Z}^- = \text{BF}_4^-, \text{PF}_6^-, \text{and SbF}_6^-$, has been studied in the temperature range 0–40° in CH_2Cl_2 , CD_2Cl_2 , CHCl_3 , and CDCl_3 . The reaction is first order in $\text{trans-}[\text{PtMe}(\pi\text{-allene})(\text{PMe}_2\text{Ph})_2]^+\text{Z}^-$ and shows an anion dependence in the thermodynamic properties (ΔH^\ddagger) of the activated complex: $\text{SbF}_6^- \sim \text{BF}_4^- > \text{PF}_6^-$. The addition of the neutral donor or anionic ligands I^- , NO_3^- , pyridine, CO, and PPh_3 leads to displacement of the π -bonded allene ligand: no insertion occurs. Addition of allene leads to rapid exchange of free and coordinated allene on the nmr time scale and suppresses the overall rate of insertion. General schemes for Pt-H and Pt-C insertion reactions based on (i) five-coordinate intermediates and (ii) four-coordinate intermediates are discussed. The importance of coordination to an electrophilic metal center is stressed if Pt-H and Pt-C insertion reactions are to be favored.

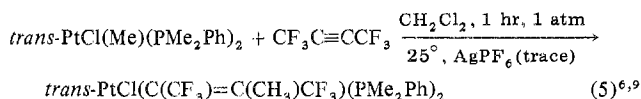
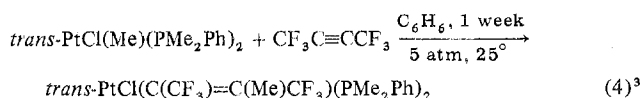
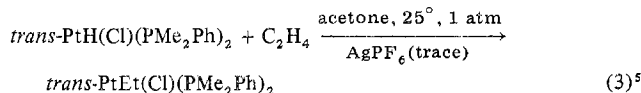
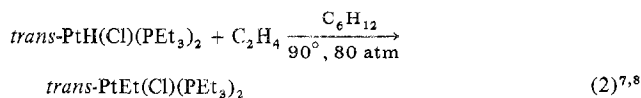
Initial coordination of an unsaturated molecule followed by insertion into a metal-hydrogen or metal-carbon bond is believed¹ to form the basis for most metal-catalyzed reactions of unsaturated hydrocarbons. In the field of d^8 transition metal chemistry five-coordinate π complexes of type I have often been

invoked² as the reactive intermediates in insertion reactions of type (1). Consistent with this proposal was the finding by Clark and Puddephatt³ that hexafluorobut-2-yne, $\text{CF}_3\text{C}\equiv\text{CCF}_3$, reacted with $\text{trans-PtCl}(\text{Me})(\text{AsMe}_2\text{Ph})_2$ to give the insertion product $\text{trans-PtCl}(\text{CCF}_3=\text{C}(\text{CH}_3)\text{CF}_3)(\text{AsMe}_2\text{Ph})_2$



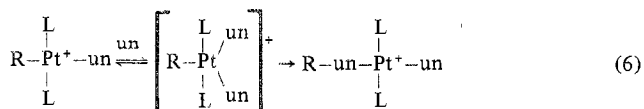
by way of a five-coordinate π complex of type I. In this study the authors were able to isolate and fully characterize⁴ the five-coordinate intermediate $PtCl(Me)(CF_3C\equiv CCF_3)-(AsMe_2Ph)_2$.

More recently a cationic mechanism has been found to facilitate the insertion of unsaturated hydrocarbons into Pt-H⁵ and Pt-C⁶ bonds. This is shown by reactions 2-5.



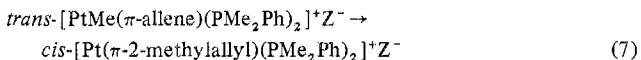
A curious feature of the cationic mechanism is that trans intermediates have often been detected or even isolated, e.g., $trans-[PtH(C_2H_4)L_2]^+$ ^{5,10} and $trans-[PtMe(un)L_2]^+$ ⁶.

While formation of trans intermediates of the above type can be understood in terms of the high trans influence¹¹ of groups such as H⁻ and CH₃⁻, it is not clear how this geometry can promote a reaction between trans ligands. A plausible rationale for the importance of trans intermediates is that the coordination of a strongly π -bonded ligand such as an olefin or acetylene promotes the formation of a five-coordinate π complex of type I involving the addition of another mole of the unsaturated hydrocarbon,¹² e.g., as shown in (6).



This model is consistent with the trans-effect theory in which strongly π -accepting ligands are believed to stabilize five-coordinate intermediates of platinum(II) and thus lead to facile substitution processes.¹³ This model allows insertion to proceed via a simple ligand migration involving mutually cis ligands and is, moreover, consistent with the 16-18-electron rule.¹⁴

In order to investigate the role of intermediates of the type $trans-PtR(un)L_2^+$ in organoplatinum insertion reactions we have undertaken a study of the methyl-platinum insertion reaction 7.¹⁵ This reaction has several attractive features:



it is quantitative and irreversible and it occurs at a convenient rate at or around room temperature. Furthermore, both the starting material and the product are air-stable crystalline solids. This paper describes our studies of this and related reactions. In the light of these studies the role of trans cationic intermediates in promoting Pt-H and Pt-C insertion reactions is discussed.

