and dried over molecular sieves. The preparation of iodobis(triphenylphosphine)(4-nitrophenyl)palladium was described previously.[1] Platinum complexes were prepared as described below. Triphenylphosphine was a product of the Ventron Corp. and it was used without further purification.

Tetrakis(triphenylphosphine)platinum(0). To a solution of 6.55 g (0.025 mol) of triphenylphosphine in 50 mL of warm absolute ethanol was added under argon a solution of 2.59 g (0.005 mol) of chloroplatinic acid hexahydrate dissolved in 7 mL of absolute ethanol. After about 5 min of stirring, 15 mL of 85% hydrazine hydrate was added. The milky solution immediately turned yellow and the product crystallized. After the mixture was cooled to room temperature, the product was filtered and washed with warm ethanol, with cold water, and finally with cold ethanol. After drying was done under reduced pressure, 5.88 g (92%) of the product was obtained.

General Procedure for Preparation of Platinum Complexes. A two- to threefold excess of aryl halide was stirred with a solution of the tetrakis(triphenylphosphine)platinum(0) complex in benzene (2.4 g in 35 mL was generally used). The clear solutions were stirred at room temperature for about 3 h and heated at reflux temperature for about 2 h more. On cooling of the mixtures, the yellow-orange crystalline products were separated by filtration, washed with ether, and dried under reduced pressure. Yields were 40–90% of theory. Analyses and melting points are given in Table V. The ν_{CO} observed in the carbonylation product is also listed (Table V).

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Registry No. 4-$CH_3OCOC_6H_4(I)Pt(PPh_3)_2$, 67226-47-5; 4-$ClC_6H_4(I)Pt(PPh_3)_2$, 67254-03-9; $C_6H_5(I)Pt(PPh_3)_2$, 67254-04-0; 4-$CH_3OC_6H_4(I)Pt(PPh_3)_2$, 67254-05-1; 4-$CH_3C_6H_4(I)Pt(PPh_3)_2$, 67254-06-2; 2-$CH_3OCOC_6H_4Pt(PPh_3)_2I$, 67226-48-6; 4-$O_2NC_6H_4Pd(PPh_3)_2Br$, 67254-07-3; 4-$O_2NC_6H_4Pd(PPh_3)_2I$, 67254-08-4; 4-$CH_3OCOC_6H_4Pd(PPh_3)_2I$, 67226-49-7; 4-$CH_3OC_6H_4I$, 696-62-8; C_6H_5I, 591-50-4; 4-$CH_3OCOC_6H_4I$, 619-44-3; 2-$CH_3OCOC_6H_4I$, 610-97-9; $C_6H_5CH_2OH$, 100-51-6; $C_6H_5CH_2NH_2$, 100-46-9; $PdCl_2(PPh_3)_2$, 13965-03-2; CO, 630-08-0.

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Mechanism of Electrophilic Cleavage of the Platinum–Carbon Bond in Platinum(II)–Diaryl Complexes

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A kinetic study is described of the electrophilic cleavage by the proton of one Pt–C σ bond in complexes of type *cis*-$[Pt(PEt_3)_2(YC_6H_4)_2]$ (Y = *p*-NMe_2, *p*-Me, *p*-OMe, H, *m*-OMe, *p*-F, *p*-Cl, *m*-F, *o*-Me, *o*-Et, *m*-CF_3) yielding *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ and YC_6H_5 in methanol and aqueous methanol. Electron-releasing substituents in the platinum-bonded aromatic rings increase the rates of electrophilic attack and a fairly good LFER is observed on plotting log k_{rel} vs. the Hammett σ parameter of the substituent Y in both solvents. Steric retardation occurs when the Pt–C bond is crowded by a neighboring ortho group. A large (ca. 6) kinetic isotope effect is observed on carrying out the Pt–C bond cleavage with DCl in MeOD/D_2O (90/10% v/v). The rates decrease with increasing water content of the solvent mixture. A mechanism is proposed which involves rate-determining direct attack of the proton on the Pt–C bond with release of YC_6H_5 in a three-center transition state. The resulting transient intermediate may be either converted to *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ by scavenging chloride ion (if present) or isomerized to *trans*-$[Pt(PEt_3)_2(YC_6H_4)S]^+$ in the absence of good nucleophiles (S = solvent). The mechanism is discussed within the framework of general acidolysis of metal–carbon bonds in organometallic compounds.

Introduction

The cleavage of non-transition-metal–carbon bonds (*demetalation*) has been extensively investigated and its mechanism elucidated in detail.[1] When alkyl groups are being cleaved in a bimolecular process, electrophilic substitution at the saturated carbon may take place via an open transition state (S_E2). A cyclic mechanism (S_Ei) may also occur through a cyclic transition state by concurrent attack of the two ends of the reagent on the polarized metal–carbon bond. This

$$X_n\text{–M–alkyl} + \text{E–N} \longrightarrow \left[X_n\text{–M}\cdots\text{alkyl} \right]^{\ddagger} \longrightarrow \text{alkyl–E} + \text{N–M}X_n \quad (S_Ei)$$

mechanistic view applies particularly to the cleavage of the metal–carbon bond in group 2B and 4B organometallics. In particular, for protonolysis reactions the driving force of the electrophilic attack is in any case the rate-determining proton transfer to the substrate. The extent of interaction of the proton with the alkyl group and of the nucleophile with the metal will depend on the charge separation being developed on both the cleaved group and the metal moiety, as well as

$$X_n\text{–M–alkyl} + \overset{\delta+}{\text{E}}\text{–}\overset{\delta-}{\text{N}} \rightarrow [X_n\text{–M}\cdots\text{alkyl}\cdots\text{E}\cdots\text{N}]^{\ddagger} \rightarrow \text{alkyl–E} + \text{N}^- + MX_n^+ \quad (S_E2)$$

