Contribution from the Department of Chemistry,
The University of Western Ontario, London, Ontario, Canada

Insertion of Ethylene into a Cationic Hydrido(acetone)platinum(II) Complex. Kinetics and Mechanism

H. C. CLARK* and C. R. JABLONSKI

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A kinetic study of the reversible insertion of ethylene into the Pt-H bond of the cationic complex *trans*-PtH(acetone)-$(PEt_3)_2^+$ to give *trans*-$Pt(C_2H_5)(acetone)(PEt_3)_2^+$ under pseudo-first-order conditions in olefin gave a rate law of the form (a). k_{obsd} was found to depend on olefin concentration according to (b) over a 20-fold variation in $[C_2H_4]$. At high

$$-d[Pt\text{-}H]/dt = k_{obsd}[Pt\text{-}H] \qquad (a)$$

$$k_{obsd} = k'[C_2H_4]/(1 + K[C_2H_2]) \qquad (b)$$

ethylene concentrations the reaction becomes zero order in ethylene according to (b) with $k_{obsd}(\lim) = 15.0 \times 10^{-4}$ sec^{-1}. Equations a and b are consistent with a mechanism involving a rapid reversible substitution of acetone by ethylene to give *trans*-$PtH(C_2H_4)(PEt_3)_2^+$ followed by a slow, rate-determining insertion step. The intermediate *trans*-$PtH(C_2H_4)(PEt_3)_2^+$ has been observed at low temperature using pmr techniques.

Chatt and Shaw[1] have shown that ethylene reacts with the square-planar platinum(II)-hydrido complex *trans*-PtCl-$[P(C_2H_5)_3]_2$, I, to give the ethyl derivative, II, in 25% yield (see eq 1). The hydride complex I is a model for a large number of coordinatively unsaturated d^8 hydrido complexes thought to be active intermediates in catalytic hydrogenation.[2-4]

$$\underset{\text{I}}{trans\text{-}PtHCl(PEt_3)_2} + C_2H_4 \xrightarrow[40\ atm]{90°} \underset{\text{II}}{trans\text{-}PtEtCl(PEt_3)_2} \qquad (1)$$

Reaction 1 is reversible at higher temperature and it has been assumed[5,6] that both insertion and β elimination proceed through a five-coordinate hydrido(olefin) complex.

Although the proposition of a coordinatively saturated hydrido(olefin) complex is intuitively justified by a consideration of the associative nature of substitution reactions of square-planar platinum(II) complexes[7] and by the isolation of such an intermediate from the reaction of tetracyanoethylene with *trans*-$PtHCN(PEt_3)_2$,[8] some very recent work indicates that the actual insertion reaction may be somewhat more complicated. Thus, the hydrido(acetone) complex, III, prepared by silver ion induced halide abstraction from *trans*-$PtHCl(PMePh_2)_2$, rapidly coordinates ethylene even at −50° to give a square-planar hydrido(olefin) complex, IV.[9]

The same reaction carried out at room temperature results in facile insertion to give, after halide quench, the alkyl product V.

$$trans\text{-}PtHCl(PMePh_2)_2 + AgPF_6 \xrightarrow[acetone]{CH_2Cl_2}$$

$$\underset{\text{III}}{trans\text{-}PtH(acetone)(PMePh_2)_2^+PF_6^-}$$

$$\begin{tikzcd} & \underset{\text{IV}}{trans\text{-}PtH(CH_2{=}CH_2)(PMePh_2)_2^+PF_6^-} \\ III + C_2H_4 \arrow[ur, "-50°"] \arrow[dr, "+25°", "+X^-"'] & \\ & \underset{\text{V}}{trans\text{-}Pt(C_2H_5)X(PMePh_2)_2} \end{tikzcd}$$

Further, the reactions with the cationic hydrido(acetone) complex IV operate catalytically. Insertion products can be isolated in good yield from solutions of the hydrido chloride and C_2H_4 containing a catalytic amount of $AgPF_6$, or to which a catalytic amount of III is added.

While the substitution of a tertiary phosphine for coordinated acetone in III blocks the insertion reaction with ethylene under the same mild conditions,[9] ethylene,[9] norbornadiene, or methyl vinyl ketone[10] insert readily when NO_3^- is the leaving group. It is then appropriate to assume that in these examples, the ease of insertion is related to the ease of substitution to give III.

The reaction of ethylene with *trans*-$PtHNO_3(PEt_3)_2$ is reported to result in an analogous substitution and the square-planar hydrido(olefin) complex VII was isolated as its BPh_4^- salt.[10]

$$\underset{\text{VI}}{trans\text{-}PtHNO_3(PEt_3)_2} + C_2H_4 \xrightarrow{NaBPh_4}$$

$$\underset{\text{VII}}{trans\text{-}PtH(CH_2{=}CH_2)(PEt_3)_2^+BPh_4^-}$$

Attempts to cause the reaction of ethylene with VII to obtain the expected inserted product analogous to V failed, giving instead a product resulting from phenylation by BPh_4^-. The fact that insertion occurs readily for VI in the absence of BPh_4^- indicates that the activation energy associated with insertion from the reactive hydrido(olefin) intermediate is greater than that for phenyl migration.

