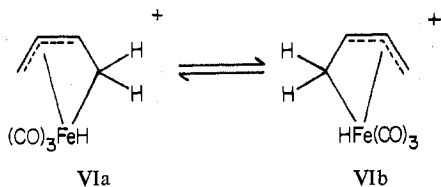


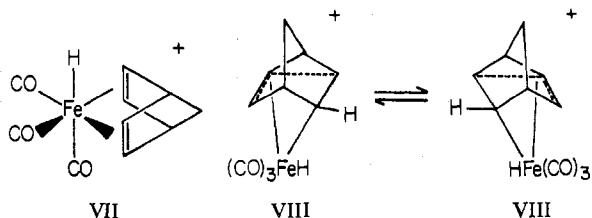
is intramolecular as required and involves no exchange of protons with solvent acid. The slower intramolecular scrambling of H_c, H_d, H_e, H_f, and H_g can be accounted for by equilibration *via* σ - π rearrangement of the two degenerate species VIa and VIb coupled with the faster three-proton scrambling.



The butadiene complex, III, has been considered in detail; application of analogous reactions can explain observations made for the other dieneiron tricarbonyl complexes reported.^{2,5}

Additional cases involving protonation of dieneiron tricarbonyl complexes where σ , π species must now be considered as possible intermediates are the reports by Whitesides of the stereospecific deuterium exchange of the endo protons of cyclohexadieneiron tricarbonyl⁶ and the exchange of the terminal protons of dieneiron tricarbonyl complexes⁷ in trifluoroacetic-*d*₁ acid. The observed sites of exchange result if the scrambling processes described above are coupled with proton (deuterium) exchange with the trifluoroacetic acid.

The structure of protonated norbornadieneiron tricarbonyl⁸ can also be formulated in terms of a σ , π species. The nmr spectral data, in which the coupling of the iron-bound proton with two olefinic protons of the ring is 13 Hz, are consistent both with the structure VII as proposed by Lillya and Rausch⁸ and with a rapidly equilibrating σ , π species VIII in which the π -allyl moiety is a homoallyl system.



Other cases in which σ , π species may likely play a role as intermediates include the proton scrambling processes in the protonated cyclohexadiene(cyclopentadienyl)rhodium,⁹ the

(5) The only datum reported which is not in agreement with the proposed scheme is the integrated area of the methylene region for the species produced by protonation of cyclohexadieneiron tricarbonyl in excess HSO₃F. The reported integral corresponds to 6 H; our mechanism predicts a 5 H integral. However, the corresponding integral (4.7 H) in DSO₃F is in accord with our mechanism (4.5 H).

(6) T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, **93**, 5296 (1971).

(7) T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *J. Amer. Chem. Soc.*, **95**, 5792 (1972).

(8) D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, **89**, 6387 (1967).

(9) (a) B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J. Chem. Soc., Chem. Commun.*, 235 (1972); (b) B. F. G. Johnson, J. Lewis and D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 2084 (1972).

stereospecific endo protonation of cyclooctatetraenemolybdenum tricarbonyl,¹⁰ and the 1,4 hydrogen shifts and deuterium-exchange reactions of π -allyliron tetracarbonyl cations.¹¹

Acknowledgments. This work was supported in part by the National Science Foundation (Grant GP-29580) and the Materials Research Center, University of North Carolina, under Grant No. GH-33632 from the National Science Foundation.

(10) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, **87**, 3267 (1965).

(11) D. H. Gibson and R. L. Vonnahme, *J. Chem. Soc., Chem. Commun.*, 1021 (1972).

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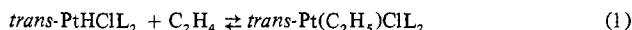
Received November 14, 1973

Mechanism of Insertion of Olefins into Platinum-Hydrogen Bonds

AIC30846A

Sir:

The uncatalyzed insertion of C₂H₄ into *trans*-PtHClL₂ (1), where L = P(C₂H₅)₃, to form the corresponding ethylplatinum complex (2) according to eq 1, has been reported to