E = electrophilic end, N = nucleophilic end } of the reagent

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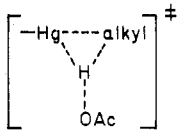
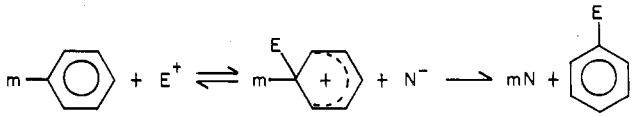
on the solvent polarity. Thus, for the protonolysis of alkylmercury bonds in acetic acid a three-center transition state has been proposed.[2]



As for the cleavage of non-transition-metal–aryl bonds, there is a body of evidence to show that electrophilic attack on the substrate produces a labile σ complex of the Wheland type:



The proton attack is rate determining; that is, subsequent reaction of the intermediate with the nucleophile is faster than its reversal to starting reactants.[1b]

The mechanism of electrophilic cleavage of metal–carbon bonds in transition-metal complexes is especially intriguing since here the problem arises of the selectivity of attack.[1c,3] This may in principle take place by (i) direct attack on the metal–carbon bond, (ii) attack on the aromatic ring in the case of metal–aryl derivatives, and (iii) a prior oxidative addition on the central metal followed by reductive elimination. The latter pathway is strictly related, inter alia, to the oxidation state of the metal and its promotional energy. An oxidative addition mechanism has been proposed, for instance, for the protonolysis of *trans*-$[Pt(PEt_3)_2MeX]$[3b] and of dialkylaurate(I) species, R_2Au^-.[4] By contrast, acidolysis of trialkyl(phosphine)gold(III) or dialkylmercury(II) is assumed to involve rate-determining proton transfer to carbon and concomitant breaking of the bond to the metal.[5]

For the specific case of platinum–carbon organometallic compounds, the wealth of preparative and structural data available, while not militating against the oxidative addition mode of electrophilic cleavage, cannot give by itself unambiguous and clear-cut clues as to the intimate mechanism of the process. The latter, as a matter of fact, receives little support from the mere knowledge of reaction products whose nature is governed by both kinetic and thermodynamic factors. On the other hand, the assessment of a mechanism cannot be made to the neglect of all the experimental evidence on hand, inclusive of kinetic and extra-kinetic findings.

The only mechanistic investigations on platinum complexes known so far were made by P.U. and U.B.[3] in 1967 when studying the kinetics of electrophilic cleavage of the Pt–C bond by the proton in substrates of type *trans*-$[Pt(PEt_3)_2Ph_2]$ and *trans*-$[Pt(PEt_3)_2MeX]$ (X = Cl, I).

Along these lines, we have undertaken a systematic study of the cleavage of the first Pt–C bond in *cis*-$[Pt(PEt_3)_2(YC_6H_4)_2]$ by the proton to yield *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ and YC_6H_5, where the substituent Y encompasses a wide range of electron-donating ability. The aim was to exploit the changes of electronic density on the platinum–carbon bond as a means of ascertaining the site of electrophilic attack and possibly to outline a general mechanistic pattern for these reactions.[6]

Experimental Section

Materials. Benzene and diethyl ether were dried over sodium wire. Anhydrous methanol was obtained by distillation of the reagent grade solvent over $Mg(OCH_3)_2$. $LiClO_4$ "anhydrous" (99.8%) was purchased from K&K Fine and Rare Chemicals. All other reagents were used without further purification. The starting material *cis*-$[Pt(PEt_3)_2Cl_2]$ was prepared by Chatt and Wilkins' method.[7]

Diaryl Substrates. Some of the complexes *cis*-$[Pt(PEt_3)_2(YC_6H_4)_2]$ were prepared by literature methods, Y (reference number): *p*-OMe (8), *p*-Me (9), H (9), *p*-F (10), *m*-F (10), *o*-Me (9), *o*-Et (11).

The following are new.

***cis*-$[Pt(PEt_3)_2(m\text{-}CF_3C_6H_4)_2]$.** *cis*-$[Pt(PEt_3)_2Cl_2]$ (1 g) suspended in dry benzene (20 mL) was treated with Grignard reagent prepared from magnesium (0.48 g), *m*-trifluoromethylbromobenzene (2.8 mL), a trace of iodine, and diethyl ether (30 mL). The mixture was stirred at 20 °C for 2 h and then hydrolyzed with ice and dilute hydrochloric acid. The crude product isolated from the organic layer by evaporation was chromatographed on alumina. Elution with petroleum ether (bp 40–70 °C) containing ether (10%) afforded *cis*-$[Pt(PEt_3)_2(m\text{-}CF_3C_6H_4)_2]$ as needles (0.25 g) from petroleum ether, mp 135–137 °C. Anal. Calcd for $C_{26}H_{38}F_6P_2Pt$: C, 43.27; H, 5.30. Found: C, 43.44; H, 5.35.