It is not clear, however, how the square-planar trans hydrido(olefin) complexes lead to the final insertion products since in each case the isolation of alkyl products *follows* addition of a ligand X^- or L.[11]

We report here the results of a kinetic study of the insertion

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(1) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

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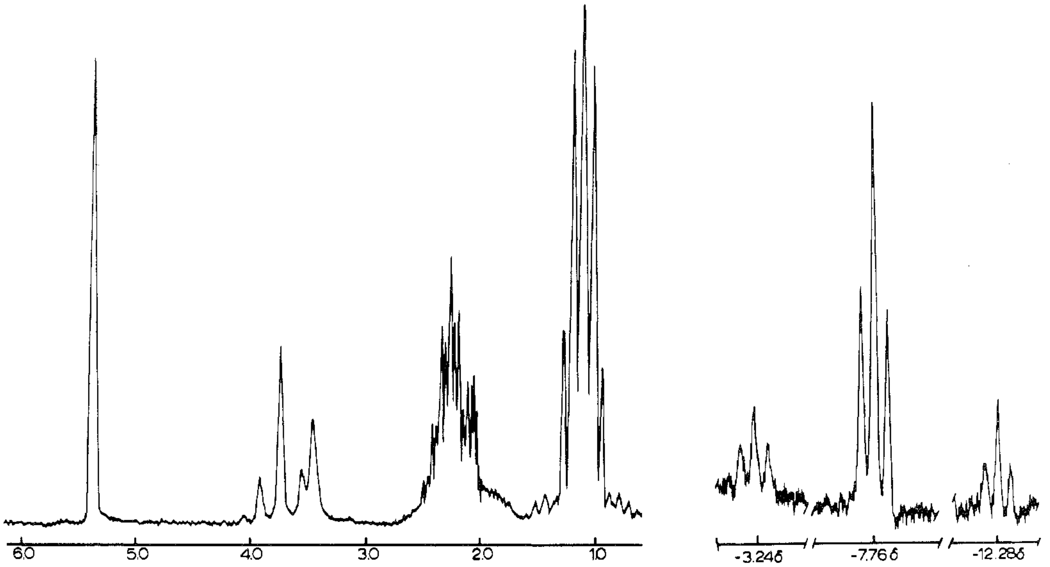
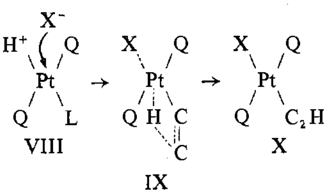


Figure 1. Pmr spectrum of *trans*-$PtH(C_2H_4)(PEt_3)_2^+PF_6^-$ in acetone-d_6 at −10°. The signals at δ 3.4 and 2.1 arise from water and acetone-d_5.



reaction (2) which was undertaken in an attempt to clarify the

$$trans\text{-}PtH(acetone)(PEt_3)_2^+ + C_2H_4 \xrightarrow[\text{acetone}]{25°} trans\text{-}PtC_2H_5(acetone)(PEt_3)_2^+ \quad (2)$$

XI XII

nature of the insertion from cationic square-planar hydrido(olefin) complexes.

Experimental Section

Nmr spectra were obtained using a Varian Associates T-60 or HA-100 spectrometer. Melting points were taken by capillary methods and are uncorrected. *trans*-Hydridochlorobis(triethylphosphine)platinum(II), I, was prepared by hydrazine reduction of *cis*-dichlorobis(triethylphosphine)platinum(II) according to the literature method[12] and was sublimed at 80° (10^{-4} mm) before use. Ethylene was obtained from Matheson Co. and was used without further purification. Silver hexafluorophosphate was obtained from Alfa Inorganics or Cationics Inc. and was used without purification. Acetone was distilled from $CaCO_3$ immediately before use.

Preparation of *trans*-$PtH(acetone)(PEt_3)_2^+PF_6^-$, XI. Standard solutions of the hydrido(acetone) complex were prepared by adding a solution of 50.6 mg of $AgPF_6$ in 5 ml of acetone to 93.5 mg of *trans*-$PtHCl(PEt_3)_2$ in 1 ml of acetone at room temperature, removal of the resulting AgCl precipitate by centrifugation, and diluting the clear, colorless supernatent to 10.0 ml.

The pmr spectrum of samples prepared in acetone-d_6 showed the characteristic pattern for two mutually trans triethylphosphine groups,[13] δ($-CH_2-$) 1.93 and δ($-CH_3$) 1.18, as well as an unresolved high-field signal at δ −24.4 with platinum satellites; $J = 1450$ Hz due to the hydride.

