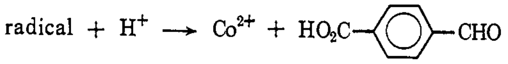
assumed either to make internal transfer possible or to form R_4. If we let proton loss from carbon represent the formation of R_4, the only alternative is proton loss from oxygen to form III. Arguments have already been presented which tend to rule out the alkoxy form as an intermediate. These arguments may, however, not be entirely valid. It is perhaps possible that the alkoxy form undergoes proton loss, this being coupled to electron transfer. If this is so, it could play the role of R_3.

Irrespective of the nature of the intermediate which shows competition between internal electron transfer and further reaction with external oxidant, the data do lead to an estimate of the specific rate of the internal electron-transfer act. If the specific rate for the reaction of O_2 with R_4 is assumed to be 10^7 M^{-1} sec^{-1} (*i.e.*, of the order of that observed for the tetralin radical with O_2), for reaction 12 to be competitive with it its specific rate must be $\sim 10^4$ M^{-1} sec^{-1} (note that the solubility of oxygen in air-saturated water at 25° is *ca.* 10^{-3} M). Even if the reaction of O_2 with the radical is assumed to be diffusion controlled, or *ca.* 10^{10} M^{-1} sec^{-1}, the specific rate for reaction 13 would be of the order only of 10^7 M^{-1} sec^{-1}, and the lifetime of the radical, when the external oxidant does not intervene, would therefore be *ca.* 10^{-7} sec. The internal electron-transfer process is therefore not extremely rapid and requires some activation of the intermediate radical. This feature makes it likely that $(NH_3)_5Co^{(III)}$ or some similar group can be a very useful probe in exploring the mechanism of oxidation of functions suitably connected to the polar group bearing the oxidizing center. It is likely that the Co(III) group, at least when the function being oxidized is several bonds removed, affects the oxidation processes at that group only by virtue of its charge, and not by acting as an oxidizing agent in concert with the external oxidizing agents. The effect of the charge on the rates can be explored by kinetic studies, and the suggestion made can be tested by substituting for Co(III) a substitution-inert ion which cannot readily undergo reduction in the way Co(III) does.



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Acknowledgment. Financial support by the National Institutes of Health, Grant GM 13638-01, is gratefully acknowledged.

The Mechanism of Electrophilic Reactions of Carbon–Metal Bonded Platinum(II) Complexes. A Comparsion between Transition and Post-Transition Organometallic Compounds

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Contribution from the Istituto di Chimica Generale dell'Università di Padova, Padua, Italy. Received June 19, 1967

Abstract: Kinetic data for the reactions of *trans*-$[Pt\{P(C_2H_5)_3\}_2(CH_3)X]$ (X = Cl or I) with hydrogen chloride in methanol to give *trans*-$[Pt\{P(C_2H_5)_3\}_2ClX]$ are reported. The reactions obey the following rate law: rate = $(k_2[H^+] + k_3[H^+][Cl^-])$[complex]. A two-step mechanism is proposed involving the formation of labile platinum(IV) intermediates of the type $[Pt\{P(C_2H_5)_3\}_2(CH_3)(H)XY]$ (X = Cl or I; Y = Cl or solvent) followed by slow elimination of methane and rearrangement to *trans*-$[Pt\{P(C_2H_5)_3\}_2ClX]$ in the rate-controlling step. A comparison of electrophilic reaction mechanisms of post-transition and transition metal–carbon compounds is presented.

It is known that d^8 transition metal ion complexes (*e.g.*, of Rh(I),[1] Ir(I),[2] and Pt(II)[3,4]) are active catalysts in the homogeneous hydrogenation of unsaturated compounds containing olefinic and acetylenic linkages,[5–8] and labile species with metal-to-hydrogen bonds have been postulated as intermediates in these processes. These catalytic reactions, in fact, quite often involve transfer of hydrogen to an olefin *via* a metal–hydrido species. For example, the activation of $RhCl_3$, which occurs during rhodium-catalyzed olefin addition reactions, is claimed to proceed through a process which consists of an oxidation of the Rh(I) (obtained from Rh(III) in a preliminary step) by a proton (especially from HCl) to a hydridorhodium(III) complex which then coordinates an olefin to give a alkylrhodium(III) species.[9] This process, as well as other d^8-catalyzed reactions, involves an oxidative addition of hydrogen chloride to a four-coordinated planar complex followed by a coordination of the

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[1] J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 131 (1965).

[2] L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).

[3] R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *ibid.*, **85**, 1691 (1963).

[4] J. C. Bailar and H. Itatani, *ibid.*, **89**, 1592 (1967).

[5] M. F. Sloane, A. S. Matlack, and D. S. Breslow, *ibid.*, **85**, 4014 (1963).

[6] J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965).

[7] R. S. Nyholm, "Proceedings of the 3rd International Congress on Catalysis, Vol. 1, North Holland Publishing Co. Amsterdam, 1965, p 25; see also J. Halpern, *ibid.*, p 146.

[8] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., Sect A*, 1711 (1966).

[9] R. Cramer, *J. Am. Chem. Soc.*, **87**, 4717 (1965); **89**, 1633 (1967).

olefin, the catalytic effectiveness depending upon thermodynamic as well as kinetic factors.