***cis*-$[Pt(PEt_3)_2(p\text{-}ClC_6H_4)_2]$.** This was prepared in an analogous way, from *cis*-$[Pt(PEt_3)_2Cl_2]$ in benzene and *p*-ClC_6H_4MgCl in THF. The crude product was recrystallized twice from methanol and then chromatographed on alumina. Elution with petroleum ether (40–70 °C) containing ether (10%) gave the product as colorless needles from methanol, mp 151–153 °C. Anal. Calcd: C, 44.05; H, 5.85. Found: C, 44.32; H, 6.07.

***cis*-$[Pt(PEt_3)_2(p\text{-}CF_3C_6H_4)_2]$.** *cis*-$[Pt(PEt_3)_2Cl_2]$ (0.7 g) in dry benzene (25 mL) was reacted with 20 mL of an ethereal solution of *p*-$CF_3C_6H_4Li$ 0.2 M (prepared from *p*-$CF_3C_6H_4Br$ by halide–metal interchange with *n*-butyllithium[12]). After 2 h of stirring at room temperature, the mixture was hydrolyzed with ice. The crude product isolated from the organic layer was washed with petroleum ether (40–70 °C) and chromatographed on alumina. Elution with petroleum ether containing ether (10%) gave the product as white needles from ethanol, mp 159–162 °C. Anal. Calcd: C, 43.27; H, 5.30. Found: C, 43.06; H, 5.20.

***cis*-$[Pt(PEt_3)_2(Me_2N\text{-}p\text{-}C_6H_4)_2]$.** *cis*-$[Pt(PEt_3)_2Cl_2]$ (1 g) suspended in dry benzene (20 mL) was treated with an ether solution (20 mL; 0.7 M) of *p*-$Me_2NC_6H_4Li$. After 30 min of stirring at room temperature, benzene and water were added. The brown crude product isolated from the organic layer was washed with small amounts of petroleum ether and then recrystallized from ethyl alcohol as white needles, mp 162–163 °C. Anal. Calcd: C, 50.06; H, 7.50; N, 4.06. Found: C, 50.18; H, 7.81; N, 4.17.

***cis*-$[Pt(PEt_3)_2(m\text{-}MeOC_6H_4)_2]$.** This was prepared in an analogous way from *cis*-$[Pt(PEt_3)_2Cl_2]$ and *m*-methoxyphenyllithium (20% excess).[12] After stirring for 1 h, benzene and water were added. The pale yellow oil resulting from evaporation of the organic layer was converted into a solid product over P_2O_5 in vacuo. This was crystallized from ethanol, mp 107–110 °C. Anal. Calcd: C, 48.35; H, 6.85. Found: C, 48.18; H, 6.80.

Cis Monoaryl Complexes. Some of the complexes *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ were prepared by literature methods, Y (reference number): H (9), *o*-Me (9), *p*-Me (9), *m*-F (10), *p*-F (10), *o*-Et (11).

The following new compounds (Y = *m*-OMe; *p*-OMe; *p*-Cl; *m*-CF_3; *p*-CF_3) were prepared using the general procedure described by Chatt and Shaw.[9] Thus, a weighed amount of the corresponding diaryl compound in dry benzene was treated with a stoichiometric quantity of dry HCl in diethyl ether. After evaporation of the solvent the residue was crystallized as a white compound from a benzene–petroleum ether mixture.

Anal. Calcd for *cis*-$[Pt(PEt_3)_2(m\text{-}MeOC_6H_4)Cl]$ (mp 117–120 °C), $C_{19}H_{37}ClOP_2Pt$: C, 39.75; H, 6.50. Found: C, 40.18; H, 6.69. Calcd for *cis*-$[Pt(PEt_3)_2(p\text{-}MeOC_6H_4)Cl]$ (mp 113–115 °C), $C_{19}H_{37}ClOP_2Pt$: C, 39.75; H, 6.50. Found: C, 39.65; H, 6.44. Calcd for *cis*-$[Pt(PEt_3)_2(p\text{-}ClC_6H_4)Cl]$ (mp 145–150 °C), $C_{18}H_{34}Cl_2P_2Pt$: C, 37.40; H, 6.09. Found: C, 37.46; H, 5.97. Calcd for *cis*-$[Pt(PEt_3)_2(m\text{-}CF_3C_6H_4)Cl]$ (mp 150–152 °C), $C_{19}H_{34}F_3ClP_2Pt$: C, 37.29; H, 5.60. Found: C, 37.02; H, 5.43. Calcd for *cis*-$[Pt(PEt_3)_2(p\text{-}CF_3C_6H_4)Cl]$ (mp 159–162 °C), $C_{19}H_{34}F_3ClP_2Pt$: C, 37.29; H, 5.60. Found: C, 37.50; H, 5.62.