2

occur only slowly even under vigorous conditions (20 hr, 100°, 80 atm).^{1,2} On the other hand the corresponding reactions of C₂H₄ with *trans*-PtH(NO₃)L₂ (3) [to form *trans*-Pt(C₂H₅)(NO₃)L₂ (4)] and with *trans*-PtH(acetone)L₂ (5) (to form 2 after work-up with methanolic LiCl) occur readily at room temperature and atmospheric pressure, as does reaction 1 in the presence of catalytic amounts of AgPF₆.³

The latter observations have been interpreted in terms of the cationic intermediate *trans*-PtH(C₂H₄)L₂⁺ (6) formed through the facile replacement by C₂H₄ of the weakly bound trans NO₃⁻ and acetone ligands of 3 and 5, respectively, or through the corresponding Ag⁺-assisted displacement of the trans Cl⁻ ligand of 1. Salts of 6, for example, [*trans*-PtH(C₂H₄)L₂]⁺BPh₄⁻, have in fact been isolated and the *trans* configuration of the cation in solution has been established by nmr spectroscopy.^{3,4}

This interpretation is consistent with the widely accepted view that insertion of olefins into transition metal-hydrogen bonds requires prior coordination of the olefin to the metal ion but not, on the face of it, with the further implied requirement of *cis* rather than *trans* disposition of the hydride and olefin ligands.⁵ The purpose of this communication is to examine this apparent inconsistency and to suggest possible explanations for its origin. Two such explanations that have occurred to us and that we have examined are encompassed by the mechanistic Schemes I and II, respectively (where S = solvent and X⁻ = NO₃⁻, etc.).⁶

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

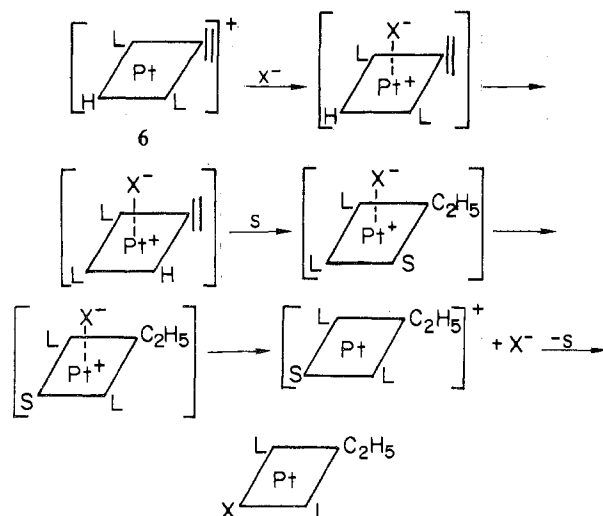
(2) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. A*, 190 (1968).

(3) H. C. Clark and H. Kurosawa, *Inorg. Chem.*, **11**, 1275 (1972).

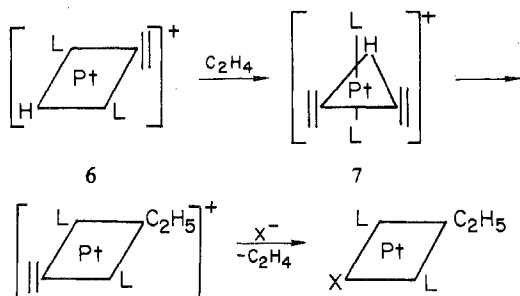
(4) A. J. Deeming, B. F. G. Johnson and J. Lewis, *Chem. Commun.*, 598 (1970).

(5) See for example, R. F. Heck, *Advan. Chem. Ser.*, No. 49, 181, 208 (1965).

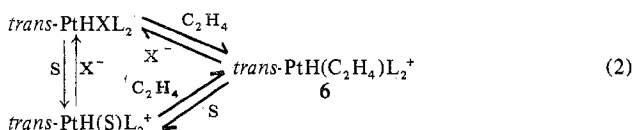
Scheme I



Scheme II



Both schemes invoke the cation $\text{trans-PtH}(\text{C}_2\text{H}_4)_2\text{L}_2^+$ (6), formed through reaction 2, as the initial intermediate. In



