served in the nickel(II) and copper(II) complexes of glycylhistidine.[16]

Failure to observe this reaction in imidazole is somewhat surprising, but it is possible that the charge donation of the nickel(II) ion makes the pyrrole nitrogen less basic and complexing does not occur, whereas in histidine the added amino group provides greater charge neutralization of the metal ion and the latter does not influence the basicity of the pyrrole nitrogen.

Finally it may be noted that the rate constants in Table III show a strong correlation with net ligand charge. This type of correlation has been discussed recently[6b] for other nickel(II) systems and is qualitatively consistent with Eigen's proposed ion-pair mechanism for these reactions.[6b]

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Ligand-Exchange Reactions in Platinum–Acetylene Complexes

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Ligand-exchange reactions in complexes of the type $(P(C_6H_5)_3)_2Pt(ac)$, where ac is a phenylacetylene, have been reinvestigated, and the previously suggested mechanism has been modified.

Introduction

Substitution and addition reactions of complexes having the general formula $(P(C_6H_5)_3)_2Pt(un)$, where un is an olefin or acetylene, have been said[1] to involve the intermediate $(P(C_6H_5)_3)_2Pt$. Nmr spectroscopy, however, has failed to provide evidence for the dissociation of the acetylenic[2] or olefinic complexes and recently we[3] have proposed an alternative associative mechanism for certain reactions of $(P(C_6H_5)_3)_2PtC_2H_4$. Synthetic studies[4] on the acetylenic complexes provide further evidence for the nondissociative behavior of these complexes in solution, and in this paper we report nmr and kinetic studies on a number of complexes having the formula $(P(C_6H_5)_3)_2Pt(ac)$ where ac is a ring-substituted phenylacetylene.

Experimental Section

Preparation of Ligands. (i) **Perdeuteriotriphenylphosphine.**—A 50-g sample of bromobenzene-d_5 was prepared by the usual method.[5] It was metalated by lithium wire in ether solution,[6] after which an equivalent amount of phosphorus trichloride was added with cooling and stirring. The crude product was recrystallized from ethanol–water (mp 79–79.5°). The C–D stretch was found at 2295–2300 cm^{-1}. The nmr spectrum showed no proton signals.

(ii) **Ring-Deuterated Phenylacetylene.**—A 10-g sample of ring-deuterated acetophenone was prepared by the Friedel–Crafts method.[7] A slight molar excess of phosphorus pentachloride was added to the acetophenone and the mixture was refluxed for 20 min. The α,α-dichloroethane was dehydrochlorinated by alcoholic potassium hydroxide.[8] After separation in the usual manner the crude product was distilled at 142°. The yield of pure product (nmr) was 2 g.

(iii) **Perdeuteriophenylacetylene.**—Compound ii (1 g) in cold (0°) ether solution was treated with a slight excess of *n*-butyllithium (hexane). After 1 hr of stirring, deuterium oxide was added dropwise after which the organic layer was separated, washed, dried, and distilled. The product distilling at 142° showed a very weak nmr signal at τ 7.10 resulting from H–D exchange in the washing process.[9]

The 3- or 4-monosubstituted phenylacetylenes were prepared by standard methods.[10]

The platinum complexes were synthesized by reported methods[11] and were analytically pure.

The nmr spectra were obtained on a Varian Associates A-56/60 or HA 100 spectrometer and were calibrated by frequency modulation; low-temperature readings were corrected by means of the methanol spectrum according to the procedure developed by Varian Associates.

Kinetic measurements were made using a Cary 16 spectrophotometer with a thermostated cell chamber. Pseudo-first-order conditions were employed throughout and good linear plots of log $(A_t - A_\infty)$ *vs.* time were obtained, where A_t are the absorbances at times t covering at least 3 half-lives of the reaction. The rate coefficients obtained were reproducible to within 5%.

Results and Discussion

The nmr spectrum of bis(perdeuteriotriphenylphosphine)(ring-deuterated phenylacetylene)platinum reveals the sharp 12-line pattern resulting from $^{1}H-^{195}Pt$ (33%) and $^{1}H-^{31}P$ (100%) couplings to the acetylenic proton (Figure 1). We are able to identify and analyze the acetylenic protons of other bis(perdeuteriotriphenylphosphine(monosubstituted phenylacetylene)-platinum complexes similarly and the relevant data are recorded in Table I.