The stereochemistry of both diaryl and monoaryl cis complexes was established by the method of Goggin and Goodfellow.[13] The IR spectra (measured on Nujol mulls with a Perkin-Elmer 577 spectrophotometer) showed two Pt–P stretching frequencies in the region between 410 and 440 cm^{-1} whereas only one is expected for the trans derivatives. In the *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ complexes the Pt–Cl

Table I. Pseudo-First-Order Rate Constants, k_{obsd}/s^{-1}, for the Reactions: *cis*-$[Pt(PEt_3)_2(C_6H_4Y)_2] \xrightarrow[(+Cl^-)]{H^+}$ *cis*-$[Pt(PEt_3)_2(C_6H_4Y)Cl]$ + C_6H_5Y in Methanol and 90% Aqueous Methanol at 30 °C (Ionic Strength = 0.3 M ($LiClO_4$), Complex = 2.0×10^{-4} M)

	methanol			90% aqueous methanol		
Y	$[H^+]$, M	$[Cl^-]$, M	$10^4 k_{obsd}/s^{-1}$	$[H^+]$, M	$[Cl^-]$, M	$10^4 k_{obsd}/s^{-1}$
p-OMe	0.001	0.05	22.3	0.005	0.05	9.5
	0.002	0.05	41.1	0.01	0.05	14.2
	0.004	0.05	72.4	0.02	0.05	26.8
	0.006	0.05	115.0	0.03	0.05	37.2
	0.008	0.05	148.0	0.04	0.05	46.2
				0.05	0.00	59.7
				0.05	0.001	57.6
				0.05	0.01	57.0
				0.05	0.05	58.0
				0.05	0.20	58.4
				0.06	0.05	70.6
				0.07	0.05	82.5
p-Me	0.0025	0.05	9.10	0.005	0.00	2.31
	0.0050	0.005	16.97	0.005	0.05	2.33
	0.0050	0.01	17.10	0.0075	0.05	3.42
	0.0050	0.05	16.90	0.02	0.05	8.60
	0.0075	0.05	26.70	0.03	0.05	13.40
	0.010	0.05	35.80	0.04	0.05	16.90
				0.05	0.05	22.30
				0.06	0.05	26.00
				0.07	0.05	30.50
H	0.002	0.005	1.09	0.05	0.05	4.13
	0.002	0.05	1.10	0.07	0.05	5.92
	0.002	0.10	1.11	0.08	0.05	6.49
	0.005	0.05	2.70	0.10	0.05	8.01
	0.01	0.05	5.60			
	0.02	0.05	11.10	0.14	0.05	11.4
	0.03	0.05	17.20	0.16	0.05	13.3
	0.05	0.05	28.10	0.20	0.00	15.6
				0.20	0.005	16.5
				0.20	0.05	16.6
				0.20	0.10	16.1
m-OCH_3	0.005	0.05	3.10	0.05	0.05	2.30
	0.0075	0.05	4.20	0.08	0.05	3.90
	0.010	0.05	6.00	0.10	0.05	4.90
	0.025	0.05	14.20	0.16	0.05	8.01
	0.050	0.05	29.10	0.25	0.05	12.50
p-F	0.01	0.05	1.40	0.05	0.05	1.54
	0.02	0.05	3.05	0.08	0.05	2.30
	0.03	0.05	4.75	0.10	0.05	2.86
	0.04	0.05	6.43	0.14	0.05	3.90
	0.05	0.05	7.90	0.16	0.05	4.40
				0.20	0.00	5.52
				0.20	0.01	5.73
				0.20	0.05	5.65
				0.20	0.10	5.62
				0.23	0.05	6.55
p-Cl	0.05	0.05	1.70	0.06	0.05	0.28
	0.05	0.10	1.72	0.10	0.05	0.55
	0.05	0.20	1.80	0.14	0.05	0.76
	0.10	0.10	2.50			
	0.20	0.20	5.52			
	0.25	0.25	6.88	0.26	0.05	1.33
m-F	0.05	0.05	0.70	0.05	0.05	0.12
	0.125	0.125	1.65	0.10	0.05	0.28
	0.166	0.166	2.27	0.25	0.05	0.57
	0.20	0.200	2.74			
o-Me	0.05	0.05	4.41			
	0.10	0.10	7.40			
	0.15	0.15	10.90			
	0.20	0.20	15.20			
	0.25	0.25	19.10			
o-Et	0.05	0.05	1.64			
	0.10	0.10	2.79			
	0.15	0.15	4.12			
	0.20	0.20	5.24			
	0.25	0.25	6.50			
m-CF_3	0.10	0.10	0.27			
	0.15	0.15	0.40			
	0.186	0.186	0.48			
	0.28	0.28	0.75			
p-CF_3	0.10	0.10	0.10			
	0.15	0.15	0.21			
	0.25	0.25	0.29			

Table II. Second-Order Rate Constants for the Reactions *cis*-$[Pt(PEt_3)_2(C_6H_4Y)_2] + H^+ + Cl^- \rightarrow$ *cis*-$[Pt(PEt_3)_2(C_6H_4Y)Cl] + C_6H_5Y$ at 30 °C[a]

Y	isosbestic points, nm	wavelength for kinetics, nm	methanol 10^2k_2,[b] M^{-1} s^{-1}	90% aqueous methanol 10^2k_2,[b] M^{-1} s^{-1}
p-OMe	254, 264	274	180 ± 5	11.2 ± 0.1
p-Me	292, 304	274	36 ± 1	4.34 ± 0.05
o-Me	245, 258, 283, 305	268	0.74 ± 0.03	
o-Et	243, 258, 283, 305	268	0.24 ± 0.003	
H	258, 288, 305	274	5.66 ± 0.04	0.83 ± 0.01
m-OMe	242, 267, 286, 307	258	5.79 ± 0.07	0.510 ± 0.003
p-F	238, 258, 290, 298	268	1.64 ± 0.02	0.277 ± 0.005
p-Cl	285, 300	268	0.28 ± 0.01	0.051 ± 0.003
m-F	244, 258, 284, 300	270	0.136 ± 0.004	0.022 ± 0.003
m-CF_3	258, 280, 303	266	0.027 ± 0.001	
p-CF_3	280, 301	260	0.012 ± 0.003	

[a] Ionic strength 0.3 M ($LiClO_4$). Uncertainties quoted are estimated standard errors. [b] Slopes of plots of k_{obsd} vs. $[H^+]$.