Experimental Section

Preparation of π -Allene Cations. The preparation of $trans-[PtMe(\text{allene})(PMe_2Ph)_2]^+PF_6^-$ has been described previously.¹⁵ The BF_4^- and SbF_6^- salts were prepared in an analogous manner involving $AgBF_4$ and $AgSbF_6$ as chloride ion abstractors. Analytical and other

Table I. Analytical and Characterization Data

Compd	% carbon		% hydrogen		Mp, ^a °C
	Calculated	Found	Calculated	Found	
<i>trans</i> -PtCH ₃ (C ₃ H ₄)-(PMe ₂ Ph) ₂ ⁺ BF ₄ ⁻	39.16	38.94	4.73	4.62	85, 130
<i>trans</i> -PtCH ₃ (C ₃ H ₄)-(PMe ₂ Ph) ₂ ⁺ PF ₆ ⁻	35.77	35.50	4.36	4.65	98, 152
<i>trans</i> -PtCH ₃ (C ₃ H ₄)-(PMe ₂ Ph) ₂ ⁺ SbF ₆ ⁻	31.52	31.81	3.67	3.79	93, 100
<i>cis</i> -Pt(η^3 -C ₄ H ₇)-(PMe ₂ Ph) ₂ ⁺ BF ₄ ⁻	39.16	39.20	4.73	4.65	131
<i>cis</i> -Pt(η^3 -C ₄ H ₇)-(PMe ₂ Ph) ₂ ⁺ PF ₆ ⁻	35.77	35.68	4.36	4.56	152
<i>cis</i> -Pt(η^3 -C ₄ H ₇)-(PMe ₂ Ph) ₂ ⁺ SbF ₆ ⁻	31.52	31.38	3.67	3.72	102

^a See discussion in text.

characterization data are given in Table I.

Kinetic Assays. When dissolved in chloroform or dichloromethane at room temperature $trans-[PtMe(\eta^2-C_3H_4)(PMe_2Ph)_2]^+Z^-$ readily undergoes insertion leading to formation of $cis-[Pt(\eta^3-C_4H_7)(PMe_2Ph)_2]^+Z^-$. Experiments were performed to determine the rate of insertion of allene into the Pt-CH₃ bond as a function of Z⁻, solvent, various substrates, and temperature.

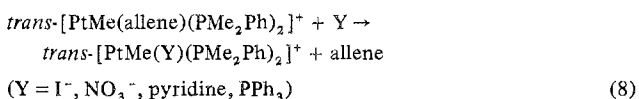
The rate of reaction was followed by measuring the concentration of $trans-[PtMe(\eta^2-C_3H_4)(PMe_2Ph)_2]^+$ as a function of time. This concentration at time *t* was determined from the ¹H nmr spectra of the Pt-CH₃ group. During the course of the insertion reaction this signal does not lose its coupling to ¹⁹⁵Pt and ³¹P, nor does its resolution change. Because the amplitude of this signal may fluctuate with time due to factors attributable to the spectrometer, an internal reference of hexamethyldisiloxane (HMDS) was introduced into the reaction solution.¹⁶ Thus the concentration of $trans-[PtMe(\eta^2-C_3H_4)(PMe_2Ph)_2]^+$ is defined by the following ratio: (intensity of Pt-CH₃ resonance)/(intensity of HMDS resonance). In these experiments [Pt-CH₃]/[HMDS] is defined as (height of primary Pt-CH₃ signal)/(height of HMDS signal). This is justifiable for two reasons: (i) the relative intensities of the nine peaks of the Pt-CH₃ group due to coupling to ¹⁹⁵Pt and ³¹P are constant and (ii) the signals are triangular insofar as experimental measurements can be made. The width of the base of both the Pt-CH₃ and HMDS signals does not change significantly during 2 half-lives of the reaction.

In a standard sample preparation 0.1 mmol of $trans-[PtMe(\eta^2-C_3H_4)(PMe_2Ph)_2]^+Z^-$ was placed in a 5-mm thin-walled nmr tube; this was dissolved in 0.25 ml of solvent and 1 μ l of HMDS was added as an internal calibrant.

For kinetic assays above 29° the samples were prepared in an ice bath to prevent insertion from occurring and were then placed into the variable-temperature probe of a Varian A-60 nmr spectrometer. The temperature was determined using the temperature-dependent shift of ethylene glycol. Temperatures were maintained with a variable-temperature control unit equipped with a thermocouple and digital read-out. Spectra of the Pt-CH₃ and HMDS resonances were recorded every 1-5 min during the course of the reaction for a length of time in excess of 1 half-life.