These types of reactions are common to many other catalytic processes, such as dimerization and hydrogenation of olefins.[6]

In this context, it is important to study (i) the chemistry of the addition of olefins to hydrido–transition metal ion complexes and (ii) the electrophilic attack by a proton on carbon–metal bonded and olefin–metal complexes of transition metal ions.

In this paper we describe a detailed investigation of electrophilic reactions of carbon–metal bonded platinum(II) complexes of the type *trans*-[Pt{P(C_2H_5)$_3$}$_2$(CH_3)X] in which the methyl group is cleaved by hydrogen chloride in protic solvents.

Experimental Section

Materials. *trans*-Bis(triethylphosphine)chloro(methyl)platinum(II) was prepared by the method of Chatt and Shaw[10] from methylmagnesium chloride and *trans*-bis(triethylphosphine)dichloroplatinum(II) in ether. The mixture was stirred for 1 hr and then hydrolyzed with ice and hydrochloric acid. The residue from evaporation of the dried ether layer was chromatographed on alumina. Elution with a mixture of light petroleum and ether yielded *trans*-[Pt{P(C_2H_5)$_3$}$_2$(CH_3)Cl], which was obtained as white needles after recrystallization from light petroleum.

trans-Bis(triethylphosphine)iodo(methyl)platinum(II) was prepared by a metathetical reaction from the corresponding chloro compound and tetrabutylammonium iodide in methanol.[10]

The compounds were characterized by their ultraviolet spectra, melting points, and elemental analysis.

All other chemicals were commercial products or reagent grade and recrystallized when necessary.

Kinetics. Fresh solutions of complex and acid HA ($A^- = Cl^-$, ClO_4^-, and *p*-toluenesulfonate), in the presence of lithium chloride and/or lithium or tetraethylammonium perchlorate, were prepared and stored separately in a thermostat. The reaction was started by mixing known volumes of the two solutions in a 1-cm quartz cell placed in a thermostated cell compartment of an Optica CF4 or Beckman DK-2A recording spectrophotometer. The reaction was followed by scanning the spectra in the ultraviolet region (330–270 mμ) from time to time. In some kinetic runs the initial molar concentration of ionic species was changed in order to study the effect of the ionic strength. The pseudo-first-order rate constants (Table I) were determined from the slope of log ($A_\infty - A_t$) against the time (A_t is the optical density at time t and A_∞ is the optical density of the reaction mixture after seven to eight half-lives). In each series of kinetic runs the acid and the chloride concentration covered a seven- to eightfold range. All reactions were followed in the presence of a large excess of acid and chloride in order to provide pseudo-first-order conditions and to force the reactions to completion. Kinetic measurements were carried out in methanol at 40° in the presence of *p*-toluenesulfonic acid, which, under these experimental conditions, may be considered to be completely dissociated.

Results and Discussion

The process studied is represented by the following equation

$$\textit{trans}\text{-}[\mathrm{Pt}\{\mathrm{P(C_2H_5)_3}\}_2(\mathrm{CH_3})\mathrm{X}] + \mathrm{H^+} + \mathrm{Cl^-} \longrightarrow \textit{trans}\text{-}[\mathrm{Pt}\{\mathrm{P(C_2H_5)_3}\}_2\mathrm{ClX}] + \mathrm{CH_4} \quad (1)$$

$$\mathrm{X^-} = \mathrm{Cl^-} \text{ or } \mathrm{I^-}$$

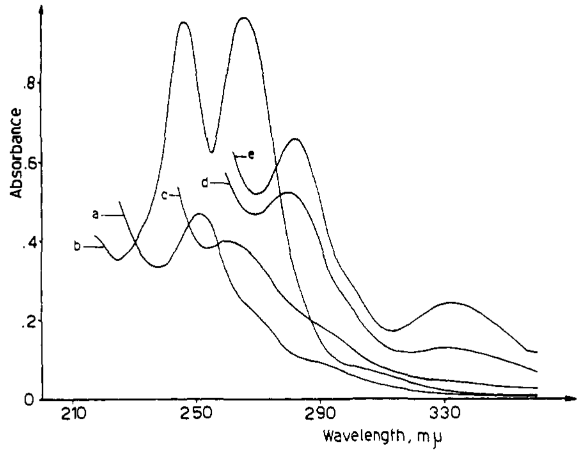

Figure 1. Spectra in the ultraviolet region of some complexes of the type *trans*-[Pt{P(C_2H_5)$_3$}$_2$RX] 10^{-4} *M* in methanol at 30°: (a) R = CH_3, X = Cl; (b) R = Cl, X = Cl; (c) R = CH_3, X = I; (d) R = Cl, X = I; (e) R = I, X = I.

The reaction of the iodo complex was followed at 330 mμ and the final product was isolated and identified as the *trans*-[Pt{P(C_2H_5)$_3$}$_2$ClI] complex. The reaction, incidentally, provides a useful means of preparing these otherwise inaccessible compounds with mixed anionic ligands. In Figure 1 the spectrum of *trans*-[Pt{P(C_2H_5)$_3$}$_2$ClI] is shown, together with spectra of other platinum(II) complexes.