Scheme I insertion of the coordinated C_2H_4 into the Pt-H bond is accomplished through the X^- -assisted isomerization to the corresponding $\text{cis-PtH}(\text{C}_2\text{H}_4)_2\text{L}_2^+$ complex which is expected to undergo the migratory insertion rearrangement readily. An implied requirement for this mechanism is a trans ligand X^- which can be readily replaced by S or C_2H_4 to yield 6 (eq 2), yet which is sufficiently nucleophilic to "coordinate" to the axial position in order to effect the trans to cis isomerization. NO_3^- , but not Cl^- or ClO_4^- , is expected to satisfy these conditions. At the same time the solvent should be sufficiently polar (e.g., acetone) to accommodate the formation of the proposed ionic intermediates, yet not so polar that its solvation effects will prevent the effective interaction of X^- with the cation 6. Both of the above expectations are consistent with the experimental evidence.³ This mechanism also derives plausibility from its close parallel with that recently proposed by Cooper and Powell,⁷ on the basis of convincing evidence, for the phosphine-catalyzed cis-trans isomerization of PtX_2L_2 complexes via tetragonal $\text{PtXL}_3^+ \cdot \text{X}^-$ intermediates analogous to those of Scheme I.

(6) The two alternative mechanistic schemes were originally proposed and favored by the Western Ontario and Chicago groups, respectively. The present communication reflects a collaborative effort to assess their validity.

(7) D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, **95**, 1102 (1973).

In Scheme II, the essential role of the coordinated C_2H_4 ligand of 6 is not necessarily that of undergoing insertion itself but rather that of stabilizing the five-coordinate configuration of Pt(II) thereby promoting the coordination of a second C_2H_4 molecule to form the trigonal-bipyramidal intermediate 7, in which one of the cis-coordinated C_2H_4 ligands would be expected to undergo rapid migratory insertion into the Pt-H bond. The ability of π -back-bonding ligands such as C_2H_4 to stabilize five-coordinate Pt(II) complexes is well recognized and is reflected, for example, in the trans-labilizing influence of such ligands.⁸

Various experiments, designed to discriminate between these two alternative mechanistic schemes, have been attempted. Kinetic measurements⁹ on the reaction of 5 with C_2H_4 in acetone (to yield 2 after quenching with methanolic LiCl), in which $[\text{C}_2\text{H}_4]$ was varied from 4.5×10^{-3} to 7.5×10^{-2} M, yielded the rate law of eq 3, where $[\text{PtH}]_{\text{total}} = [\text{5}]$

$$\frac{-d[\text{PtH}]_{\text{total}}}{dt} = \frac{k[\text{PtH}]_{\text{total}}[\text{C}_2\text{H}_4]}{1 + k'[\text{C}_2\text{H}_4]} \quad (3)$$

+ [6]. Unfortunately, this result fails to discriminate between the two alternative mechanisms. According to Scheme I the C_2H_4 dependence can be accommodated by the displacement of the preequilibrium of eq 2 from $\text{trans-PtH}(\text{acetone})_2\text{L}_2^+$ to $\text{trans-PtH}(\text{C}_2\text{H}_4)_2\text{L}_2^+$. However, while not altogether expected the rate law is also compatible with Scheme II if 6 is assumed to be a five-coordinate complex containing a coordinated solvent ligand, i.e., $\text{PtH}(\text{S})(\text{C}_2\text{H}_4)_2\text{L}_2^+$ which reacts with C_2H_4 to form 7, by a dissociative mechanism involving loss of S.

Another experiment designed to distinguish between the two alternative mechanisms by means of isotopic tracers also failed to yield a definitive result.⁹ $[\text{PtH}(\text{C}_2\text{H}_4)_2\text{L}_2]^+ \cdot \text{PF}_6^-$ was prepared in pure form and was treated with an excess of C_2D_4 in acetone to yield the ethyl-insertion product which was converted to $\text{Pt}(\text{C}_2\text{H}_n\text{D}_{5-n})\text{IL}_2$ by addition of LiI. Reaction with I_2 resulted in cleavage of the Pt-C bond to yield $\text{C}_2\text{H}_n\text{D}_{5-n}\text{I}$ which was analyzed mass spectrometrically. The formation of either $\text{Pt}(\text{C}_2\text{H}_5)\text{IL}_2$ or of a 1:1 mixture of $\text{Pt}(\text{C}_2\text{D}_4\text{H})\text{IL}_2$ and $\text{Pt}(\text{C}_2\text{H}_5)\text{IL}_2$ as the major products would have constituted strong support for either Scheme I or II, respectively. However, the actual result, namely, the formation of $\text{Pt}(\text{C}_2\text{D}_4\text{H})\text{IL}_2$ as the major initial product, was inconclusive indicating, not unexpectedly, that exchange of $\text{PtH}(\text{C}_2\text{H}_4)_2\text{L}_2^+$ with C_2D_4 was faster than insertion.