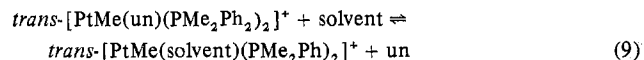
At temperatures below 29° samples were prepared in a methanol-Dry Ice bath and placed into the nmr probe at -20°. Seven to fourteen spectra of the Pt-CH₃ and HMDS resonances were recorded. The Pt-CH₃:HMDS peak height ratios were averaged; this average defined the concentration of $trans-[PtMe(\eta^2-C_3H_4)(PMe_2Ph)_2]^+$ at *t* = 0. The samples were then placed in a constant-temperature bath at the appropriate temperature for the kinetic assay. At various times during the course of the reaction the samples were removed from the constant-temperature bath, quenched in a methanol-Dry Ice bath, and spectroscopically analyzed as above. Assays were performed for more than 1 half-life and in some cases up to 4 half-lives. In all cases the reaction was found to be clean and irreversible.

Noninsertion Reactions. The addition of a 1 molar equiv of I⁻, NO₃⁻ (added as (*n*-C₄H₉)₄N⁺ salts), CO, pyridine, or PPh₃ led to displacement of allene according to reaction 8. No insertion occurred.



When a standard preparation of *trans*-[PtMe(η^2 -C₃H₄)(PMe₂Ph)₂]⁺Z⁻ was sealed in an nmr tube under an atmosphere of allene (0.1–0.5 mmol), insertion was suppressed. At 30° for an allene to platinum ratio of 5:1 the half-life was *ca.* 1 week; *cf.* $t_{1/2} \approx 30$ min in the absence of added allene. Addition of allene in these reactions led to the formation of a polymer—probably polyallene. Production of polyallene has been noted¹⁷ with the rhodium(I) compounds *trans*-RhX(C₃H₄)(PPh₃)₂ where X = Cl, Br, or I.

Miscellaneous Reactions. Addition of 1 molar equiv of THF, dioxane, or acetone, known⁸ to compete for coordination to the methylplatinum cation according to eq 9, was found to have no



(un = C₂H₄, MeC≡CMe; solvent = acetone, THF)

observable effect on the rate of the insertion reaction 7, nor was any allene displacement observed. Addition of 1 molar equiv of Z⁻, added in the form of product, *i.e.*, *cis*-[Pt(η^3 -C₄H₇)(PMe₂Ph)₂]⁺Z⁻, had no effect on the rate of insertion.

Results and Discussion

Characterization of η^2 -Allene and η^3 -Allyl Cations. Analytical and other characterization data are shown in Table I. Of note is the observation that the η^2 -allene compounds melt, crystallize, and then remelt at temperatures similar to the melting points of their respective η^3 -allyl (insertion) products. By placing *trans*-[PtMe(η^2 -C₃H₄)(PMe₂Ph)₂]⁺BF₄⁻ in an nmr tube, heating it to its first melt at 86°, and subsequently recording a low-temperature nmr spectrum in CH₂Cl₂, it was shown that an apparently quantitative insertion does indeed occur on the initial melting.

Previously¹⁵ reported nmr data for *trans*-[PtMe(η^2 -C₃H₄)(PMe₂Ph)₂]⁺PF₆⁻ are applicable to the BF₄⁻ and SbF₆⁻ salts except in one facet. The variable-temperature ¹H nmr spectra of the phosphine methyl resonances are anion dependent. Coalescence temperatures for the processes PMe(Me')Ph → PMe₂Ph are -10° (SbF₆⁻), -30° (PF₆⁻), and *ca.* -60° (BF₄⁻). It is tempting to correlate the coalescence temperatures with the rate of the process equivalencing the phosphine methyl groups. However, the very small chemical shift difference between the phosphine methyl proton resonances in the low-temperature limiting spectra also appears to be temperature dependent: $\Delta = 3$ Hz for SbF₆⁻, 2 Hz for PF₆⁻, and *ca.* 1 Hz for BF₄⁻. A clear correlation between rate and anion is not warranted in view of the uncertainties in the spectral data.

Previously¹⁵ the process leading to the apparent plane of symmetry about the MePt₂ moiety was considered to involve rotation about the Pt- η^2 -C₃H₄ bond; *cf.*¹⁵ rotation about the Pt-olefin bond in *trans*-[PtMe(propene)(PMe₂Ph)₂]⁺. However, we now find evidence that alternative explanations must be considered. At 0° the ¹H nmr spectrum of the π -allene cation shows the inequivalence of the allene methylene groups, consistent with coordination to Pt *via* only one of the olefinic double bonds. As the temperature is raised, the allene methylene resonances initially lose their distinct couplings (to ¹⁹⁵Pt, ³¹P, and ¹H) and finally, at 40°, collapse into the base line. Although insertion is occurring rapidly at 40°, the loss of the allene signal cannot be attributed to complete insertion since the methylplatinum and phosphinemethyl resonances retain their triplet patterns. The loss of the allene proton resonances may be attributed to either a "hopping" of the allene-platinum bond, as first noted by Ben-Shoshan and Pettit¹⁸ for (Me₂C=C=CMe₂)Fe(CO)₄, or a rapid dissociative-associative process involving the platinum-allene moiety. In the case of (Me₂C=C=CMe₂)Fe(CO)₄ the authors were able to distinguish between these processes since (i) the rate of the process equivalencing of the allene methylene resonances was independent of added allene and (ii) free and coordinated allene did not exchange on the nmr time scale.