Preparation of *trans*-$PtHNO_3(PEt_3)_2$. The title compound was prepared by adding an aqueous solution of $AgNO_3$ to a solution of *trans*-$PtHCl(PEt_3)_2$ in methanol according to the procedure of Chatt and Shaw.[1] Recrystallization from pentane gave the product as white needles, mp 49.5-50°.

Preparation and Characterization of *trans*-$PtH(C_2H_4)(PEt_3)_2^+PF_6^-$. A solution of *trans*-$PtH(acetone)(PEt_3)_2^+PF_6^-$ was prepared as described above and concentrated to *ca.* 0.3 ml in an nmr tube. The sample was then cooled to −78°, evacuated, pressurized to 1 atm with ethylene, and finally sealed. The pmr spectrum is shown in Figure 1. Pmr parameters are similar to those previously reported for *trans*-$PtH(C_2H_4)(PEt_3)_2^+BPh_4^-$.[10]

Product Isolation. Excess methanolic lithium chloride was added *via* a syringe to the residual acetone solution of *trans*-$PtH(acetone)(PEt_3)_2^+$ and ethylene contained in the reactor described below after completion of sampling for kinetic analysis.

Removal of solvent at room temperature left a white gum which was triturated with benzene. Evaporation of the benzene extracts after drying over anhydrous K_2CO_3 left a colorless oil which solidified upon standing. Thin layer chromatographic analysis on silica gel plates eluted with benzene showed that the crude product contained only trace amounts of *trans*-$PtHCl(PEt_3)_2$ resulting from unreacted hydride species. The major product had an R_f value identical with that of authentic *trans*-$PtC_2H_5Cl(PEt_3)_2$. Recrystallization of the crude product from pentane gave white needles with mp 49.5-51.5°, identified as *trans*-$Pt(C_2H_5)Cl(PEt_3)_2$ (lit.[1] mp 53-55°) by comparison of ir spectra. A Nujol mull showed a band at 1200 cm^{-1} assigned to a $Pt-CH_2CH_3$ deformation and was transparent at 2220 cm^{-1}.

Demonstration of the Reversibility of the Insertion Reaction. Ten milliliters of a 0.02 *M* solution of *trans*-$PtH(acetone)(PEt_3)_2^+PF_6^-$ was held under an atmosphere of ethylene (400 mm) in the reactor described below for 24 hr. Approximately half the solution was removed *via* syringe and evaporated to dryness at room temperature. After 0.5 hr excess methanolic lithium chloride was added. Removal of solvent, followed by benzene extraction and work-up as above, gave a colorless oil which solidified upon cooling. Infrared analysis (Nujol) showed the presence of both *trans*-$PtHCl(PEt_3)_2$ and *trans*-$Pt(C_2H_5)Cl(PEt_3)_2$ in an approximate ratio of 1:2 as evidenced by characteristic bands at 2220 and 1200 cm^{-1}, respectively.

The remaining portion was quenched by adding excess methanolic lithium chloride directly to the reactor under an atmosphere of ethylene. Work-up and analysis as above gave nearly pure *trans*-$Pt(C_2H_5)Cl(PEt_3)_2$ with only traces of *trans*-$PtHCl(PEt_3)_2$ evident.

Kinetic Analysis. The rate of insertion according to reaction 2 was obtained by monitoring the decrease in total Pt-H species by following the decrease in intensity of ν_{Pt-H} as a function of time. Initial conditions used $[PtH(acetone)(PEt_3)_2^+PF_6^-] = 0.02\,M$ prepared as previously described. Ten milliliters of this solution was injected into a gas-stirred reactor[14] shown in Figure 2 which was thermostated at 25° and contained a known partial pressure of ethylene. The reactor was ballasted with nitrogen to give a total pressure of 1 atm to allow easy sampling. The volume of the reactor (*ca.* 2 l.) ensured that ethylene was present in large excess even at the lower pressures used.

Aliquots (0.25 ml) were then removed through the serum cap using a 0.25-ml syringe and quenched by injection into serum-stoppered vials containing 5 mg of NaCl, LiCl, NaBr, or NaI which were cooled to liquid nitrogen temperature. Sampling and quenching required an average of 10 sec.

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[12] G. W. Parshall, *Inorg. Syn.*, 12, 26 (1970).

[13] H. C. Clark, K. R. Dixon, and W. Jacobs, *J. Amer. Chem. Soc.*, 90, 2259 (1968).

[14] We thank Dr. A. Shaver for suggesting a reactor of this type.

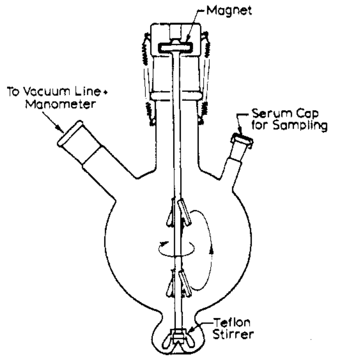

Figure 2. Gas-stirred reactor. Total volume is approximately 2 l.