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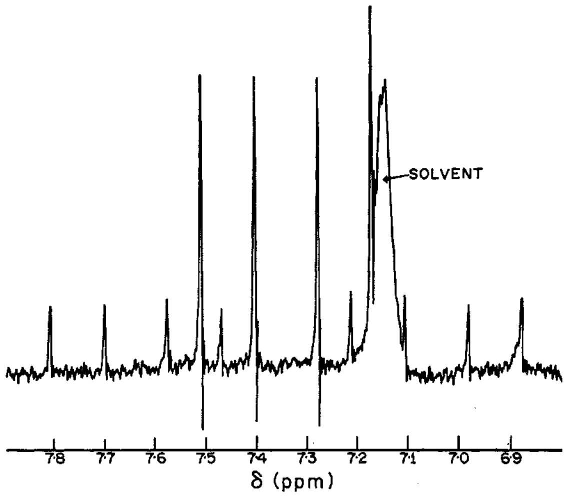

Figure 1.—The 100-MHz nmr spectrum of $(P(C_6H_5)_3)_2Pt(C_6D_5CCH)$ in C_6D_6 at 30°. TMS as internal reference.

TABLE I

THE NMR PARAMETERS (100 MHz) OF L_2Pt(X-SUBSTITUTED PHENYLACETYLENE) in C_6D_6 AT 30°
(L = PERDEUTERIOTRIPHENYLPHOSPHINE)[a]

X	τ(C–H)	J_{Pt-H}, Hz	$J_{cis\ P-H}$, Hz	$J_{trans\ P-H}$, Hz
p-CH_3O	2.53	62.6	10.6	23.1
m-CH_3O	2.40	59.1	10.6	22.9
p-CH_3	2.53	60.5	10.8	23.1
m-CH_3	2.54	60.9	10.8	23.1
H	2.51	60.4	10.8	22.9
p-F	2.55	58.2	10.6	22.6
p-Cl	2.51	57.3	10.8	22.6
m-Cl	2.46	56.6	10.8	22.6
p-NO_2	2.31	52.9	11.3	21.9
m-NO_2	2.73	53.2	11.4	21.8

[a] Internal reference TMS.

TABLE II

TEMPERATURE DEPENDENCE OF OBSERVED FIRST-ORDER RATE COEFFICIENTS k_{obsd} OF L_2Pt(ac) AND ac′ IN CYCLOHEXANE
(L = TRIPHENYLPHOSPHINE)

ac = Phenylacetylene, ac′ = *p*-Nitrophenylacetylene

Temp, °K	286.1	297.6	303.4	305.8	310.5	301.8[a]
10^4k_{obsd}	1.89	8.51	17.94	25.60	44.60	15.5[a]

ac = Phenylacetylene, ac′ = *p*-Methoxyphenylacetylene

Temp, °K	299.1	299.6	305.7	301.8[a]
10^4k_{obsd}	10.12	10.60	25.7	14.0[a]

[a] Taken from ref 1.

The ability to differentiate, over a temperature range of −40 to +110°, between $J_{cis\ P-H}$ and $J_{trans\ P-H}$ (assuming the former to be smaller[2]) in the spectra leads us to believe, along with others,[2] that the acetylenic ligand is held firmly by the metal atom in a square-planar configuration and that neither dissociation nor rotation of the coordinated acetylene is occurring in solution.

In the light of this finding it was evidently of interest to reexamine substitution reactions of the type

$$(P(C_6H_5)_3)_2Pt(ac) + ac' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (P(C_6H_5)_3)_2Pt(ac') + ac$$

where ac and ac′ are various ring-substituted phenylacetylenes and for which a dissociative rate-determining step was postulated[1] earlier.

As found previously, the rate of substitution is insensitive to the nature and concentration of the reagent acetylene and although our rate coefficients were obtained under pseudo-first-order conditions, whereas they were earlier obtained from the rate of approach to equilibrium, the agreement was satisfactory (Table II).

An Arrhenius plot using the above data yielded an activation energy for the reaction of 23.5 kcal/mol.