Addition of allene to *trans*-[PtMe(η^2 -C₃H₄)(PMe₂Ph)₂]⁺ leads to rapid exchange of free and coordinated allene. This exchange is only frozen out on the nmr time scale below -60°. The differences between (allene)Fe(CO)₄ and methylplatinum allene cations are not surprising in view of the lability of four-coordinate square-planar platinum(II) complexes toward substitution reactions.¹³ Thus the process leading to the equivalencing of the phosphine methyl groups could involve (i) Pt- η^2 -allene bond rotation, (ii) Pt- η^2 -allene bond "hopping,"¹⁸ or (iii) Pt- η^2 -allene bond dissociation followed by association. Unfortunately the kinetics and spectroscopic properties of the present system do not lend themselves to a ready distinction between these processes.

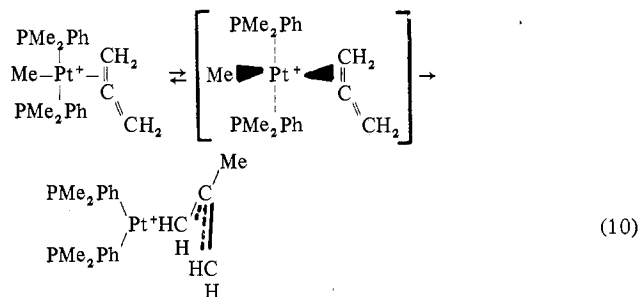
Analysis of Kinetic Data. The experimental data conformed to the interpretation that reaction 7 is at least pseudo first order in the concentration of *trans*-[PtMe(η^2 -C₃H₄)(PMe₂Ph)₂]⁺Z⁻. A plot of ln [Pt-CH₃]/[HMDS] vs. time gave a straight line of slope -*k*(*T*). Standard deviations were calculated from a least-squares fit to a line $Y = A + BX$. Values of *k*(*T*) calculated in this manner are given in Table II. The energy of activation (*E*_a) of the insertion reaction was calculated using the Arrhenius form for the temperature dependence of rate constants

$$k(T) = Ae^{(E_a/RT)}$$

The thermodynamic properties of the activated complex were calculated using absolute rate theory.¹⁹ These are given in Table III.

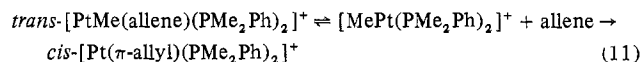
Mechanistic Implications of Kinetic Data. The observation of first-order kinetics for the insertion reaction 7 rules out the possibility that the reaction is bimolecular, involving the participation of two platinum complexes in the activated state. The following mechanisms are consistent with the observation of first-order kinetics.

(1) Insertion may proceed *via* a tetrahedral transition state as shown in (10). This clearly brings the methyl and allene

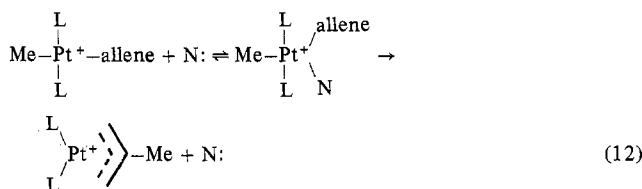


groups into a *cis* configuration.

(2) Insertion may occur by a dissociative process in which platinum-allene bond rupture occurs initially to give a three-coordinate methylplatinum cation. Subsequent association may then occur and lead to a geometry favorable to insertion. This is represented by (11).



(3) Insertion may proceed *via* a five-coordinate transition state as indicated by reaction (12). No specific geometry is



ascribed to the five-coordinate transition state except in that it brings the methyl and allene groups into a *cis* configuration. The fifth ligand, N, may be (i) the anion, (ii) the solvent, or