Table I reports the pseudo-first-order rate constants for the reaction of the chloro complex (which could be

Table I. Pseudo-First-Order Rate Constants, k_{obsd} (sec^{-1}), in Methanol at 40°[a]

$$\textit{trans}\text{-}[\mathrm{Pt}\{\mathrm{P(C_2H_5)_3}\}_2(\mathrm{CH_3})\mathrm{X}] \xrightarrow[(-\mathrm{CH_4})]{+(\mathrm{H^+},\ \mathrm{Cl^-})} \textit{trans}\text{-}[\mathrm{Pt}\{\mathrm{P(C_2H_5)_3}\}_2\mathrm{XCl}]$$

Expt no.	Acid concn × 10^3, *M*	[LiCl] × 10^3, *M*	[N(C_2H_5)$_4$ClO$_4$] added × 10^3, *M*	10^4k_{obsd}, sec^{-1}
		X = Cl		
1	20	10	28	9.4
2	15	10	33	7.65
3	12.5	10	35.5	6.3
4	10	10	38	4.42
5	8	10	40	4.4
6	8	10	40[b]	4.0
7	8	10	12[b]	5.65
8	8	10	...	5.75
9	5	10	43	2.5
10	3	10	45	1.54
11	8	20	30	6.2
12	8	15	35	4.6
13	8	8	42	3.35
14	8	5	45	2.5
15	8	3	47	2.14
16	16	18	24	11.3
17	16	9	33	7.3
18	16	3.6	38.4	4.6
		X = I		
19	25	5	28	1020
20	20	5	33	790
21	14	5	39	550
22	11	5	42	420
23	8	5	45	335
24	5	5	48	210
25	3	5	50	130
26	11	12.6	34.4	392
27	11	25	22	390

[a] Substrate concentration *ca.* 5 × 10^{-4} *M;* HA = *p*-toluenesulfonic acid. [b] $LiClO_4$ added.

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(10) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

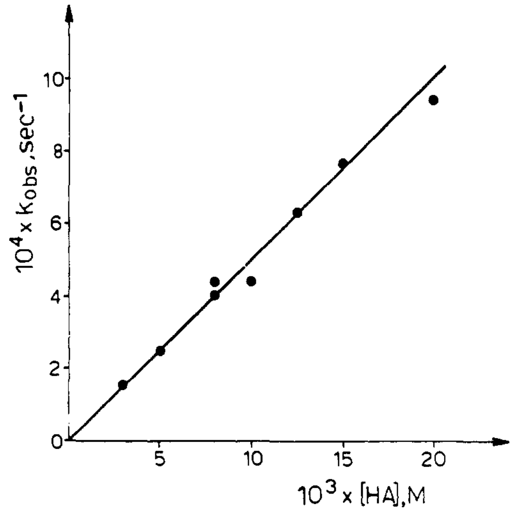

Figure 2. Dependence of the k_{obsd} values on the acid concentration for the reaction of *trans*-[Pt{P(C$_2$H$_5$)$_3$}$_2$(CH$_3$)Cl] in methanol at 40°: ionic strength = 5.8 × 10^{-2} *M;* chloride concentration = 10^{-2} *M;* slope ($k_2 + k_3$[Cl$^-$]) = 5 × 10^{-2} M^{-2} sec^{-1}.

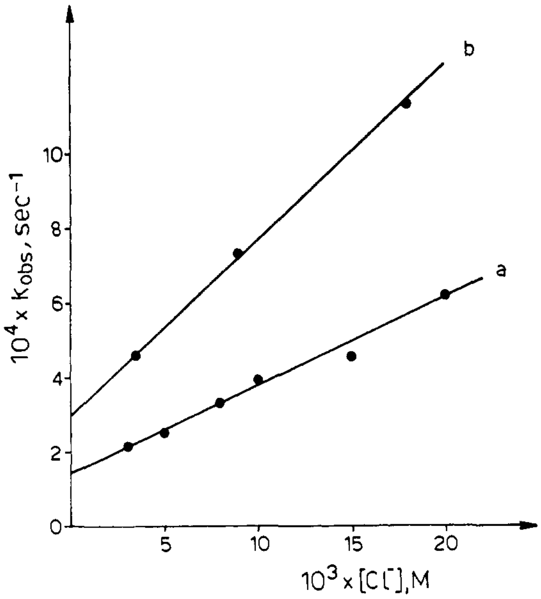

Figure 3. Dependence of the k_{obsd} values on the chloride concentration for the reaction of *trans*-[Pt{P(C$_2$H$_5$)$_3$}$_2$(CH$_3$)Cl] in methanol at 40°: ionic strength = 5.8 × 10^{-2} *M;* acid concentration = 8 × 10^{-3} *M* (curve a) and 16 × 10^{-3} *M* (curve b); intercept (k_2) = 1.78 × 10^{-2} M^{-1} sec^{-1}; slope (k_3) = 3 M^{-2} sec^{-1}.

studied most systematically) and their dependence on the acid and chloride concentration.