The aliquots were then warmed to room temperature and transferred *via* syringe to an NaCl solution cell through a Teflon valve. The intensity of the Pt-H stretch was then determined on a Perkin-Elmer Model 621 spectrometer using a blank acetone reference in an adjustable path length cell. An independent check using standard solutions of *trans*-$PtHCl(PEt_3)_2$ in acetone verified Beer's law for the Pt-H stretch in the concentration range studied.

Samples obtained in this manner showed good pseudo-first-order kinetics over 2.5-3.0 half-lives. The data were plotted as the usual function log $(A_t - A_\infty)$ *vs.* time where A_t is absorbance at time t and A_∞ is absorbance at infinity (*ca.* 10 half-lives). Infinity samples showed, in most cases, only very small concentrations of hydride species remaining so that the reverse reaction can be neglected in the kinetic analysis.

The design of the gas-stirred reactor shown in Figure 2 ensures that the rates obtained are not diffusion controlled[15] according to

$$CH_2CH_{2(g)} \rightleftharpoons CH_2CH_2\,(soln) \qquad (3)$$

Direct proof that (3) is not rate determining is provided by two observations: (a) the rate is independent of stirrer speed and (b) solutions of $PtH(PEt_3)_2PF_6^+$ prepared in CH_2Cl_2, which are yellow and become colorless with the formation of an intermediate hydrido-(olefin) complex (*vide infra* pmr), show an instantaneous bleaching when injected into the reactor and the stirrer is turned on.

The actual concentration of ethylene in solution in the reactor under the conditions of the kinetic study was determined using the gas chromatographic method described by Swinnerton, *et al.*[16]

A plot of $[C_2H_4]_{soln}$ *vs.* $P_{C_2H_4}$ (mm) was linear over the concentration range studied ($[C_2H_4] = 1.906 \times 10^{-4}P_{C_2H_4}$ (mm)).

Results.

Stoichiometry of the Reaction. Product analysis after methanolic LiCl quench of equilibrated mixtures of *trans*-$PtH(acetone)(PEt_3)_2^+PF_6^-$ and excess ethylene in acetone solution gave only a single major product which was identified, by comparison of melting point and ir data with literature values,[1] as *trans*-$Pt(C_2H_5)Cl(PEt_3)_2$. Thin-layer chromatographic analysis failed to show any other products except traces of starting hydrido chloride.

The cationic insertion reaction (2) was shown to be readily reversible at 25°. Both *trans*-$PtHCl(PEt_3)_2$ and *trans*-$Pt(C_2H_5)Cl(PEt_3)_2$ can be isolated from equilibrated samples of *trans*-$PtH(acetone)(PEt_3)_2^+PF_6^-$ and ethylene which had been evacuated to dryness before quenching with methanolic LiCl. Treatment of *trans*-$Pt(C_2H_5)Cl(PEt_3)_2$ in an analogous manner does not, however, result in any significant hydride formation. The reverse reaction has, however, been reported for the chloro derivative at much higher temperatures.[5]

Determination of the Rate Equation. Plots of log $(A_t - A_\infty)$ *vs.* time were linear indicating a first-order dependence of the rate on [Pt-H]. Figure 3 shows the ir data used to generate the pseudo-first-order plots shown in Figure 4. The slope of the lines obtained as in Figure 4 gives k_{obsd}. The dependence of k_{obsd} on $[C_2H_4]$ (Table I) shows that the rate approaches a limiting value with increasing olefin concentration and suggests the analytical form

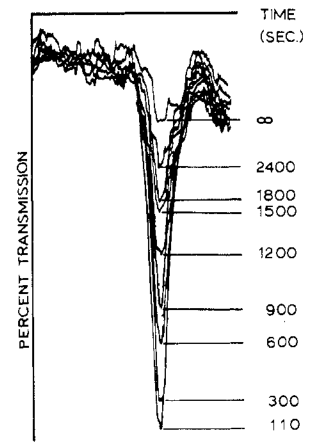

Figure 3. Time dependence of ν_{Pt-H} in acetone at 25° and 100 mm of ethylene.

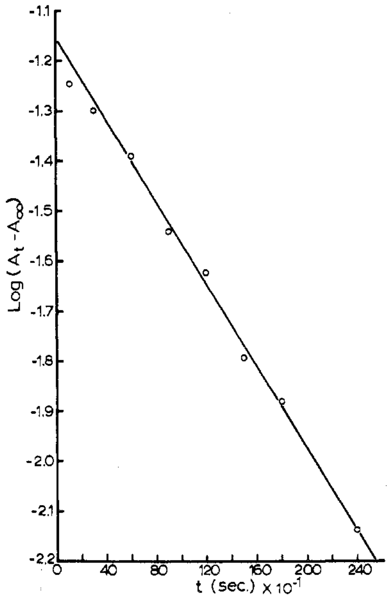

Figure 4. Plot of log $(A_t - A_\infty)$ *vs.* time for reaction 2 at 25° and 100 mm of ethylene.