Table III. Effect of the Water Content of the Solvent Methanol on the Pseudo-First-Order Rate Constants, k_{obsd}, for the Reaction

$$cis\text{-}[Pt(PEt_3)_2(p\text{-}MeC_6H_4)_2] \xrightarrow{H^+,\ Cl^-} cis\text{-}[Pt(PEt_3)_2(p\text{-}MeC_6H_4)Cl] + MeC_6H_5$$

([HCl] = 0.05 M; μ = 0.3 ($LiClO_4$); 30 °C)

vol % of water	10^3k_{obsd}, s^{-1}	vol % of water	10^3k_{obsd}, s^{-1}
0.0	18.0	6.2	2.5
0.7	11.8	8.2	2.1
1.7	6.1	10.2	2.1
3.2	3.6	13.2	2.1
4.2	3.0		

stretch is centered at 280 ± 3 cm^{-1}. A clear-cut confirmation of the cis geometry for these latter compounds arises from the fact that all of them undergo spontaneous cis-to-trans isomerization in protic solvents.[11] A kinetic study of these processes will be published in a forthcoming paper.[14]

The ^1H NMR spectra were determined on a Hitachi Perkin-Elmer R 24 B spectrometer with $CDCl_3$ as the solvent and Me_4Si as an internal reference. The number of protons, determined by integration, were in agreement with the assigned structures. In the diaryl compounds the methyl peaks of the coordinated phosphine overlap the methylene absorptions. In the complexes *cis*-$[Pt(PEt_3)_2(YC_6H_4)Cl]$ the methyl protons of PEt_3 give a much more complex pattern which is still distinguishable from the very characteristic quintet exhibited by the trans isomers.[10,15]

Kinetics. The kinetics were followed spectrophotometrically in anhydrous methanol or aqueous methanol (up to a 10% v/v water content) under pseudo-first-order conditions at a constant ionic strength of 0.3 M $LiClO_4$ at 30 °C. For the runs in anhydrous methanol the desired proton and chloride concentrations were obtained by transferring into a standard volumetric flask the appropriate amounts of standardized solutions of dry hydrogen chloride, LiCl, and anhydrous $LiClO_4$ (99.8%) in methanol. For the runs in aqueous methanol the solution of reagents other than the complex was made up in the same way, except that the proton concentrations were obtained by dissolving the appropriate amounts of a standardized solution of $HClO_4$. For the kinetic isotope effect experiments, the solutions of DCl made up in MeOD–D_2O (10%) were titrated to determine their precise concentrations.

The reactions were carried out in a silica cell in the thermostated cell compartment of a double-beam Optica CF 4 spectrophotometer where the temperature remained constant to ±0.05 °C. The reagent solution was brought to reaction temperature in the spectrophotometer and the reaction was started by adding a weighed amount of a finely powdered sample of the complex and shaking the solution rapidly. The spectrum between 330 and 230 nm was scanned from time to time and in all the cases well-defined isosbestic points were found (see Table II). Faster reactions were followed at a single wavelength at which the absorbance change was largest by using a Beckman DU spectrophotometer, equipped with a Saitron 301 photometer and a Servogor S recording potentiometer.

Final spectra after completion of kinetic runs were identical with those of the corresponding cis monoaryl chlorides prepared independently. The pseudo-first-order rate constants, k_{obsd}, were obtained from a nonlinear least-squares fit of experimental data to $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obsd}t)$ with A_0, A_∞, and k_{obsd} as the parameters to be optimized (A_0 = absorbance after mixing of reactants, A_∞ = absorbance at completion of reaction). This procedure proved especially useful for the slowest reactions for which experimental observation of A_∞ was unfeasible. The cleavage of the second Pt–C σ bond was sufficiently slow under the experimental conditions described to allow the rates of cleavage of the first one to be easily followed.

Geometry of the Final Monoaryl Complexes: Role of Scavenging Agents. *cis*-$[Pt(PEt_3)_2Ph_2]$ (70 mg) in 10 mL of MeOH was reacted with 0.25 mL of a 0.5 M $HClO_4$ solution in MeOH at room temperature, the reaction progress being monitored by spectrophotometry in the UV–vis region. *Once the reaction was complete* excess lithium chloride was added and *trans*-$[Pt(PEt_3)_2(Ph)Cl]$ was isolated in virtually quantitative yield [identified by melting point (105–106 °C; lit.[9] 105–107 °C) and IR spectrum].

These cis–trans isomerizations accompanying Pt–C cleavage to monoaryl complexes in the absence of chloride ion were also followed kinetically for aryl = *p*-$MeOC_6H_4$ and *p*-MeC_6H_4: the reaction rates proved to be identical with those in the presence of Cl^- at the same proton concentrations but the UV spectra of the reaction mixtures below 260 nm were different, confirming that the monoaryl products had trans configuration (see Discussion).