Plots of the dependence of k_{obsd} on the acid concentration (see Figure 2) and on the chloride concentration (see Figure 3) indicate a rate law of the form

$$-\frac{d[\text{complex}]}{dt} = (k_2[H^+] + k_3[H^+][Cl^-])[\text{complex}] \qquad (2)$$

The intercept from Figure 3 divided by the acid concentration gives the value of the second-order rate constant, k_2 = 1.78 × 10^{-2} M^{-1} sec^{-1}, which can be ascribed, ignoring the role of the solvent, to a bimolecular electrophilic attack by the proton on the chloro complex. The slope of this plot, divided by the acid concentration, gives a value of 3 M^{-2} sec^{-1} for the third-order rate constant, k_3, which can be identified with a substitution reaction in which the complex, the electrophile H$^+$, and the nucleophile Cl$^-$ are present in the transition state. The same values of rate constants k_2 and k_3 are obtained by changing the acid concentration (see Figure 3a and 3b). The slope of the linear plot of the pseudo-first-order rate constants, k_{obsd} (sec^{-1}) *vs.* the acid concentration, at [Cl$^-$] = 10^{-2} *M* (Figure 2), gives for the ($k_2 + k_3$[Cl$^-$]) term the value of 5 × 10^{-2} M^{-1} sec^{-1}, which is in excellent accord with that (4.78 × 10^{-2} M^{-1} sec^{-1}) calculated by using the values of the rate constants, independently determined.[11] Data in Table II (expt 28–30) show that the rate of the reaction decreases on increasing the water content of the reaction mixture (Figure 4). This is probably due to the larger solvation of the reactant species (H$^+$ and Cl$^-$) in the presence of increasing amounts of water.

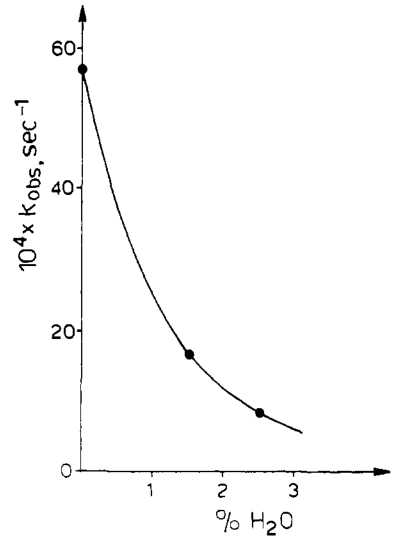

Figure 4. Effect of the content in water on the rate of the reaction (k_{obsd} (sec^{-1})) for the reaction in methanol of *trans*-[Pt{P(C$_2$H$_5$)$_3$}$_2$(CH$_3$)Cl]: *p*-toluenesulfonic acid = 0.1 *M;* lithium chloride = 0.1 *M;* temperature 30°.

Table II. Pseudo-First-Order Rate Constants, k_{obsd} (sec^{-1}), in Methanol–Water at 30°[a]

$$trans\text{-}[Pt\{P(C_2H_5)_3\}_2(CH_3)Cl] \xrightarrow[(-CH_4)]{+(H^+,\ Cl^-)} trans\text{-}[Pt\{P(C_2H_5)_3\}_2Cl_2]$$

Expt no.	Acid concn × 10³, *M*	LiCl × 10³, *M*	H$_2$O, vol. %	10^4k_{obsd}, sec^{-1}
28	100	100	0	57
29	100	100	1.5	16.4
30	100	100	2.5	8.1

[a] Substrate concentration *ca.* 5 × 10^{-4} *M;* HA = *p*-toluenesulfonic acid.

Experiments no. 5–8 examine the effect of changing the ionic strength of the reaction mixture and indicate a

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[11] In fact, from Figure 3 we have obtained k_2 = 1.78 × 10^{-2} M^{-1} sec^{-1} and k_3 = 3 M^{-2} sec^{-1}. At [Cl$^-$] = 10^{-2} *M*, (k_2 + k_3[Cl$^-$]) = (1.78 ×10^{-2}) + (3 × 10^{-2}) = 4.78 × 10^{-2} M^{-1} sec^{-1}.

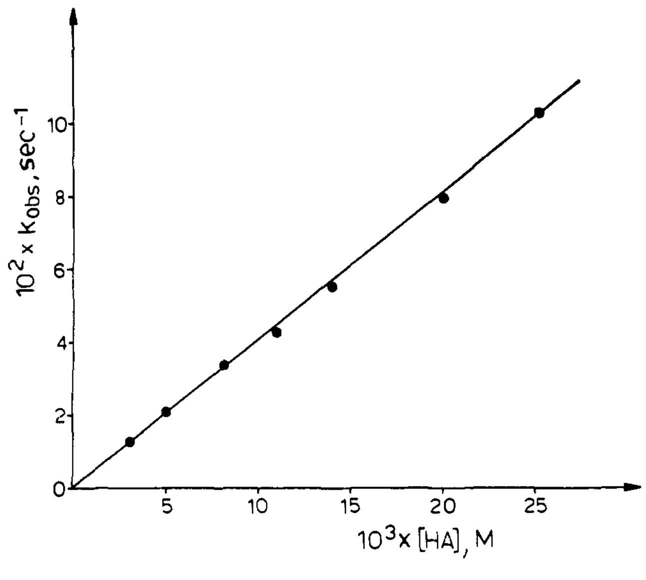

Figure 5. Dependence of the k_{obsd} values on the acid concentration for the reaction of *trans*-[Pt{$P(C_2H_5)_3$}$_2(CH_3)I$] in methanol at 40°: ionic strength = 5.8×10^{-2} *M;* slope (k_2) = 4.1 M^{-1} sec^{-1}.

negative salt effect on the rate of the reaction. This suggests a decreasing ionic character on going from the starting materials to the activated complex. No reaction is observed between *trans*-[Pt{$P(C_2H_5)_3$}$_2(CH_3)Cl$] and glacial acetic acid or nitrous acid at 40° in methanol.

