

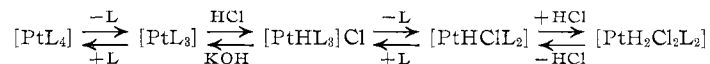
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## Reactions of Inorganic Acids with Zerovalent Platinum, Palladium, and Nickel Compounds Having Triphenylphosphine or 1,2-Bis(diphenylphosphino)ethane as Ligands<sup>1</sup>

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Reactions of compounds  $[ML_4]$ ,  $[ML_3]$ , and  $[ML'_2]$  ( $M = Pt, Pd, Ni$ ;  $L = (C_6H_5)_3P$ ;  $L' = [(C_6H_5)_2PCH_2]_2$ ) with acids are described. For  $[PtL_4]$  the following equilibria were found



while  $[PdL_4]$ ,  $[NiL_4]$ , and  $[ML'_2]$  reacted with acids yielding hydrogen; here no hydride was isolated, only the corresponding bivalent metal salts. The infrared spectra of the hydrides are discussed and an explanation for the basic properties is suggested.

It is known that some transition metal complexes show basic behavior; that is, they add a proton reversibly to yield hydrides.

These complexes which can be protonated belong to either of two classes. The first one includes cyclopentadienyl<sup>2</sup> and cyclopentadienylhydrido<sup>3</sup> complexes; the other includes complexes where the metal is in a low valency state and where the ligands have weaker  $\pi$ -acceptor properties than carbon monoxide, such as phosphines or arenes.<sup>4,5</sup> Planar  $d^8$  complexes of monovalent iridium and rhodium, such as  $[Rh((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$ ,<sup>5</sup>  $[IrCl(CO)((C_6H_5)_3P)_2]$ ,<sup>6</sup>  $[IrH(CO)((C_6H_5)_3P)_2]$ ,<sup>7</sup> and  $[Ir((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]Cl$ <sup>8</sup> should be in the latter class; they take up acids reversibly and form octahedral  $d^6$  complexes. Since we believed that some zerovalent platinum,<sup>9,10</sup> palladium,<sup>11,12</sup> and nickel<sup>12</sup> complexes with phosphine or diphosphine as ligands should belong to the second mentioned class, we were interested to try to support this hypothesis by means of protonation reactions on these complexes.

### Experimental Section

Zerovalent platinum, palladium, and nickel compounds were prepared as described in the literature.<sup>9-12</sup> Infrared spectra were recorded on a Perkin-Elmer 237 spectrophotometer; details are given in Table I.

Melting points were determined in the air and were not cor-

rected. Molecular weights (Table II) were measured with a Mechrolab osmometer. Analytical and other data are collected in Table II. The compounds were prepared according to one of the following patterns.

**$PtH((C_6H_5)_3P)_3Cl$ .**— $[Pt((C_6H_5)_3P)_4]$  or  $[Pt((C_6H_5)_3P)_3]$  (2 or 1.5 g) was suspended in alcohol (30 ml) and the stoichiometric quantity of 15% alcoholic HCl was slowly added; alternatively, a stream of gaseous HCl (15 bubbles/min) was passed through until solution was complete.  $(C_6H_5)_3P$ -saturated hexane was added and the compound (1.1 g) was collected and found to be insoluble in benzene.

Other compounds were obtained similarly, alcoholic aqueous acid being used for obtaining compounds 2–6, 13, 14, 16–20, while alcoholic acid was used for obtaining 11 and 15, and gaseous acids were used to obtain 9 (also in benzene solution), 12, and 15 (which can be obtained also from 13 or 14). Compounds 2, 3, 11, 13–20 were insoluble in the reaction medium and were collected by filtration. Compound 12 was isolated by precipitation with hexane (saturated with HCl) after 2 hr of bubbling in either benzene or ethanol solution.

**$[PtH((C_6H_5)_3P)_3][(C_6H_5)_3B]$ .**—To an ethanol solution of either 1, 4, or 6 an ethanol solution of sodium tetraphenylborate was added slowly with stirring; a white precipitate formed, which was insoluble in common organic solvents except  $CH_2Cl_2$  and  $CHCl_3$ . Similarly, compounds 9 and 10 were prepared from either 1, 4, or 5 and compound 2 from 1.