A distinguishing feature of Scheme II is the expectation that the role of the C_2H_4 ligand in 6 could be assumed by other ligands which are effective in stabilizing the five-coordinate configuration of Pt(II) and thereby promoting the coordination and subsequent insertion of an olefin molecule. The trans-labilizing influence of the SnCl_3^- ligand and its tendency to stabilize five-coordinate Pt(II) complexes [e.g., $\text{Pt}(\text{SnCl}_3)_5^{3-}$ and $\text{PtH}(\text{SnCl}_3)_2(\text{PEt}_3)_2^{10}$ are well known and, indeed, the catalysis of reaction 1 by SnCl_2 [presumably via $\text{PtH}(\text{SnCl}_3)_2\text{L}_2$] has previously been reported.¹¹ We have, accordingly, examined the kinetics of this reaction, together with the accompanying equilibria, in methanol solution and

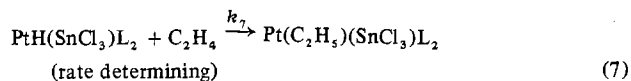
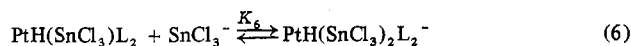
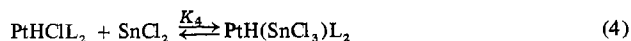
(8) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 351.

(9) H. C. Clark and C. Jablonski, details to be submitted for publication.

(10) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, **87**, 658 (1965).

(11) R. Cramer and R. V. Lindsey, *J. Amer. Chem. Soc.*, **88**, 3534 (1966).

obtained results that are quantitatively in accord with the mechanism described by eq 4-8 where $K_4 = (1.7 \pm 0.3) \times$



$10^3 M^{-1}$, $K_5 = 9 \pm 1 M^{-1}$, $K_6 = (1.8 \pm 0.3) \times 10^5 M^{-1}$, and $k_7 = (3.0 \pm 0.5) \times 10^{-1} M^{-1} \text{sec}^{-1}$.^{12,13} The failure of excess Cl^- to inhibit the SnCl_2 catalysis¹³ conclusively rules out the previously admissible alternative interpretation which attributes the catalytic role of SnCl_2 (in a manner analogous to that for Ag^+)³ to the formation of the cationic complex $\text{PtH}(\text{C}_2\text{H}_4)\text{L}_2^+$ by promoting displacement of the Cl^- ligand as SnCl_3^- .

While Scheme II does derive some support from the above parallel, the alternative interpretation of Scheme I has not been ruled out and the mechanism of the insertion reactions involving the cationic $\text{PtH}(\text{C}_2\text{H}_4)\text{L}_2^+$ complex still remains to be conclusively established.

Acknowledgments. Support of this research through grants from the National Research Council of Canada and the National Science Foundation and through Postdoctoral Fellowships (to T. A. W.) from the National Cancer Institute and (to A. M.) from the Accademia dei Lincei is gratefully acknowledged.

(12) T. A. Weil, A. Mantovani, and J. Halpern, details to be submitted for publication.

(13) These experiments, performed at 25° and an ionic strength of $5.0 \times 10^{-3} M$, maintained with LiClO_4 , encompassed the concentration ranges 1×10^{-4} – $3 \times 10^{-4} M$ PtHClL_2 , 5×10^{-5} – $2.5 \times 10^{-3} M$ SnCl_2 , 9×10^{-3} – $9 \times 10^{-2} M$ C_2H_4 , and 1×10^{-4} – $5 \times 10^{-3} M$ LiCl .