In the case of the reaction of *trans*-[Pt{$P(C_2H_5)_3$}$_2(CH_3)I$] with *p*-toluenesulfonic acid in methanol (Figure 5) the rate was independent of the concentration of chloride (expt no. 22, 26, and 27). Unfortunately, the easy oxidation of iodide under these conditions prevented any studies of the dependence of rate on the concentration of iodide.

The proposed reaction mechanism for the electrophilic substitution of *trans*-[Pt{$P(C_2H_5)_3$}$_2(CH_3)Cl$] can be represented as shown in Figures 6a and b. In this mechanism it is thought that an electrophilic interaction occurs between the proton and a filled (originally $5d_{z^2}$) orbital of the four-coordinated platinum(II) in a preliminary reversible protonation step. As a consequence of the reduction of the d-electron charge by the added electrophile (H^+), the interaction between a nucleophilic reagent (the σ donor solvent or the competitive Cl^-) and the filled d_{z^2} orbital should also be reduced. Therefore the vacant orbital (originally $6p_z$) becomes available for bonding in the subsequent reversible nucleophilic attack. Thus, a labile six-coordinated platinum intermediate (IIa and/or IIb), in which the metal ion can be assigned the formal oxidation state IV, should be formed in a preliminary stepwise reaction, and the elimination of the alkyl group followed by rearrangement to a *trans* configuration should be the rate-controlling step.

Experiments carried out by using deuterio species should probably give some information concerning the extent of the bond breaking between platinum and hydrogen in the transition state (in Figure 6a).[8,12,13]

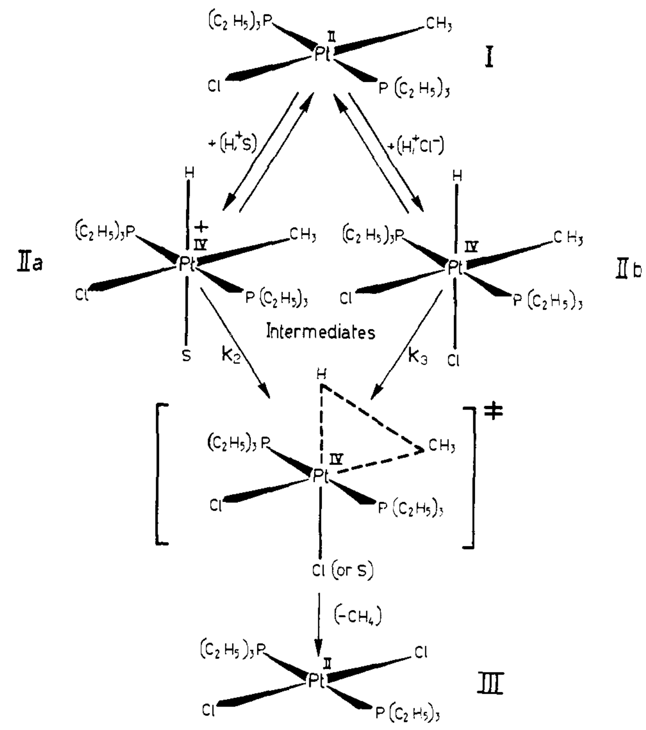

Figure 6a. Proposed reaction mechanism (S = solvent).

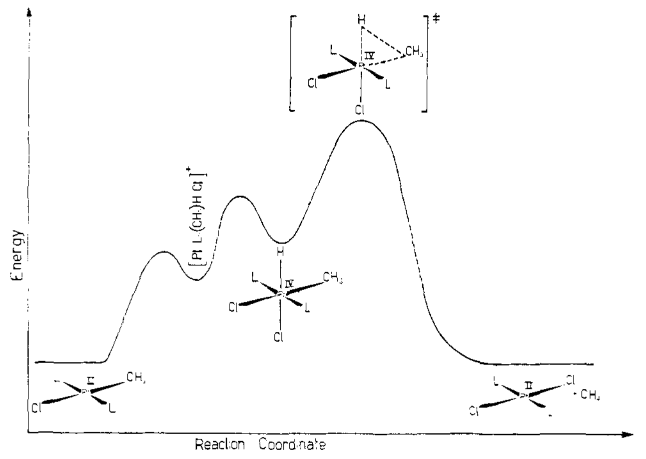

Figure 6b. Profile of the reaction (L = $P(C_2H_5)_3$).

It is pertinent to note that, on changing the ligand R, the reaction rate varies in the order $R^- = CH_3^- > C_6H_5^-$, reflecting the decreasing basicity of the carbanion as the pK_a values on the McEwen–Streitwieser–Applequist–Dessy (MSAD) scale for methane and benzene, are 40 and 37, respectively.[14]

This mechanism is, in part, very similar to that proposed by Halpern and Falk[15] for the deuterium–hydrogen exchange on *trans*-[Pt{$P(C_2H_5)_3$}$_2(H)Cl$], in which a reversible addition of both D^+ and Cl^- to form the labile platinum(IV) intermediate [Pt{$P(C_2H_5)_3$}$_2(H)(D)Cl_2$] is involved. In reaction 1 we have a similar intermediate, but we are looking at an alternative

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(12) (a) J. F. Harrod and A. J. Chalk, *Nature*, **205**, 280 (1965); (b) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(13) R. P. Bell, *Discussions Faraday Soc.*, **39**, 16 (1965).