The mechanism derived earlier for the reaction was

$$(P(C_6H_5)_3)_2Pt(ac) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (P(C_6H_5)_3)_2Pt + ac$$

$$(P(C_6H_5)_3)_2Pt + ac' \xrightarrow{k_2} (P(C_6H_5)_3)_2Pt(ac') \qquad (1)$$

and it is possible to test the postulate by studying the effect on the rate of adding the retarding acetylene (ac). If sufficient ac is added that its concentration is unaffected by ac leaving the complex (ac at least 20 times the complex concentration) and ac′ is adjusted so that the reaction goes to completion, then using (1) it can be shown that

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{k_{-1}}{k_2k_1}\frac{[ac]}{[ac']} \qquad (2)$$

A plot of $1/k_{obsd}$ against [ac]/[ac′] was found to be linear and as can be seen from Table III the derived values for 10^4k_1 agree well internally (*e.g.*, runs I and III) as well as with the values listed in Table II for the unretarded experiments. However, microscopic reversibility demands that for a pair of reactions such as III and IV k_{-1}/k_2 for III must equal k_2/k_{-1} for IV, and for sets of reactions as I, II, and III then $(k_{-1}/k_2)_{II} = (k_{-1}/k_2)_I/(k_{-1}/k_2)_{III}$.

It is evident that such relationships do not hold and we must conclude that the simple mechanism proposed by Allen and Cook should be modified.

An alternative mechanism consistent with our observations is as follows. In the presence of the reagent acetylene there is a rate-determining stereo-

TABLE III

10^4k_{obsd} OF THE REACTION ($YC_6H_4C{\equiv}CH$) + $L_2Pt(XC_6H_5C{\equiv}CH)$ IN THE PRESENCE OF $XC_6H_4C{\equiv}CH$ AT 32.7° (L = TRIPHENYLPHOSPHINE)[a]

Run	Substituents	10^4k_{obsd}, sec^{-1}					k_{-1}/k_2	10^4k_1
I	X = H	21.8	18.8	16.3	11.5	9.72	0.091	25.6
	Y = *p*-NO_2	(1.48)	(4.44)	(6.71)	(13.3)	(20.0)		
II	X = *p*-CH_3O	33.20	27.44	22.26	18.80	. . .	0.079	40.1
	Y = *p*-NO_2	(1.36)	(4.08)	(8.16)	(12.23)	. . .		
III	X = H	23.9	22.2	21.1	19.10	17.3	3.80	25.7
	Y = *p*-CH_3O	(1.45)[b]	(4.36)[b]	(6.55)[b]	(9.16)[b]	(13.0)[b]		
IV	X = *p*-CH_3O	4.14	4.06	3.98	3.83	. . .	0.48	41.6
	Y = H	(1.22)[c]	(4.58)[c]	(9.17)[c]	(18.3)[c]			

[a] Concentration ratios [$XC_6H_4C{\equiv}CH$]/[$YC_6H_4C{\equiv}CH$] are expressed in parentheses under respective k_{obsd}'s. Cyclohexane is the solvent. Concentration ranges: complexes, 4×10^{-5}–8×10^{-5} *M*; *p*-$NO_2C_6H_4CCH$, 1×10^{-3}–3×10^{-3} *M*; *p*-$CH_3OC_6H_4CCH$, 4×10^{-3}–2×10^{-2} *M*; C_6H_5CCH, 5×10^{-3}–1×10^{-2} *M*. [b] $\times 10^{-2}$. [c] $\times 10^{-1}$.

chemical change in the original complex, possibly involving rotation through 90° of the coordinated acetylene, to give a pseudotetrahedral complex. This internal rearrangement is followed by the coordination of *either* ac *or* ac′. Loss of the originally coordinated acetylene (with concomitant rotation of the remaining acetylene into the plane) completes the sequence.

The overall mechanism may be represented as a reaction coordinate–potential energy diagram and this is shown in Figure 2; the rate law corresponding to the proposed mechanism may be derived from

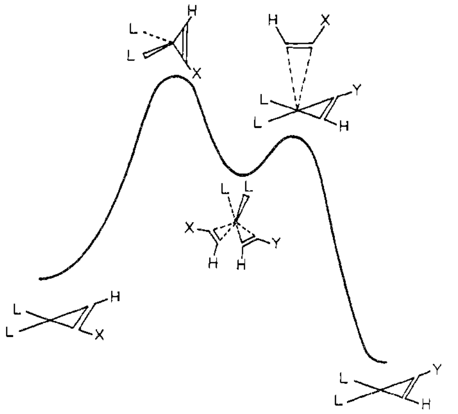

Figure 2.—Energy profile for substitution reactions of $(P(C_6H_5)_3)_2Pt(ac)$ with ac′ (ac = $XC{\equiv}CH$, ac′ = $YC{\equiv}CH$).