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Geometrical Distortion and Spin-Orbit Splitting in Excited Transition Metal Complexes¹

AIC308527

Sir:

During the last few years the use of transition metal compounds in photochemical and energy-transfer experiments has rapidly expanded. The interpretation of the results often depends upon a knowledge of the relative energies of various excited levels in the systems. Such values are usually estimated from the locations of band maxima of absorption and sometimes of emission spectra. Because huge Stokes shifts are found for d-d transitions in these molecules, as well as un-

comfortably large values of the spin-orbit coupling constants ζ , we decided to perform a detailed analysis to determine the energies, geometries, decay parameters, and spin-orbit splittings of the lowest excited levels of a few simple complexes. We report here the results for crystalline $\text{K}_3\text{Co}(\text{CN})_6$. Experiments on ruthenium(II), osmium(II), iridium(III), and rhodium(III) hexacyanides are also in progress.

Figure 1 shows the 4.2°K emission spectrum of $\text{K}_3\text{Co}(\text{CN})_6$. The smoothed curve is a computer-generated fit that yields information about the lowest excited level [$E(^3T_1)$] geometry, the M-CN stretching force constant, and the magnitude of the totally symmetric metal-carbon stretching frequency in both the ground and lowest excited (emitting) level. The fitting procedure was carried out on a function that represented a superposition of all possible vibronic transitions originating from the lowest vibrational state of the lowest excited electronic level [$E(^3T_1)$]. The transitions were assumed to terminate on levels possessing 1 quanta of allowing mode and any number of quanta of the totally symmetric (a_1) M-CN vibrational mode of the [$A_1(^1A_1)$] electronic ground state. Each vibronic transition was assumed to have a frequency dependence of the form $g(\omega) = \omega^4 e^{-(\omega - \omega_m)^2/a^2}$ where ω_m is the frequency at which the maximum of that vibronic transition intensity occurs and a is an average value for the width of a vibronic transition. The relative intensities of the vibronic transition were assigned using Franck-Condon factors. To calculate these Franck-Condon factors a harmonic oscillator model was used that permitted different frequencies and equilibrium positions to be possessed by the a_1 (M-CN) modes of the ground and excited [$E(^3T_1)$] levels.

Our spectral fitting technique has yielded the following information. (a) The equilibrium nuclear geometry of the $E(^3T_1)$ excited level is approximately octahedral, but the molecule is expanded. We estimate an increase of about 0.10 Å in the M-C equilibrium distance over the 1.89 Å ground-state value.² (b) The a_1 (M-CN) vibrational frequency of the excited $E(^3T_1)$ level is 35% lower than that of the corresponding totally symmetric ground-state vibration. (c) The energy of the nonvertical $A_1 \rightarrow E(^3T_1)$ zero-zero transition lies at or higher than 17.1 kK. Its exact location depends upon whether there is a nontotally symmetric enabling mode for the transition. (d) Our value, calculated from the electronic emission band, for the a_1 (M-CN) ground-state frequency is $420 \pm 5 \text{ cm}^{-1}$. This compares favorably with the latest report of 414 cm^{-1} obtained from ir spectroscopy.^{2,3}

With this information we may calculate the approximate position of the band maximum of the absorption corresponding to the $A_1 \rightarrow E(^3T_1)$ transition; that is, we can calculate the energy of the vertical transition from the ground state to the $E(^3T_1)$ level. This transition is difficult, if not impossible, to observe. The vertical absorption requires approximately $1/2 k_u (\Delta Q_a)^2$ more energy than that needed for the zero-zero transition [k_u is the force constant for the upper level and equals $\sqrt{0.65(2.62 \text{ mdyne/Å})^3}$]. The band maximum in absorption is predicted to occur $\sim 3.3 \text{ kK}$ higher than the zero-zero transition or at approximately 20.3 kK. The observed emission maximum appears at $\sim 14.0 \text{ kK}$. This means that where the vertical transition energy is of importance, an error of 18.3 kcal is introduced by using the emission band maximum to compute its energy. Conversely, for states that are seen only in absorption, an error of half this magnitude may result when it is the zero-zero energy of the relaxed

(1) Research supported by AFOSR(NC)-OAR, Grant 72-2207.

(2) L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962).

(3) I. Nakagawa, *Can. J. Spectrosc.*, **18**, 1 (1973).