Results and Discussion

Cleavage of the first Pt–C σ bond in complexes of the type *cis*-$[Pt(PEt_3)_2(YC_6H_4)_2]$ by electrophilic attack in the presence of chloride ion takes place according to the reaction

$$cis\text{-}[Pt(PEt_3)_2(YC_6H_4)_2] + H^+ + Cl^- \xrightarrow[\text{MeOH or MeOH/H}_2\text{O}]{30\ ^\circ C} cis\text{-}[Pt(PEt_3)_2(YC_6H_4)Cl] + YC_6H_5 \quad (1)$$

where Y = *p*-OMe, *p*-Me, H, *m*-OMe, *p*-F, *p*-Cl, *m*-F, *o*-Me, *o*-Et, *m*-CF_3, and *p*-CF_3

The pseudo-first-order rate constants, k_{obsd}, were linearly dependent on proton concentration but independent of chloride concentration at constant ionic strength (0.3 M, $LiClO_4$), and fitted rate law (2). The k_{obsd} values are listed in Table I for

$$k_{obsd} = k_2[H^+] \quad (2)$$

the solvents methanol and 10% aqueous methanol (v/v). The values of k_2, from linear regression analysis of rate law (2), are set forth in Table II (uncertainties are standard errors of estimates).

Addition of water to the solvent methanol effectively depresses the rates which level off to a constant value at a water content of about 5% in volume; this is shown typically by the

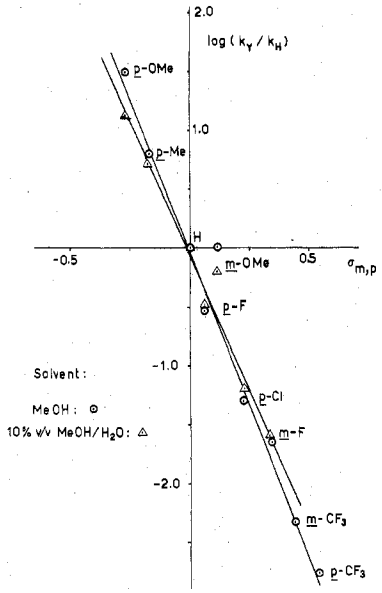


Figure 1.

dependence of k_{obsd} on the solvent's water content for Y = *p*-Me in Table III.

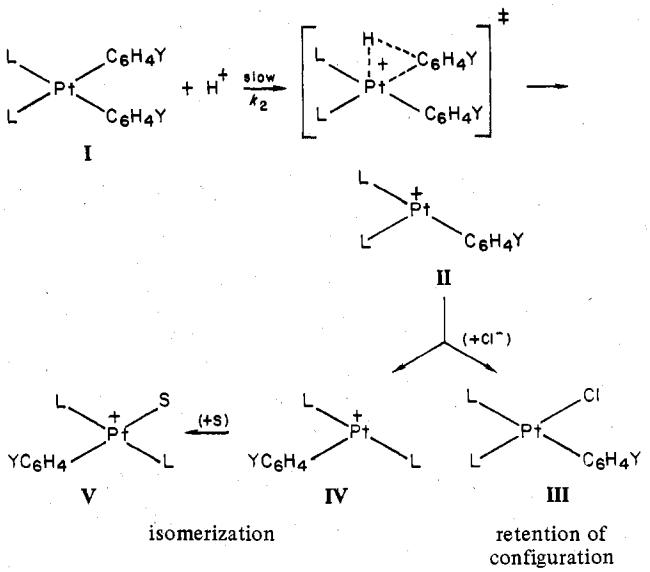
When reactions (eq 1) are carried out in the presence of excess chloride ion, the final monoaryl complexes retain the same cis configuration at the platinum center as their bisaryl parent substrates. In the absence of chloride ion, the cleavage of the first Pt–C σ bond is accompanied by isomerization to the trans monoaryl analogues.

The values of log (k_Y/k_H) in Table III fit a fairly good linear relationship with Hammett's σ parameters of the Y substituents in the platinum-bonded aromatic rings of the substrates, in the sense that *the rates of electrophilic attack increase markedly with increasing electron-donating ability of the Y substituent* both in methanol ($\rho = -5.1 \pm 0.3$; $r = -0.9856$) and in 10% aqueous methanol ($\rho = -4.5 \pm 0.4$; $r = -0.9845$) (Figure 1).[18] The rates appear to be markedly depressed by increased steric hindrance in the vicinity of the Pt–C bond (cf. k_2 values for Y = *p*-Me vs. *o*-Me in Table II).

A large (ca. 6) overall kinetic isotope effect is observed on carrying out the Pt–C bond cleavage with DCl in MeOD/D_2O (90%/10% v/v), as shown typically for Y = *p*-MeO and *p*-Me in Table IV.