Table I. Kinetic Data for the Insertion Reaction at 25.0° in Acetone; $[PtH(acetone)(PEt_3)_2{}^+PF_6{}^-] = 0.02\,M$

$P_{C_2H_4}$,[a] mm	$[C_2H_4]_{soln}$,[b] M	(k_{obsd} ± 0.3) $\times 10^4$,[c] sec^{-1}	Correln coeff	No. of points
25	0.0045	3.59	0.995	5
50	0.0090	5.07	0.997	8
100	0.0185	7.31	0.995	8
100	0.0185	7.68	0.997	8
100	0.0185	9.09[d]	0.998	8
200	0.0370	11.19	0.997	8
250	0.0465	12.26	0.981	8
350	0.0655	13.41	0.998	8
350	0.0655	13.32	0.990	8
400	0.0750	13.49	0.999	8

[a] Ballasted to 760 mm vapor pressure in acetone at 25° with N_2. [b] Determined *via* gas chromatographic analysis; see Experimental Section. [c] Observed pseudo-first-order rate constant; least-squares analysis. [d] Solution contained 1 equiv of NH_4PF_6 (0.02 M).

$$k_{obsd} = \frac{k'[C_2H_4]}{1 + K[C_2H_4]} \qquad (4)$$

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(15) P. V. Dankwerts, "Gas Liquid Reactions," McGraw Hill, New York, N. Y., 1970.

(16) J. W. Swinnerton, J. L. Linnenbom, and C. H. Cheek, *Anal. Chem.*, 34, 483 (1962).

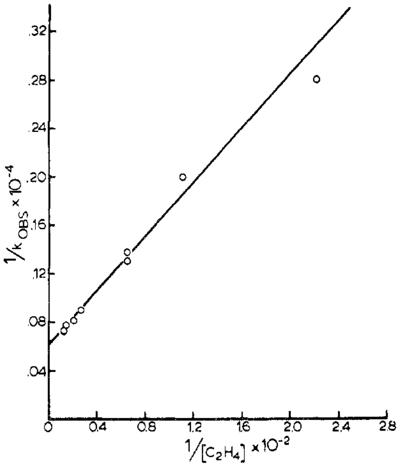


Figure 5. Plot of $1/k_{\text{obsd}}$ for reaction 2 *vs.* $1/[C_2H_4]$ in acetone at 25°.

Rearranging the expression shows that a plot of the reciprocal olefin concentrations *vs.* $1/k_{\text{obsd}}$ should be linear with a slope of $1/k'$ and intercept K/k'.

$$1/k_{\text{obsd}} = \frac{1}{k'[C_2H_4]} + \frac{K}{k'} \tag{5}$$

Figure 5 shows that, to a good approximation, eq 5 fits the data. The values of k' and K obtained from a linear regression analysis are $(9.93 \pm 0.5) \times 10^{-2}$ sec^{-1} M^{-1} and $66 \pm 15\ M^{-1}$, respectively.

Discussion

The overall rate equation is then described by

$$\text{rate} = \frac{-\text{d}[\text{Pt-H}]}{\text{d}t} = \frac{k'[C_2H_4][\text{Pt-H}]}{1 + K[C_2H_4]} \tag{6}$$

which is inconsistent with an insertion involving concerted coordination of added chloride ion. If chloride ion were involved in the insertion step, it is clear that the experimental method described above (see Experimental Section) would not have given pseudo-first-order plots. The form of (6) suggests the formation of a reactive intermediate in a preliminary equilibrium step defined by K.

Further, the preequilibrium satisfying (6) is identified as initial substitution of solvent by ethylene in the hydrido(acetone) complex to give *trans*-$\text{PtH}(C_2H_4)(\text{PEt}_3)_2^+$.

$$\underset{\text{XI}}{\textit{trans}\text{-PtH(acetone)(PEt}_3)_2^+} + C_2H_4 \overset{K}{\rightleftharpoons} \underset{\text{XIII}}{\textit{trans}\text{-PtH}(C_2H_4)(\text{PEt}_3)_2^+}$$

^{1}H nmr analysis of acetone solution of mixtures of XI and ethylene at low temperatures revealed that equilibrium mixtures of XI, ethylene, and the hydrido(ethylene) complex were present (*cf.* Figure 1). Integration of signals corresponding to free and complexed ethylene as well as phosphine ethyl groups allowed estimation of K. Data taken at −90 through −30° in 10° intervals was extropolated to give $K_{298} \simeq 10^2$. Although the determination of K from pmr data in this system is of limited precision, fair agreement with the value of 66 obtained kinetically is obtained. Attempts to determine K in acetone solution using uv methods were unsuccessful due to strong solvent absorption in the region of interest.