**$[PtHCl((C_6H_5)_3P)_2]$ .**—Gaseous HCl was bubbled into a solution of  $[Pt((C_6H_5)_3P)_4]$  (1 g) or  $[Pt((C_6H_5)_3P)_3]$  (0.8 g) in benzene (30 ml) till the solution became colorless. It was then concentrated under vacuum to 15 ml; hexane was added, and white crystals were collected; mp 215–218°, lit.<sup>13</sup> 215–220°; soluble in benzene,  $CHCl_3$ , and acetone; insoluble in ethanol.

**Reactions of  $[Pd(H_2O)((C_6H_5)_3P)_3](ClO_4)_2$  with  $(C_6H_5)_3P$ .**—Compound 13 and excess  $(C_6H_5)_3P$  were melted together under nitrogen for 1 hr. The cooled mixture was washed with alcohol and crystallized from  $CHCl_3$  and hexane, to yield yellow  $[PdCl_2((C_6H_5)_3P)_2]$ , mp 289°.

### Results

First we allowed  $[Pt((C_6H_5)_3P)_3]$ <sup>9</sup> to react with acids, because it may be considered unsaturated from the point of view of its coordination. The reaction products were different according to the acid or to the reaction medium used.

When aqueous or dilute alcoholic acid was reacted with a suspension of the zerovalent platinum compound,

(13) J. Chatt and B. L. Shaw, *ibid.*, 5075 (1962).

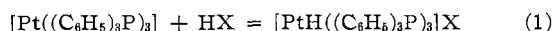
- (1) Preliminary note: F. Cariati, R. Ugo, and F. Bonati, *Chem. Ind. (London)*, 1714 (1964).
- (2) T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5249 (1960).
- (3) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958); M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *ibid.*, 4854 (1961).
- (4) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *ibid.*, 3653 (1962).
- (5) A. Sacco and R. Ugo, *ibid.*, 3274 (1964).
- (6) L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).
- (7) M. Angoletta and G. Caglio, *Rend. Ist. Lombardo Sci. Lettere*, **A97**, 823 (1963).
- (8) A. Sacco and R. Ugo, unpublished results.
- (9) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958); L. Malatesta and R. Ugo, *ibid.*, 2080 (1963).
- (10) J. Chatt and G. A. Rowe, *Nature*, **191**, 1101 (1961).
- (11) L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).
- (12) J. Chatt, F. A. Hart, and H. R. Watson, *ibid.*, 2537 (1962).

TABLE I  
INFRARED DATA<sup>a</sup>

Compd	$\nu_{\text{PtH}}$ , cm <sup>-1</sup>	$\delta_{\text{PtH}}$ , cm <sup>-1</sup>	Other frequencies	Anion symmetry
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]Cl	2102	817		
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]NO <sub>3</sub>	2107	813 <sup>c</sup>	1337 ( $\nu_{\text{as}} \text{NO}_3^-$ ) 822 <sup>c</sup> ( $\delta_{\text{NO}_3^-}$ )	D <sub>3h</sub>
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]ClO <sub>4</sub>	2112	809	1094 ( $\nu_{\text{as}} \text{ClO}_4^-$ )	T <sub>d</sub>
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]BF <sub>4</sub>	2112	726	1054 ( $\nu_{\text{as}} \text{BF}_4^-$ )	T <sub>d</sub>
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]CH <sub>3</sub> OSO <sub>3</sub>	2102	824	2972 ( $\nu_{\text{as}} \text{CH}_3$ )-2922 ( $\nu_s \text{CH}_3$ ) 1257-1227 ( $\nu_{\text{as}} \text{SO}_3$ )-1057 ( $\nu_s \text{SO}_3$ ) 1017 ( $\nu_{\text{SO}}$ )	C <sub>3v</sub>
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]HSO <sub>4</sub>	2112	827	3420 ( $\nu_{\text{OH}}$ ) 1252-1227 ( $\nu_{\text{as}} \text{SO}_3$ ) 1057 ( $\nu_s \text{SO}_3$ ) 1017 ( $\nu_{\text{SO}}$ )	C <sub>3v</sub>
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	2122	...		
[PtHCl((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>2</sub> ] <sup>d</sup>	2210	824		
[PtH(CN)((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>2</sub> ]	2062	829	2142 ( $\nu_{\text{CN}}$ )	
[PtH(SCN)((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>2</sub> ]	2247	822 <sup>b</sup>	2092 ( $\nu_{\text{CN}}$ ) 872 ( $\nu_{\text{CS}}$ )	
[PtH <sub>2</sub> Cl <sub>2</sub> (P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> ]	2272-2262 2232			
[PtHCl(As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> ]	2147	803		
[Pd(H <sub>2</sub> O)((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	...	...	3400 ( $\nu_{\text{H}_2\text{O}}$ ) 1094 ( $\nu_{\text{as}} \text{ClO}_4^-$ )	T <sub>d</sub>
[Pd(H <sub>2</sub> O)((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ](BF <sub>4</sub> ) <sub>3</sub>	...	...	3400 ( $\nu_{\text{H}_2\text{O}}$ ) 1054 ( $\nu_{\text{as}} \text{BF}_4^-$ )	T <sub>d</sub>
[Pd(NO <sub>3</sub> ) <sub>2</sub> ((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>2</sub> ]	...	...	1480-1510 ( $\nu_{\text{as}} \text{NO}_2$ ) 1270-1130 ( $\nu_s \text{NO}_2$ ) 1020 ( $\nu_{\text{NO}}$ *) 806 ( $\delta_{\text{NO}_2}$ )	C <sub>2v</sub>
[Pd(SO <sub>4</sub> )((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>2</sub> ]	...	...	1265 ( $\nu_{\text{as}} \text{SO}_2$ ) 1155 ( $\nu_s \text{SO}_2$ ) 1110 ( $\nu_{\text{as}} \text{SO}_2^*$ ) 920 ( $\nu_s \text{SO}_2^*$ )	C <sub>2v</sub>
[Pt{((C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	...	...	1054 ( $\nu_{\text{as}} \text{ClO}_4^-$ )	T <sub>d</sub>
[Pd{((C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	...	...	1054 ( $\nu_{\text{as}} \text{ClO}_4^-$ )	T <sub>d</sub>
[Ni{((C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	...	...	1054 ( $\nu_{\text{as}} \text{ClO}_4^-$ )	T <sub>d</sub>