A mechanism which is consistent with this body of evidence is shown in Scheme I. Structural and spectroscopic studies on platinum–aryl complexes indicate that there is substantial interaction of the metal d orbitals with the aryl π system. Thus, the simplest way of envisaging the attack by the proton is to consider the Pt–aryl bond as the reaction site. The protonation will then involve a perturbation of the delocalized metal–aryl bonding orbital with concomitant loosening of the Pt–carbon linkage, in a three-center transition state. No nucleophilic assistance is required by the activation process and therefore the rate is independent of chloride ion concentration. The rate will increase with increasing electron density on the Pt–C axis, as determined by the electron-donating ability of the substituent Y on the aromatic ring. This is in line with the highly negative value of ρ in the Hammett relationship observed. Also, the rate increases with the ease of electron detachment from platinum, as measured by anodic oxidation potentials of the metal substrates from cyclic voltammetry experiments to be described in a forthcoming publication. These arguments support the view that the platinum center is involved in the activation process, although they fall short of establishing a full-fledged oxidative addition to platinum(IV).

Scheme I



(L = PEt_3; S = solvent)

Table IV. Pseudo-First-Order Rate Constants, k_{obsd}, for the Reactions

$$cis\text{-}[Pt(PEt_3)_2(YC_6H_4)_2] \xrightarrow[+Cl^-]{D^+} cis\text{-}[Pt(PEt_3)_2(YC_6H_4)Cl] + YC_6H_4D$$

in MeOD/D_2O (10% v) at 30 °C. Complex concn 20 × 10^{-4} M

Y	[DCl], M	$10^4 k_{obsd}$, s^{-1}	$10^2 k_2$, M^{-1} s^{-1}
p-OMe	0.0125	2.75	2.06 ± 0.05
	0.032	6.75	
	0.061	12.10	
	0.092	19.50	
	0.125	25.7	
p-Me	0.011	0.732	0.71 ± 0.006
	0.031	2.23	
	0.062	4.36	
	0.085	5.97	
	0.119	8.47	

In this connection it is worth mentioning that cleavage of the first Pt–C bond by protonolysis in *cis*-[$Pt(PEt_3)_2Me_2$] is ca. 10^6 times faster than in *cis*-[$Pt(PEt_3)_2(aryl)_2$] under comparable conditions, whereas the same reaction on *cis*-[$Pt(PEt_3)_2(C_6F_5)_2$] is immeasurably slow;[14] this reactivity order—Me >> aryl > C_6F_5—reflects a decreasing electron density at the protonation site compounded with an increasing Pt–C bond strengthening. The large kinetic isotope effect (ca. 6) observed is near to the highest one expected when the proton is half transferred and *provides unmistakable evidence that the driving force of protonolysis is the rate determining transfer to the substrate,*[16] *as shown in Scheme I*, with the bulk at the protonation site playing an adverse role (cf. the rate-depressing effect of ortho substituents). Such a large isotope effect is hardly in agreement with any alternative mechanism, such as the following one, which we had proposed[6] in a preliminary account of this work at a time when the kinetic isotope effect experiments had indeed not yet been carried out.

$$L_2Pt(YC_6H_4)_2 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [L_2Pt(H)(YC_6H_4)_2]^+ \xrightarrow{k_2} [L_2Pt(YC_6H_4)]^+ + YC_6H_5 \xrightarrow[+Cl^-]{fast} L_2Pt(YC_6H_4)Cl$$

This mechanism, which involves a protonated platinum species

as an intermediate and would yield the same rate law form, is likely to entail a much smaller isotope effect than observed, due to the composite nature of the associated k_{obsd} rate parameter [$k_{obsd} = k_1k_2[H^+]/(k_{-1} + k_2)$]. This would also hold true if the protonation step were a rapid preequilibrium one[16] ($k_{obsd} = K_{eq}k_2[H^+]$).

The marked decrease in rate on going from methanol to aqueous methanol is mostly due to stabilization of the electrophile H^+ through solvation by the more polar water. In this context it would be tempting to quantify this effect in terms of the reduction in free energy of H^+ on addition of water. The free energy of transfer of H^+ from methanol to aqueous methanol, ΔF_T, may be obtained by interpolation from data given by Feakins et al.[17] and the rate decrease corresponding to this free energy may be taken as $\exp(\Delta F_T/RT)$. However, when this procedure is applied to data in Tables II and III the calculated rate constant ratios are somewhat different from the experimental, indicating that different solvation of the starting complexes on changing the solvent may play some role in producing this solvent effect.[19]

For the steps following the first rate-determining protonolysis, we propose a pathway similar to the mechanism that has been assumed[11] for the uncatalyzed cis–trans isomerization in Pt(II) complexes. The intermediate resulting from electrophilic attack is taken to be a three-coordinate species, II, whose fate is governed by the presence of nucleophiles in the system. When chloride ion is present, the vacant coordination site in II is blocked before the intermediate isomerizes to its "trans-like" counterpart, IV, thereby leading to retention of configuration in the ensuing monoaryl platinum product, III; in the absence of good nucleophiles (viz., when perchlorate ion is available) cis to trans isomerization, II → IV, can take place and the final monoaryl complex has trans configuration (addition of chloride at this stage will allow its isolation as *trans*-[$Pt(PEt_3)_2$(aryl)Cl], see Experimental Section). However, since we lack direct experimental evidence other than product analysis at this juncture, we cannot rule out the possibility that the intermediate II is a four-coordinate solvento species, *cis*-[$Pt(PEt_3)_2$(aryl)S]$^+$ (S = solvent) from which chloride ion, if present, will displace the solvent before isomerization to *trans*-[$Pt(PEt_3)_2$(aryl)S]$^+$ can take place.