A preliminary rate determination for the insertion of ethylene (p = 100 mm) into the Pt-H bond of VI according to eq 7 indicated a pseudo-first-order hydride consumption

$$\underset{\text{VI}}{\textit{trans}\text{-PtH(NO}_3)(\text{PEt}_3)_2} + C_2H_4 \rightarrow \underset{\text{XIV}}{\textit{trans}\text{-Pt}(C_2H_5)\text{NO}_3(\text{PEt}_3)_2} \tag{7}$$

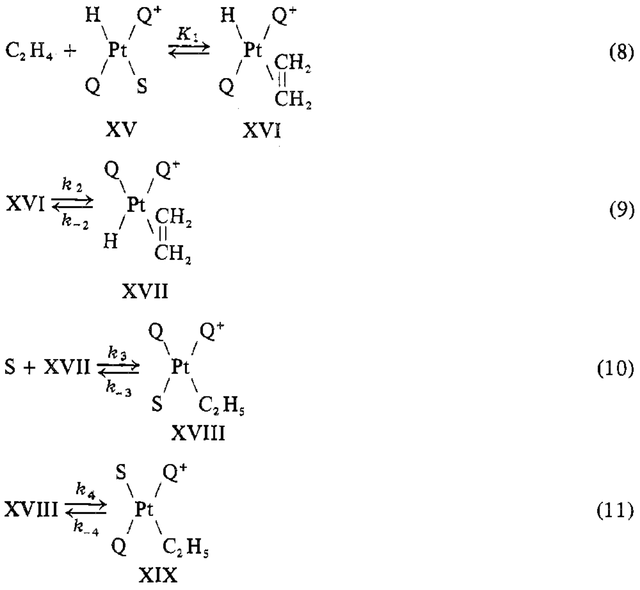
in the initial stages of reaction.

The pseudo-first-order rate constant obtained was, however, 35 times smaller than that found for the analogous insertion reaction of XI under identical conditions. Since Lewis[10] has shown that the initial step of (7) is substitution to give a hydrido(olefin) complex, the result is consistent with either a less favorable equilibrium constant for the initial rapid reversible substitution or a rate-determining substitution.

The observation of *immediate* precipitates[10] from the reaction of VI with ethylene in the presence of the large counterion BPh_4^- favors the former. The reaction of VI with ethylene or methyl acrylate in methanol has been observed[17] to occur in two stages. Ultraviolet analysis shows an initial rapid equilibrium which corresponds to the formation of *trans*-$\text{PtH}(C_2H_4)(\text{PEt}_3)_2^+$ followed by a slower rate-determining insertion.

Mechanistic Implications. A reasonable mechanism accounting for the kinetic data is shown in Scheme I.

Scheme I



S = solvent; Q = PEt$_3$

If the reverse of reaction 11 is neglected, rate = k_4 [XVIII]. Assuming that the steady-state approximation applies for XVIII and XVII, the final rate expression is (see Appendix[18])

$$\text{rate} = \frac{-\text{d}[\text{Pt-H}]}{\text{d}t} = \frac{k'[C_2H_4][\text{Pt-H}]}{1 + K_1[C_2H_4]}$$

where

$$k' = \frac{k_4k_3k_2K_1}{(k_{-3} + k_4)(k_{-2} + k_3)}$$

The Isomerization Step. A primary requirement for facile insertion is a cis arrangement of hydride and olefin in the coordination sphere. The kinetic data require only that the equilibrium concentration of cis isomer is small and cannot distinguish between an assisted and an unassisted isomerization step. It is, however, clear that trans–cis isomerization must be quite rapid.

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(17) H. C. Clark and C. Wong, unpublished results.

(18) See paragraph at end of paper regarding supplementary material.

One can identify systems where isomerization is assisted. Thus the trans–cis rearrangement XVI-XVII and XVIII-XIX of Scheme I can be accomplished by coordination of a fifth ligand which in this case may be counterion or solvent followed by a pseudorotation as suggested by Haake and Pfeiffer from their study of the cis–trans isomerization of PtQ_2Cl_2 ($Q = R_3P$) in the presence of added phosphine.[19]

A second alternative is isomerization *via* a consecutive displacement mechanism originally proposed by Basolo and Pearson[20] and recently defended by Cooper and Powell.[21] Although tertiary phosphines seem necessary to promote cis–trans isomerism in Pt(II) complexes of the form Q_2PtX_2 (Q = phosphine, X = halide), either solvent or counterion functions as an effective entering group for the more labile complex XVI. Rearrangement *via* consecutive displacements requires in this case dissociation of a phosphine so that reaction 9 may be rate determining.