(14) For references see D. J. Cram in "Fundamentals of Carbanion Chemistry," Vol. 4, Academic Press Inc., New York, N. Y., 1965, p 19.

(15) J. Halpern and C. D. Falk, "Exchange Reactions," International Atomic Energy Agency, Vienna, 1965, p 191; *J. Am. Chem. Soc.*, **87**, 3523 (1965).

decomposition of such an intermediate which, in the case of the hydride intermediate, $[Pt\{P(C_2H_5)_3\}_2(H)(D)Cl_2]$, results in a very slow elimination of hydrogen (HD). In other words, the intermediate II postulated in reaction 1 can decompose either to regenerate, in a fast reaction, the original complex or to eliminate, in a slow reaction, the molecule RH.

The value of k_{obsd}, estimated, for the hydrogen–deuterium exchange[15] of *trans*-$[Pt\{P(C_2H_5)_3\}_2(H)Cl]$ in 75% acetone–25% water at 30° is 2000×10^{-4} sec^{-1}, whereas at the same concentration of hydrogen chloride the k_{obsd} value of the *cis* elimination of molecular hydrogen in the reaction

$$\textit{trans}\text{-}[Pt\{P(C_2H_5)_3\}_2(H)Cl] \xrightarrow[(-H_2)]{+(H^+,Cl^-)} \textit{trans}\text{-}[Pt\{P(C_2H_5)_3\}_2Cl_2] \qquad (3)$$

in methanol at 40° has been found by us to be significantly smaller ($k_{obsd} = 1.2 \times 10^{-4}$ sec^{-1}), although an allowance should be made for the difference in solvent and ionic strength. This is in accord with the hypothesis that the decomposition of the intermediate dihydride is the rate-controlling step of reaction 3.

Evidence in support of the proposed mechanism is offered by the following considerations.

(i) **Basic Chemistry.** Irrespective of the finer details, the mechanism in Figure 6a requires an increase in oxidation state from the starting four-coordinate platinum(II) to a six-coordinate platinum(IV) hydrido complex, promoted by hydrogen chloride. It is well known that, for the d^8 transition metal ions, a two-electron oxidation to the six-coordinate d^6 becomes easier as one moves to the left from Au(III) (where it is not possible to get Au(V)[16]) to Ir(I). The oxidation of square-planar d^8 complexes to octahedral d^6 complexes occurs with halogens,[17,18] in some cases with hydrogen halides or alkyl halides, and in few cases with hydrogen to form unstable products. The nature of the coordinated ligands would normally affect the ease with which the $M^{n+} \rightarrow M^{(n+2)+}$ valence change occurs, the relative stabilities of the oxidation states for covalent compounds depending on the promotion energies of the involved d electrons and on the bond strengths. Moreover, platinum (in both the oxidation states II and IV) has the greatest tendency among the transition metals to form compounds with carbon–metal bonds, and the formation of stable bonds to hydrogen is a feature of d^8 metal ion chemistry. Evidence of interaction between a hydrogen of coordinated amines and the nonbonding d electron density of the metal comes from a study of N–H stretching frequencies in the complexes *trans*-$[PtL(piperidine)Cl_2]$ and from anomalous N–H stretching and deformation frequencies in complexes of the type $[Pt(NH_3)_2Cl_2]$,[19] but is not found for the analogous palladium(II) complexes. However, the X-ray structure of *trans*-diiodobis(dimethylphenylphosphine)palladium(II) indicates[20] for this compound a distorted octahedron in which one of the coordination positions is occupied by a hydrogen on the β carbon of the phenyl ring of the phosphine.

In the field of d^8 transition metal ion chemistry, Rh(I) and Ir(I) complexes react reversibly with molecular hydrogen to form stable adducts.[2,21] Examples of reversible oxidative additions by hydrogen chloride have been reported for Rh(I),[9,21,22] Ir(I)[23] (the latter giving a *cis*-(hydrogen halide)iridium(III) octahedral structure[24]), and Pt(II)[25,26] complexes. In addition four-coordinate planar Rh(I),[27] Ir(I), and isoelectronic Pt(II) complexes undergo a variety of novel addition and substitution reactions, the most significant being the reactions with alkyl halides,[19] olefins, and acetylenes.[28–31] Hydrido complexes, as well as the carbon–metal bonded compounds, of these transition elements are usually stabilized by acceptor ligands coordinated to the central atom.[10] No stable platinum(II) complexes of the type $[Pt\{P(C_2H_5)_3\}_2(R)H]$ (R = alkyl or aryl group) have been reported. Thus, the instability of similar platinum(IV) complexes in respect to the platinum(II) derivatives should be more pronounced because of the decreased effectiveness of the coordinated phosphines to withdraw nonbonding d electron density from the metal (in a higher oxidation state) *via* π bonding. This offers an interpretation for the postulated lability of the intermediates IIa and IIb (Figure 6a). It is pertinent to note that by treating $[Pt\{P(C_2H_5)_3\}_2\{Ge(C_6H_5)_3\}_2]$ with hydrogen chloride, $(C_6H_5)_3GeH$ and $(C_6H_5)_3GeCl$ have been obtained among other products, suggesting that the cleavage proceeds by way of an octahedral intermediate.[32,33]