Table II. Kinetic Data

Amt of <i>trans</i> -PtCH ₃ ⁻ (C ₂ H ₅)(PMe ₂ Ph) ₂ ⁻ Z ⁻ , mg	Substrate	Solvent	Temp, °C	<i>k</i> _{obsd} , sec ⁻¹
Z = BF ₄ ⁻				
61	None	CH ₂ Cl ₂	38.9	(2.13 ± 0.25) × 10 ⁻⁴
61	None	CH ₂ Cl ₂	36.7	(2.54 ± 0.19) × 10 ⁻⁴
61	61 mg of allyl ^a	CH ₂ Cl ₂	34.4	(1.26 ± 0.06) × 10 ⁻⁴
122	None	CH ₂ Cl ₂	34.1	(1.27 ± 0.07) × 10 ⁻⁴
61	61 mg of allyl ^a	CH ₂ Cl ₂	32.9	(1.12 ± 0.08) × 10 ⁻⁴
61	None	CH ₂ Cl ₂	29.5	(1.18 ± 0.09) × 10 ⁻⁴
61	None	CH ₂ Cl ₂	29.4	(4.90 ± 0.16) × 10 ⁻⁵
61	None	CH ₂ Cl ₂	22.7	(2.37 ± 0.18) × 10 ⁻⁵
61	None	CH ₂ Cl ₂	20.3	(1.87 ± 0.16) × 10 ⁻⁵
61	None	CH ₂ Cl ₂	13.5	(4.81 ± 0.52) × 10 ⁻⁶
61	None	CH ₂ Cl ₂	4.4	(1.09 ± 0.09) × 10 ⁻⁶
61	None	CD ₂ Cl ₂	29.5	(3.03 ± 0.16) × 10 ⁻⁴
61	None	CD ₂ Cl ₂	22.7	(5.34 ± 0.44) × 10 ⁻⁵
61	None	CD ₂ Cl ₂	20.0	(1.38 ± 0.06) × 10 ⁻⁵
61	None	CD ₂ Cl ₂	14.4	(9.87 ± 0.64) × 10 ⁻⁶
61	None	CD ₂ Cl ₂	10.3	(2.96 ± 0.14) × 10 ⁻⁵
61	None	CD ₂ Cl ₂	4.4	(2.20 ± 0.15) × 10 ⁻⁶
61	None	CHCl ₃	29.5	(6.39 ± 0.81) × 10 ⁻⁵
61	None	CHCl ₃	24.0	(2.10 ± 0.14) × 10 ⁻⁵
61	None	CHCl ₃	20.0	(1.22 ± 0.06) × 10 ⁻⁵
61	None	CHCl ₃	14.4	(6.84 ± 0.27) × 10 ⁻⁶
61	None	CHCl ₃	4.4	(1.50 ± 0.15) × 10 ⁻⁶
61	None	CDCl ₃	20.0	(1.21 ± 0.06) × 10 ⁻⁵
Z = PF ₆ ⁻				
69	None	CH ₂ Cl ₂	29.5	(3.43 ± 0.16) × 10 ⁻⁵
69	None	CH ₂ Cl ₂	25.1	(1.41 ± 0.08) × 10 ⁻⁵
69	None	CH ₂ Cl ₂	24.0	(1.49 ± 0.10) × 10 ⁻⁵
69	None	CH ₂ Cl ₂	22.5	(1.41 ± 0.15) × 10 ⁻⁵
69	None	CH ₂ Cl ₂	20.0	(8.27 ± 0.37) × 10 ⁻⁶
69	None	CH ₂ Cl ₂	15.0	(5.11 ± 0.48) × 10 ⁻⁶
69	None	CH ₂ Cl ₂	14.0	(6.43 ± 0.52) × 10 ⁻⁶
69	None	CH ₂ Cl ₂	9.9	(3.15 ± 0.23) × 10 ⁻⁶
69	None	CH ₂ Cl ₂	4.4	(1.48 ± 0.09) × 10 ⁻⁶
Z = SbF ₆ ⁻				
76	None	CH ₂ Cl ₂	38.5	(2.41 ± 0.34) × 10 ⁻⁴
76	76 mg allyl ^a	CH ₂ Cl ₂	34.5	(1.23 ± 0.20) × 10 ⁻⁴
76	None	CH ₂ Cl ₂	29.5	(3.59 ± 0.48) × 10 ⁻⁵
76	None	CH ₂ Cl ₂	25.1	(2.43 ± 0.09) × 10 ⁻⁵
76	None	CH ₂ Cl ₂	22.5	(1.50 ± 0.14) × 10 ⁻⁵
76	None	CH ₂ Cl ₂	15.0	(4.99 ± 0.45) × 10 ⁻⁶
76	None	CH ₂ Cl ₂	9.9	(1.59 ± 0.14) × 10 ⁻⁶

^a *cis*-Pt(η³-C₄H₇)(PMe₂Ph)₂Z.