$$\begin{tikzcd}
 & & L_2Pt(ac)_2 \arrow[r, "k_X'"] & L_2Pt(ac) \\
L_2Pt(ac) \arrow[r, "k_1"] & L_2Pt(ac) \arrow[ur, "k_X", "{[ac]}"'] \arrow[dr, "{[ac']}"', "k_Y"] & & \\
 & & L_2Pt(ac)(ac') \arrow[r, "k_Y'"] & L_2Pt(ac')
\end{tikzcd}$$

k_X, k_Y, k_X', and k_Y' are assumed to be fast. It is a simple matter to show that the resulting equation is of the same form as eq 1. Thus, although the general form of the rate equation, eq 2, is applicable to these reactions, the kinetics are complicated by there being two intermediates of the type $L_2Pt(ac)(ac')$.

It is interesting to note that when perdeuteriophenylacetylene is added to a benzene solution of bis(triphenylphosphine)(phenylacetylene)platinum, nmr spectroscopy detects the gradual emergence of a proton signal (τ 7.27) assignable to free phenylacetylene. From the kinetic results discussed earlier it is evident that exchange of phenylacetylene cannot result from a dissociative process involving the original complex and it is also unlikely to arise from H–D exchange[9] since the complex was dissolved in a neutral medium. We feel, therefore, that this piece of evidence demands an associative process and supports the existence in solution of the four-coordinate intermediate as postulated in the mechanistic scheme.

We have extended our investigation of the kinetics of the substitution reaction to other (monosubstituted phenylacetylene)platinum complexes (Table IV) and have established a correlation between the log k_{obsd} at 25° and Hammett σ^0 values. With the exception of m-CH_3O and m-NO_2 the points fall on a line with a gradient of −1.20. For these substitution reactions we suggest that in the rate-determining step the homolytic rupture of the Pt–C bonds is accompanied by considerable electron redistribution about the metal and acetylenic ligand, such that the latter fragment in going to the transition state rotates about the metal–ligand axis essentially as a radical-stabilized ligand. This transition state bears a resemblance to that postulated[12] for the Cope rearrangement of 1,5-hexadienes. If this view is correct, the energy barrier to rotation (*ca.* 23–25 kcal/mol) is too high to permit temperature–nmr studies capable of conclusively demonstrating the phenomenon.[13]

Table IV

Rate Coefficients and Derived Parameters for the Reaction of $L_2Pt(XC_6H_4C{\equiv}CH)$ in Cyclohexane with p-$NO_2C_6H_4C{\equiv}CH$ (L = Triphenylphosphine)[a]

X	10^4k_1(obsd), sec^{-1}				4 + log k_{298}[b]	E_a, kcal/mol	Log A
p-CH_3O	2.64 (284.1)	13.80 (297.6)	30.50 (303.6)	48.30 (307.7)	1.17	22.43	13.62
m-CH_3O	1.69 (290.6)	3.55 (296.0)	10.87 (303.7)	24.84 (311.0)	0.70	23.80	14.14
p-CH_3	3.42 (290.3)	5.65 (293.9)	19.50 (303.6)	52.20 (309.5)	0.99	22.92	13.71
m-CH_3	3.19 (290.6)	10.00 (297.8)	31.46 (306.8)	58.00 (311.1)	1.01	23.10	13.99
p-F	2.02 (292.8)	4.83 (297.8)	14.33 (306.8)	52.50 (317.5)	0.69	23.93	14.20
p-Cl	1.61 (291.3)	3.38 (297.4)	14.67 (308.6)	35.70 (315.0)	0.57	24.30	14.20
m-NO_2	1.18 (297.8)	3.45 (305.7)	10.44 (314.6)	18.63 (318.9)	0.11	25.80	15.03
p-NO_2[c]	1.28 (296.7)	2.49 (301.9)	3.91 (305.8)	13.45 (314.9)	0.14	25.95	15.14

[a] Temperatures (°K) are shown in parentheses. [b] Interpolated result at 298°K. [c] Phenylacetylene as attacking ligand.

The reaction of bis(triphenylphosphine)(phenylacetylene)platinum with p-nitrophenylacetylene was studied at various temperatures in benzene and 1-propanol as solvents; the derived E_a's (25.2 and 25.0 kcal/mol) differed so little from that found in cyclohexane that solvent assistance, and hence polar transition states, can be ruled out.

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