Comparison of Mechanisms. An alternative mechanism, involving a Wheland-type intermediate (see Introduction), would accommodate all experimental findings as well, except for the fact that in some aromatic substitutions steric bulkiness produces an *increase* in rate due to the $sp^2 \rightarrow sp^3$ hybridization change. Furthermore, unsaturated non-transition organometallics undergo proton attack faster than saturated ones, contrary to what is observed in our case.

It is worth considering at this juncture that the protonolysis of *trans*-[$Pt(PEt_3)_2$MeCl][3b] takes place by a two-term rate law which includes an additional third-order chloride-dependent path beside the second-order term: $k_{obsd} = k_2[H^+] + k_3[H^+][Cl^-]$. This can be taken to imply that protonolysis for the third-order term involves prior oxidative addition of H^+, Cl^- to the Pt(II) substrate to give a Pt(IV) adduct (stabilized by coordination of chloride ion), from which methane is slowly eliminated. In agreement with this view, we have found an inverse solvent isotopic effect ($k_H/k_D \simeq 0.5$) for this reaction, as expected for a preequilibrium proton transfer followed by a rate-determining reaction of the protonated substrate[16] (however, a small or even substantially inverse isotope effect does not rule out a rate-determining proton transfer with a product-like transition state, so that isotope effects in this range do not allow a decision between the two mechanisms).

By contrast, the protonolyses of *cis*-[$Pt(PEt_3)_2$MeCl],[14] *trans*-[$Pt(PEt_3)_2Ph_2$],[3a] and *trans*-[$Pt(PEt_3)_2$MeI][3b] follow the same second-order rate law (2) as *cis*-[$Pt(PEt_3)_2(YC_6H_4)_2$], suggesting a one-step proton transfer mechanism similar to the one in Scheme I with direct attack at the Pt–C bond.

Therefore, it would appear that there can be a variety of mechanisms for platinum–carbon bond cleavage via electrophilic attack, depending on (i) the nature of the cleaved group and (ii) the trans-activating ability of the ligand trans to the carbon group. With a weak trans ligand (such as Cl) oxidative addition to the metal would be favored, whereas with a strong trans ligand (such as I, alkyl, aryl, or PR_3) direct proton transfer in a three-center transition state will predominate.

Registry No. *cis*-[$Pt(PEt_3)_2(C_6H_4$-*p*-OMe$)_2$], 61285-90-3; *cis*-[$Pt(PEt_3)_2(C_6H_4$-*p*-Me$)_2$], 61285-91-4; *cis*-[$Pt(PEt_3)_2(C_6H_5)_2$], 15638-50-3; *cis*-[$Pt(PEt_3)_2(C_6H_4$-*m*-$OCH_3)_2$], 67049-29-0; *cis*-[$Pt(PEt_3)_2(C_6H_9$-*p*-F$)_2$], 15613-44-2; *cis*-[$Pt(PEt_3)_2(C_6H_4$-*p*-Cl$)_2$], 67049-28-9; *cis*-[$Pt(PEt_3)_2(C_6H_4$-*m*-F$)_2$], 15613-43-1; *cis*-[$Pt(PEt_3)_2(C_6H_4$-*o*-Me$)_2$], 67049-27-8; *cis*-[$Pt(PEt_3)_2(C_6H_4$-*o*-Et$)_2$], 58220-16-9; *cis*-[$Pt(PEt_3)_2(C_6H_4$-*m*-$CF_3)_2$], 67049-26-7; *cis*-[$Pt(PEt_3)_2(C_6H_4$-*p*-$CF_3)_2$], 67049-25-6; *cis*-[$Pt(PEt_3)_2(Me_2N$-*p*-$C_6H_4)_2$], 67049-24-5; *cis*-[$Pt(PEt_3)_2$(*m*-$MeOC_6H_4$)Cl], 67049-23-4; *cis*-[$Pt(PEt_3)_2$(*p*-$MeOC_6H_4$)Cl], 67112-04-3; *cis*-[$Pt(PEt_3)_2$(*p*-ClC_6H_4)Cl], 67112-05-4; *cis*-[$Pt(PEt_3)_2$(*m*-$CF_3C_6H_4$)Cl], 67049-39-2; *cis*-[$Pt(PEt_2)_2$(*p*-$CF_3C_6H_4$)Cl], 67049-38-1; *cis*-[$Pt(PEt_3)_2Cl_2$], 15692-07-6.

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(18) The value for Y = *m*-OMe is an "out-lier" in both solvent systems and we have no explanation for this at present. As for Y = *p*-NMe_2, addition of acid to *cis*-[$Pt(PEt_3)_2(Me_2N$-*p*-$C_6H_4)_2$] produces a sharp change in the original spectrum which is promptly reversed by addition of hydroxide ion in excess. At very low proton concentrations the cleavage of the *second* Pt–C bond interferes seriously with reaction I. The overall rate decreases with increasing added acid owing to increased formation of an unreactive species via protonation of the amino group in the aromatic ring to yield the highly deactivating ammonium substituent *p*-NMe_2H^+.
(19) A good agreement with the observed solvent effect has been obtained[1a] for data relating to acidolysis of *trans*-[$Pt(PEt_3)_2$(Me)Cl].[3b] Here, the reduction in free energy of H^+ and Cl^- accounts almost exactly for the observed decrease in the rate, $k_{obsd} = k_3[H^+][Cl^-]$, indicating that any solvent effect on the substrate must be offset by an exactly similar solvent effect on the transition state.