Table III. Thermodynamic Data for Eq 7

Z ⁻	Solvent	<i>E</i> _a , kcal/mol	Δ <i>H</i> [‡] , kcal/mol	Δ <i>S</i> [‡] (298°), eu	Δ <i>G</i> [‡] , kcal/mol
SbF ₆ ⁻	CH ₂ Cl ₂	29.6 ± 1.4	29.0 ± 1.4	4.6 ± 1.8	27.7 ± 1.7
PF ₆ ⁻	CH ₂ Cl ₂	19.3 ± 1.2	18.7 ± 1.2	-5.6 ± 1.0	20.3 ± 1.5
BF ₄ ⁻	CH ₂ Cl ₂	27.5 ± 1.2	26.9 ± 1.2	3.0 ± 1.1	26.0 ± 1.6
BF ₄ ⁻	CHCl ₃	23.9 ± 1.5	23.3 ± 1.5	-0.2 ± 1.3	23.3 ± 1.9
BF ₄ ⁻	CD ₂ Cl ₂	26.5 ± 7.6	25.9 ± 7.6	2.6 ± 6.5	25.7 ± 9.5

(iii) another substrate. Reactions 10–12 do not, however, accommodate the fact that *trans*-[PtMe(η²-C₃H₄)(PMe₂Ph)₂]+Z⁻ at ca. 0.5 *M* concentrations in solvents of low dielectric constant, such as CHCl₃ and CH₂Cl₂, will be severely aggregated.

Anion Dependence. The enthalpies of activation follow the order SbF₆⁻ ~ BF₄⁻ > PF₆⁻. It is of interest to note that while BF₄⁻ is a better nucleophile and coordinating group than PF₆⁻,²¹ it is PF₆⁻ that results in the lower enthalpy of activation. Moreover BF₄⁻ and SbF₆⁻ show comparable enthalpies of activation. This suggests that the size of the anion is important: the ideal participating anion requires a balance between size and charge density. Some rate dependence on the nature of the anion would be expected even if the sole role of the anion were "to get in the way to some extent."²² The observations (i) Δ*S*[‡] ≈ 0 and (ii) that addition of Z⁻ (added as *cis*-[Pt(η³-C₄H₇)(PMe₂Ph)₂]+Z⁻) has no apparent effect on the rate

of insertion argue against direct anion participation in a five-coordinate transition state as indicated by (12), where N = Z⁻.

Solvent Dependence. Solvent-dependent studies for (7) are limited by two factors. First, the cationic complexes are not soluble in nonpolar solvents such as benzene and hexane. Second, in polar solvents which may act as Lewis bases, e.g., THF and acetone, reaction 9 may successfully compete with (7).

The differences in the rates of insertion of the BF₄⁻ complex in dichloromethane and chloroform are small. The differences in the enthalpies of activation might be explained in terms of enthalpies of solvation. Of concern, however, are the results we obtained for the kinetic assays in CD₂Cl₂. Kinetic assays of the *trans*-[PtMe(η²-C₃H₄)(PMe₂Ph)₂]+BF₄⁻ insertion reaction run simultaneously (and under identical conditions) in CH₂Cl₂ and CD₂Cl₂ resulted in a *k*(*T*)(CD₂Cl₂)/*k*(*T*)(CH₂Cl₂) ratio of 2. This suggests that the deuterated solvent promotes the reaction. However, the dielectric constant, dipole moment, and size of CD₂Cl₂ should be insignificantly different from that of CH₂Cl₂.²³ The only possible difference between the two solvents could be their ability to hydrogen bond to the anions. However, variations of this ratio (*k*(CD₂Cl₂)/*k*(CH₂Cl₂)) were so large that the possibility that impurities in the CD₂Cl₂ solvent were affecting our results must be considered.²³ The increase in the rate of reaction in CD₂Cl₂

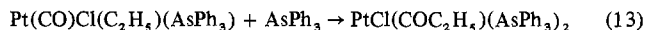
is rendered more suspect by the observation that CDCl_3 and CHCl_3 show identical rates of reaction. Our kinetic results in CD_2Cl_2 remain to be explained.

The fact that insertion reactions 7 have entropies of activation near zero argues against any direct solvent participation in the activated complex, *i.e.*, for (12) where $N = \text{solvent}$.

Related Studies. At the present there do not appear to be any quantitative studies of the insertion of olefins into metal-alkyl bonds with which we can compare our results. The most intensively studied insertion reactions are those involving a metal-alkyl and a coordinated carbonyl ligand, *e.g.*, $\text{CH}_3\text{Mn}(\text{CO})_5$,²⁵⁻²⁷ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$,²⁸ $\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3\text{CH}_3$,²⁷⁻³⁰ and $\text{Ir}(\text{CO})_2\text{Cl}_2(\text{L})\text{R}$ ^{31,31} where $\text{L} = \text{AsPh}_3$ or AsMe_2Ph and $\text{R} = \text{CH}_3$ and C_2H_5 .

Unlike insertion reaction 7, these carbonyl insertion reactions are two-step reactions involving (i) insertion resulting in a decrease in the effective coordination number of the metal and (ii) reoccupation of the vacant site by an incoming nucleophile, L . Thus a critical distinction between (7) and the above metal-carbonyl insertion reactions (aside from the intrinsic difference between allene and carbonyl ligands) involves the coordination number and stereochemistry of metal.