There are also examples of unassisted isomerization. Several recent investigations show that square-planar Pt(II) complexes may isomerize without benefit of added ligand suggesting a dissociative mechanism. Thus XX which may dissociate chloride to give a solvated cationic species readily isomerizes while XXI, which is reluctant to dissociate either phosphine or CH_3^-, does not.[22]

$$\underset{\text{XX}}{cis\text{-}PtMeCl(PEt_3)_2} \xrightleftharpoons{PEt_3} trans\text{-}PtMeCl(PEt_3)_2$$

$$\underset{\text{XXI}}{cis\text{-}PtMe_2(PEt_3)_2} \not\rightarrow trans\text{-}PtMe_2(PEt_3)_2$$

Although the lack of isomerization of XXI might be attributed to a decreased thermodynamic stability of the trans derivative, the facts that *cis*-Pt(*o*-tolyl)Cl$(PEt_3)_2$ does not isomerize in the presence of excess phosphine but readily isomerizes when $AgNO_3$ is added[23] and that the rate was repressed by added chloride[24] further support a dissociative mechanism for isomerization.

The Insertion Step. The migratory insertion rearrangement of the cis intermediate XVII may be concerted with solvent coordination or may lead to a three-coordinate intermediate which rapidly scavenges solvent or counterion. Whitesides[25] has recently demonstrated that the rate of β elimination from XXII is decreased by added phosphine or by the presence of

$$\underset{\text{XXII}}{cis\text{-}(PPh_3)_2Pt(n\text{-}C_4H_9)_2}$$

chelating phosphines. β elimination is preceded by dissociation of a phosphine, and the principle of microscopic reversibility dictates that the reverse reaction, insertion of olefin into Pt-H, proceeds from a four-coordinate intermediate.

$$\text{XXII} \xrightarrow{-Ph_3P} \underset{\text{XXIII}}{(Ph_3P)Pt(\text{-}CH_2CH_2CH_2CH_3)_2} \rightarrow \underset{\text{XXIV}}{(Ph_3P)PtH(C_4H_9)(C_4H_8)}$$

The insertion of XXV to give the acyl complex XXVI provides another example of an insertion reaction involving a four-coordinate intermediate. Even though the insertion proceeds in

$$\underset{\text{XXV}}{(Ph_3As)Pt(Et)(CO)(Cl)} + Ph_3As \rightarrow \underset{\text{XXVI}}{(Ph_3As)_2PtCl(COEt)}$$

the presence of added Ph_3As, the rate of insertion remains independent of $[Ph_3As]$. Glyde and Mawby[26] concluded that insertion occurs directly from XXV (which presumably has CO and Et in mutual cis positions) in the slow step to give a three-coordinate intermediate which then rapidly coordinates Ph_3As. Studies in solvents whose ability to coordinate to Pt(II) varies showed that insertion of XXV was independent of solvent interaction.

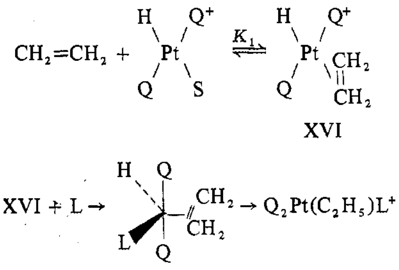
The reverse reaction, decarbonylation, has very recently been demonstrated to be strictly dissociative for the conversion of XXVII to XXVIII.[27] Thus the reaction proceeds readily when chloride is abstracted by silver ion in weakly coordinating solvents.

$$\underset{\text{XXVII}}{(Ph_3P)_2PtCl(RCO)} \xrightarrow{Ag^+} \underset{\text{XXVIII}}{(Ph_3P)_2Pt(CO)(R)^+}$$

In more strongly coordinating solvents as acetonitrile, however, the cationic acyl–acetonitrile complex is isolated.

The kinetics observed in the present study cannot distinguish between insertion from a rearranged four-coordinate intermediate (Scheme I) and an insertion which is essentially associative in nature proceeding from a five-coordinate solvent-containing complex (Scheme II). Scheme II requires a slow, rate-determining insertion step concomitant with coordination of a fifth ligand. Whether the insertion is a one-step (concerted) or two-step (synchronous) process is a moot point. The function of L is to distort the square-planar arrangement and allow a close approach of H and olefin so that the insertion can occur *via* the formation of a four-center transition state.

Scheme II



L = counterion or solvent; $Q = PEt_3$

Although a definitive distinction cannot be made at this time, we are inclined to favor Scheme I (insertion from a rearranged four-coordinate intermediate) for the insertion of the *trans*-hydrido(acetone) complex XI and VI.[17] Our reasoning follows from a number of observations. (1) The insertion reaction of XI proceeds readily in the absence of chloride or other ligands which strongly coordinate to Pt(II). (2) Added chloride *inhibits* insertion by displacement of coordinated olefin. (3) The decreased rate observed for the reaction of VI is not expected if coordination by NO_3^- is involved in the rate-determining insertion step.[28]

A slight increase in k_{obsd} for reaction 2 resulted when 1 equiv of NH_4PF_6 was added (*cf.* Table I). This result is consistent with participation of counterion as in Scheme II

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(19) P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 92, 4996 (1970).

(20) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 5.