(ii) **Mechanistic Studies.** The reaction kinetics of $[Ir^I\{P(C_6H_5)_3\}_2(CO)X]$ with hydrogen and with alkyl halides were found to obey a second-order rate law, indicating the tendency of d^8 complexes to increase their coordination number. The rates of the reactions with hydrogen halides are very fast.[34] The reaction of *trans*-$[Pt\{P(C_2H_5)_3\}_2(C_6H_5)_2]$ with acid to yield *trans*-$[Pt\{P(C_2H_5)_3\}_2(C_6H_5)Cl]$ obeys a second-order rate law. In this case, however, no dependence of the rate constant on the chloride concentration was found. Also, in this case a two-step mechanism involving a hydridoplatinum(IV) octahedral complex as intermediate was proposed.[35]

These considerations, including electrophilic catalyzed substitution reactions[36] and $SnCl_3^-$-catalyzed absorption of olefin by platinum(II) complexes,[37]

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(24) L. Vaska, personal communication.

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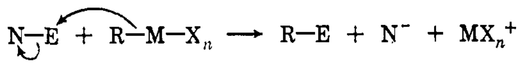
support the postulated formation of the hydridoplatinum(IV) complexes IIa and IIb, as labile reaction intermediates.

Electrophilic Attack on Post-Transition and Transition Metal–Carbon Bonded Compounds. The major part of the information available concerning electrophilic substitution comes from the extensive studies of the cleavage of carbon–metal bonds of organo compounds of post-transition elements, especially those of groups IIb and IVb.[38] Very few examples of electrophilic attack on analogous compounds of transition metal ions have been reported in the literature. Information of this type mainly concerns the reactions of tetracoordinate planar d^8 transition metal ions.

In the organometallic compounds of post-transition elements, the decidedly higher electronegativity of the carbon (2.55) with respect to the other metals is responsible for the polar character of the carbon–metal bond. This bond is therefore polarized in the sense $C^{\delta-}$–$M^{\delta+}$, the electron cloud of the bond being shifted toward the carbon atom.[39] The extent of this polarization depends, *inter alia*, on the nature of the metal and of the organic group attached to it.

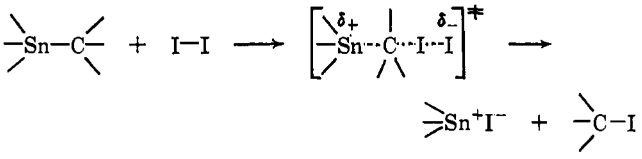
An electrophilic attack on a carbon–metal bond of compounds of post-transition elements may occur either by a unimolecular or a bimolecular process. In the first case (SE1 mechanism),[40a] the reactivity sequence is determined by the ability of the leaving group R to stabilize itself as a carbanion.[40b]

For the bimolecular electrophilic substitutions it is generally accepted that they proceed essentially by an electrophilic substitution at the saturated carbon with an open transition state (SE2 mechanism), although a closed cyclic mechanism (SF2 type) involving a concomitant nucleophilic attack at the metal atom is sometimes operative. A considerable amount of evidence is available to support the idea that electrophilic attack at the negative carbon atom and nucleophilic attack at the positive metal atom by any polar reagent are, generally, but not necessarily, concomitant processes. Representing the reagent as E–N (E is the electrophilic and N the nucleophilic end), these mechanisms can be written as[41,42]

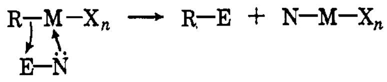


$$\text{N—E} + \text{R—M—X}_n \longrightarrow \text{R—E} + \text{N}^- + \text{MX}_n^+ \quad \text{SE2} \quad \text{(a)}$$

Thus the cleavage of tetraalkyltin compounds by iodine in polar solvents proceeds by a mechanism involving an "open" transition state, as depicted schematically below[43]

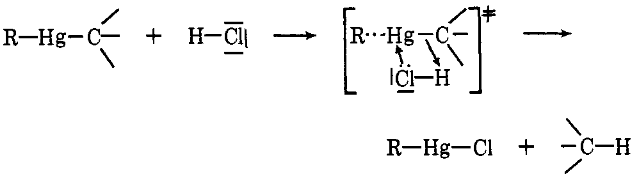


(in this process the solvent may act as a Lewis base).



$$\text{R—M—X}_n \longrightarrow \text{R—E} + \text{N—M—X}_n \quad \text{SF2 or SEi} \quad \text{(b)}$$

E.g., for the cleavage of dialkylmercury compounds by hydrochloric acid in dimethyl sulfoxide–dioxane, a cyclic mechanism has been proposed.[44,45]



Mechanism b has been also indicated[46] by the symbol SEi (internal electrophilic substitution) to denote a mechanism in which a cyclic transition state (four-, five-, or six-centered) is formed by concurrent attack of the two ends of the reagent upon the extremities of the polarized R–M bond.[46–48] Of course, one of the two modes of attack may prevail over the other. The SE2 mechanism is generally favored in polar solvents and the SF2 mechanism in nonpolar solvents because of the small charge separation in the transition state. An alternative bimolecular mechanism involves an electrophilic substitution *via* coordination (SEC)[49,50] in which the nucleophilic end coordinates to the metal in an initial step and then the alkyl group interacts with the electrophilic end of the reagent, leading to a cyclic transition state. This mechanism should be favored in cases where the central metal tends to increase its coordination number as, for example, the reactions of boron alkyl compounds.[51]

As the extent of metal–carbon bond polarization depends upon the electronegativities of the two bound atoms, the charge separation in platinum(II)–alkyl compounds should be rather small and in the direction $C^{\delta-}$–$Pt^{\delta+}$.