Glyde and Mawby³³ have studied carbonyl insertion reaction 13 which involves a square-planar platinum(II) complex. This



reaction was found to be first order in $\text{Pt}(\text{CO})\text{Cl}(\text{C}_2\text{H}_5)(\text{AsPh}_3)$. Furthermore the authors found no evidence for the involvement of either solvent or nucleophile in the rate-determining step. The latter finding is somewhat surprising in view of the availability of two vacant coordination sites and the general acceptance of five-coordinate intermediates in platinum(II) substitution reactions.¹³

Of particular interest is the stereochemical pathway of reaction 13. The stereochemistry of $\text{Pt}(\text{CO})\text{Cl}(\text{C}_2\text{H}_5)\text{AsPh}_3$ is uncertain.³³ In a further study of this and related compounds the authors assume that the ethyl and carbonyl groups must be mutually *cis* for insertion to occur and thus assume that the ground state of the complex must also have the *cis* configuration.³⁴ Methylplatinum(II) insertion reaction 7 demonstrates that this assumption of ground-state geometry does not necessarily follow.

In the preceding carbonyl insertion reactions it has been generally suggested that the major part of the energy of activation involves rupture of the metal-alkyl bond. This stems from the discovery that the insertion reaction involving $\text{CH}_3\text{Mn}(\text{CO})_5$ proceeds *via* methyl migration.³⁴ However, unlike the case for the preceding carbonyl insertion reactions, the energy of activation for (7) may arise in bringing the methyl and allene groups into a *cis* configuration. (No specific geometry is implied by the term *cis* other than one in which the reacting groups are adjacent.) The dependence of ΔH^\ddagger on anion supports this view. However, it is of note that the carbonyl insertion reactions referred to above, involving reacting groups that are mutually *cis* in the ground state, show enthalpies of activation similar to those for (7).

Conclusions

(1) The addition of anionic ligands I^- and NO_3^- and neutral donor ligands PPh_3 , CO , and pyridine to *trans*- $[\text{PtMe}(\eta^3\text{-C}_3\text{H}_4)(\text{PMe}_2\text{Ph})_2]^+\text{Z}^-$ leads to complete displacement of allene; no insertion occurs. (2) The addition of allene leads to rapid exchange of free and coordinated allene and suppresses the rate of insertion. (3) The addition of Z^- , added as *cis*- $[\text{Pt}(\eta^3\text{-C}_4\text{H}_7)(\text{PMe}_2\text{Ph})_2]^+\text{Z}^-$, has no effect on the rate of insertion. (4) $\Delta S^\ddagger \approx 0$. These four observations argue strongly against a five-coordinate transition state as implied by reaction 12 where $N = \text{I}^-$, NO_3^- , PPh_3 , CO , pyridine, Z^- or solvent. If the insertion reaction is counterion assisted, it must proceed

through a tight ion pair. Consequently it is not clear whether we should describe the transition state as a distorted square-planar four-coordinate species or a five-coordinate species in which a rehybridization of platinum orbitals has occurred to accommodate a pair of electrons from the counterion BF_4^- , PF_6^- , or SbF_6^- . In any event the activated species is electron deficient having more 16-electron character than 18-electron character since BF_4^- , PF_6^- , and SbF_6^- are not good two electron donor ligands.

We conclude that the role of cationic intermediates in promoting Pt-H and Pt-C insertion reactions is primarily one of activating the unsaturated hydrocarbon. Cationic species $[\text{PtR}(\text{solvent})\text{L}_2]^+\text{Z}^-$ promote the coordination of unsaturated hydrocarbons; activation of the coordinated unsaturated hydrocarbon by interaction with an electrophilic metal center may then lead to a variety of products.⁶ This is in contrast to the coordination of unsaturated hydrocarbons to electron-rich four-coordinate platinum complexes which lead to five-coordinate π complexes which are inert to insertion reactions. Examples of these include the pyrazolylborate complexes $\text{HB}(\text{pz})_3\text{PtMe}(\text{un})$ where *un* = allenes, acetylenes, and olefins.³⁷ As a further general example of the importance of electronic factors in governing the reactivity of π -complexed unsaturated hydrocarbons, we note the recent isolation of hydridotantalum(III) π complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{TaH}(\text{un})$ where *un* = C_2H_4 ³⁸ and $\text{C}_3\text{H}_7\text{C}\equiv\text{CC}_3\text{H}_7$.³⁹ Here all the ligands occupy *cis* coordination sites on the metal and yet insertion occurs only under forcing conditions. Finally we should note that electronic factors in the unsaturated substrate are also important. For example, insertion of acetylenes into Pt-CH₃ bonds has only been observed⁶ for activated acetylenes (*i.e.*, those bearing electron-withdrawing substituents). By contrast the insertion of simple alkenes and alkynes into Pt-H occurs much more readily. This may, however, merely reflect the different thermodynamic considerations associated with Pt-H and Pt-C systems.