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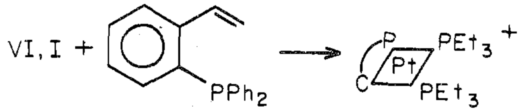
(28) To verify this k_{obsd} needs to be factored into K and $k_{insertion}$.

but changes in ionic strength can affect k_{obsd} of both Schemes I and II.

Neither Scheme I nor Scheme II detracts from the proposal that insertion follows coordination of olefin in the apical position on square-planar d^8 complexes which do not contain a good leaving group.[5,6] In fact, the results observed by Brookes[29] are compatible with just such a scheme.

Thus VI or I reacts very rapidly with diphenylstyrylphosphine to give inserted products. The mechanism probably proceeds *via* initial displacement of NO_3^- or Cl^- to give a P-bonded diphenylstyrylphosphine. Insertion can then proceed from a five-coordinate intermediate stabilized by a chelate effect. An alternative mechanism involving displacement of PEt_3 by olefin is possible but less likely in view of the bascity of tertiary alkylphosphines.



It is, however, clear from the results observed in this study that the square-planar hydrido(olefin) complex formed by initial substitution provides a lower energy pathway leading to insertion. As the leaving group trans to hydride becomes poorer, direct insertion from a five-coordinate intermediate formed by initial interaction with the olefin is expected to become competitive. In some cases, however, the rate of insertion from an initially formed five-coordinate intermediate approaches that of insertion from the reactive square-planar hydrido(olefin) intermediates of the types IV and XIII.[30]

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Registry No. C_2H_4, 74-85-1; *trans*-PtH(acetone)$(PEt_3)_2{}^+PF_6{}^-$, 51716-77-9; *trans*-PtH$(C_2H_4)(PEt_3)_2{}^+PF_6{}^-$, 51794-48-0; *trans*-Pt-C_2H_5(acetone)$(PEt_3)_2{}^+$, 51716-78-0.

Supplementary Material Available. The Appendix will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2213.

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[29] P. R. Brookes, *J. Organometal. Chem.*, 47, 179 (1973).

[30] This appears to be the case with the reaction of ethylene with *trans*-$PtHSnCl_3(PEt_3)_2$ in methanol or ethanol: H. C. Clark, C. R. Jablonski, J. Halpern, T. A. Weil, and A. Mantovani, *Inorg. Chem.*, in press.

Contribution from the Chemistry Department,
University of Tasmania, Hobart, Tasmania 7001, Australia

Single-Crystal Electronic Spectrum of Quinolinebis(acetylacetonato)copper(II) and Its Implications on the d Orbital Energies of Planar β-Ketoenolate–Copper(II) Complexes

M. A. HITCHMAN

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The single-crystal polarized electronic spectrum of the square-pyramidal complex quinolinebis(acetylacetonato)copper(II) is reported and the d-orbital energy sequence is deduced to be $d_{xy} >> d_{z^2} > d_{x^2-y^2} > d_{yz} \approx d_{xz}$. The angular overlap model is used to estimate the variation in the d-orbital energies accompanying the distortion of a planar bis(acetylacetonato)copper(II) complex to a square-pyramidal geometry. The transition energies observed for quinolinebis(acetylacetonato)copper(II) are in good agreement with the calculated values if the d-orbital energy sequence in planar bis(acetylacetonato)copper(II) is the same as that in the quinoline adduct. The intensities of the "d–d" transitions in quinolinebis(acetylacetonato)copper(II) substantiate the hypothesis that the bulk of the intensity in the "d–d" spectra of β-ketoenolate–copper(II) complexes is borrowed from charge-transfer transitions in which an electron is transferred from combinations of the essentially nonbonding lone pair electrons of the oxygen atoms to the central metal ion.

Introduction

The "d–d" electronic spectra of bis(acetylacetonato)copper(II) $(Cu(acac)_2)$ and similar complexes with substituted β-diketones have been the subject of numerous studies.[1] The close similarity of the spectra suggests that the metal–ligand bonding remains quite similar throughout this series of compounds. Despite the fact that many of the spectra have been measured using single crystals at low temperatures, the energy sequence of the d orbitals in the complexes has remained uncertain. A major reason for this ambiguity has been the fact that the selection rules for the optical transitions of a centrosymmetric complex such as $Cu(acac)_2$ provide little information which can be used to assign the spectrum.

It is known that five-coordinate adducts are formed on the addition of bases such as pyridine to solutions of copper–acetylacetonate complexes in inert solvents.[2] Several attempts have been made to use the intensity changes and energy shifts which occur on adduct formation to deduce the d-orbital energies in the complexes.[2-4] However, the ambiguity of the analysis of the broad bands into their component peaks combined with the uncertainty of the precise geometry of the species present in solution has prevented general agreement on the interpretation of the results.

The present study describes the "d–d" electronic spectrum of a single crystal of the square-pyramidal adduct bis(acetyl-

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[1] For a recent review of some of the work in this area see D. W. Smith, *Struct. Bonding (Berlin)*, 12, 50 (1972).

[2] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, 26, 1165 (1957).

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