The average electronegativity values of some elements in specified oxidation states, as calculated from the enthalpy of formation of halides, MX_n,[52] are given below.

Zn(II) 1.65	C(IV) 2.55	Sn(IV) 1.96	Pd(II) 2.28
Hg(II) 2.00	Si(IV) 1.90	Pd(IV) 2.33	Pt(II) 2.20

As the polarity of the bond decreases, one expects a parallel gradual decrease in tendency for an E–N reagent to attack the polarized metal–carbon bond as would be the case on going from the organometallic compounds of the post-transition elements to the platinum(II) compounds.

In fact, upon treatment of *cis*- or *trans*-$[Pt^{II}\{P(C_2H_5)_3\}_2(R)_2]$ (R = methyl or phenyl group) with chlorine or iodine (X_2) in carbon tetrachloride the

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octahedral $[Pt^{IV}\{P(C_2H_5)_3\}_2(R)_2X_2]$ complexes are obtained as stable products,[10,53] suggesting that both the electrophilic and nucleophilic ends of the reagent attack the central metal atom. Under similar conditions, the post-transition organometallic compounds of the type R_nM undergo an electrophilic attack by the halogens, and the stable products $R_{n-1}MX$ and RX are obtained.[38]

Finally, taking into account the observations that (i) Rh, Ir, Pd, and Pt form stable complexes in which the central atom can have electron configurations d^6 and d^8 and (ii) the low-spin complexes with more than six d electrons exhibit coordination numbers particularly sensitive to the number of d electrons, it follows that these transition metal ions have, as their most prominent feature, the ability to change their coordination numbers with changes of oxidation state.[54]

This property may favor electrophilic substitution mechanisms different from those proposed for analogous post-transition metal compounds. It would also imply that normally the carbon–metal bonded compounds of transition elements with less than eight d electrons should follow, as a general trend, the mechanistic pattern of the organometallic post-transition elements.

In this connection, it is worth noting that the reactions of the d^3 Cr(III) organometallic compounds of the type $RCH_2Cr(H_2O)_5^{2+}$ with mercuric chloride proceed by an S_E2 mechanism in which the electrophilic attack by the mercury occurs at the α-carbon atom. Thus[55]

$$RCH_2\cdot Cr(H_2O)_5^{2+} + Hg_2X \longrightarrow RCH_2\cdot HgX + XCr(H_2O)_5^{2+}$$

Furthermore, the d^8 iridium(I) and in a few cases, platinum(II) complexes react with mercuric halides to give metal-bonded compounds, *e.g.*[16]

$$[(Ph_3P)_2(CO)Ir^{I}Cl] + HgX_2 \longrightarrow [(Ph_3P)_2(CO)ClXIr^{III}\text{-}HgX]$$

It is also likely that metal–carbon bonded compounds of Bi(III) and Sb(III) ($R_{3-n}MX_n$ type) may undergo oxidative addition reactions with a mechanism similar to that found for d^8 transition metal ions.

We have attempted to illustrate the spectrum of general behavior of d^8 complexes, which includes as limiting situations (i) the case in which a preequilibrium exists between the four-coordinated complex and the electrophile leading to a five-coordinated species which should be more sensitive to nucleophilic attack to give the substituted product and (ii) the case in which an oxidative addition occurs leading to the formation of stable six-coordinated compounds.[16,18,23,56]

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The Nature of Carbon Monoxide Bonding in Some *trans*-1,3-Dichloro-2-(4-Z-pyridine and -pyridine N-oxide)carbonylplatinum(II) Complexes

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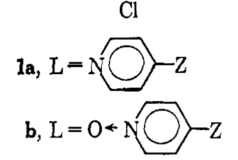
Abstract: Two series of new carbonyl complexes, **1a** and **1b**, have been prepared. The infrared and nmr spectra suggest little dπ-pπ* interaction between the carbon monoxide and platinum in these complexes. The nmr studies also indicate that the *trans*-labilizing effect of olefins is greater than that of carbon monoxide in square-planar Pt(II) complexes.

The discovery[1] that ethylene is readily replaced by carbon monoxide in the reaction



made available a large number of platinum(II) carbonyl complexes of structures **1a** and **1b**. We have determined the infrared and nmr spectra of some of these compounds in order to examine the nature of the platinum–ligand bonding. In particular, we wished to evaluate the extent of interaction between the filled d orbitals of Pt and the low-lying antibonding orbitals of CO which are concentrated on the carbon atom; this interaction presumably is responsible for the reported high *trans* effect of the carbon monoxide ligand.

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