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Registry No. *trans*- $\text{PtCH}_3(\text{C}_3\text{H}_4)(\text{PMe}_2\text{Ph})_2^+\text{BF}_4^-$, 54382-39-7; *trans*- $\text{PtCH}_3(\text{C}_3\text{H}_4)(\text{PMe}_2\text{Ph})_2^+\text{PF}_6^-$, 38466-81-8; *trans*- $\text{PtCH}_3(\text{C}_3\text{H}_4)(\text{PMe}_2\text{Ph})_2^+\text{SbF}_6^-$, 54382-38-6; *cis*- $\text{Pt}(\eta^3\text{-C}_4\text{H}_7)(\text{PMe}_2\text{Ph})_2^+\text{BF}_4^-$, 54340-41-9; *cis*- $\text{Pt}(\eta^3\text{-C}_4\text{H}_7)(\text{PMe}_2\text{Ph})_2^+\text{PF}_6^-$, 38466-82-9; *cis*- $\text{Pt}(\eta^3\text{-C}_4\text{H}_7)(\text{PMe}_2\text{Ph})_2^+\text{SbF}_6^-$, 54340-42-0.

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Synthesis and Characterization of Transition Metal Complexes Containing a Pentadentate Macrocyclic Ligand

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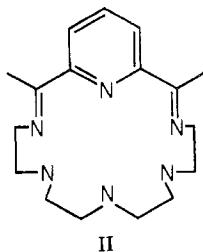
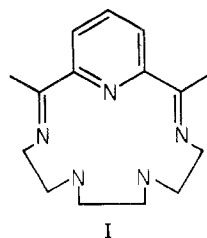
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The transition metal complexes (Fe(III), Co(III), Ni(II), and Cu(II)) with the pentadentate macrocyclic ligand 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene (abbreviated as pyaneN₅), have been prepared and characterized by elemental analyses and by spectral, magnetic, conductance, and electrochemical measurements. In the cases of the Ni(II) and Co(III) complexes, the macrocycle is folded and one additional ligand is included in the coordination sphere to form six-coordinate complexes with approximate octahedral geometry: [M(pyaneN₅)X]ⁿ⁺ (M = Ni, X = I⁻, Br⁻, Cl⁻, NCS⁻, CH₃CN, NH₃, H₂O, n = 1 or 2; M = Co, X = I, Br, Cl, NCS, N₃, NO₂, and n = 2). The average ligand field strengths (Dq = 1124 cm⁻¹ for Ni(II) and 2520 cm⁻¹ for Co(III)) are typical of those observed for hexaamminenickel(II) and -cobalt(III) systems and indicate that complexation involves little or no steric strain. The Fe(III) complexes are seven-coordinate with one bidentate or two monodentate ligands included in the coordination sphere in addition to the pentadentate ring. Oxidative dehydrogenation of the Fe(II) complexes by reaction with oxygen introduces imine linkages into the macrocyclic ligands. The Cu(II) complex is a five-coordinate species.

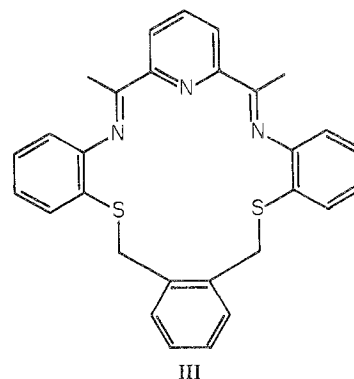
Introduction

The cyclic ligands 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (abbreviated pydieneN₅, structure I) and 2,16-dimethyl-3,6,9,12,15,21-hexaazabicyclo[15.3.1]heneicosa-1(21), 2-,15,17,19-pentaene (pydieneN₆, structure II) were the first



macrocyclic ligands to be prepared which contained more than four donor atoms.¹ Complexes of ligand I have been prepared with iron(III)² and manganese(II)³ and have been characterized as seven-coordinate, with the pentadentate macrocyclic ligand lying in a plane and with two monodentate anions occupying axial positions. This geometry has been confirmed by an X-ray crystal structure determination on the Fe^{III}-(pydieneN₅)(NCS)₂⁺ derivative.⁴ The planar nature of the pyridine ring and adjacent imines contributes to the tendency toward planar coordination by this ligand with ions having spherical electron distributions such as high-spin iron(III) and manganese(II). A second class of pentadentate macrocyclic

ligands has recently been prepared (structure III); however,



it also favors planar chelation and only its Zn(II) and Cd(II) complexes have been characterized.⁵ The study of pentadentate macrocyclic complexes of other transition metal ions, for example, those with electron distributions which favor an octahedral coordination geometry, requires a macrocyclic ligand which is flexible and large enough to fold in order to provide a nonplanar five-donor arrangement. Such a ligand and its metal complexes with several transition element ions (Fe(III), Co(III), Ni(II), Cu(II)) are reported here.

Results and Discussion

Preparation of the Ligand. The preparation of the new ligand 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene (structure IV, referred to as