<sup>a</sup> Spectra were recorded in Nujol or C<sub>4</sub>Cl<sub>6</sub> mull. Oxygens bonded to metal are marked with asterisks. <sup>b</sup> Assigned by analogy with the position of the same vibration on the other compounds of the table. <sup>c</sup> These values may be reversed. <sup>d</sup> See ref 16.

an ionic platinum(II) hydride was isolated, according to the reaction



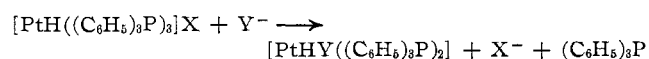
when X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, CH<sub>3</sub>OSO<sub>3</sub><sup>-</sup>.

Colorless, diamagnetic compounds were obtained (Table II) and their molar conductance in C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (Table III) is in agreement with that required by a univalent electrolyte. In an analogous way with X<sup>-</sup> = Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> similar compounds were obtained, but their molar conductance value was lower than required. When gaseous HX was bubbled through a benzene solution of [Pt((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>3</sub>], the reaction yielded a nonconducting diamagnetic hydride<sup>13</sup> according to the reaction



where X<sup>-</sup> = Cl<sup>-</sup>, CN<sup>-</sup>, and no ionic platinum(II) hydride was found.

It seems that, when X<sup>-</sup> is an anion with low coordinating power, pattern 1 is followed and ionic compounds are formed, while anions with high coordinating power afford covalent compounds, according to pattern 2. This view finds additional support in the reaction

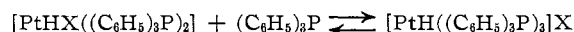


when X<sup>-</sup> = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>OSO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup> and Y<sup>-</sup> = CN<sup>-</sup>, SCN<sup>-</sup>. It should be noted that when X<sup>-</sup> = (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B<sup>-</sup>, *i.e.*, the anion employed has virtually no coordinating power, there was a simple exchange of the anion, and [PtH((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>3</sub>][(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B] was isolated.

When X<sup>-</sup> was an anion with intermediate coordinating power, such as Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>, either ionic [PtH-

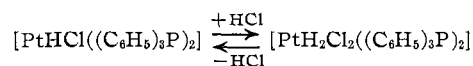
((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>3</sub>]Cl or covalent [PtHCl((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>2</sub>] was isolated, according to the reaction conditions. Further, these ionic compounds (X<sup>-</sup> = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>) displayed a lower value of molar conductance in nitrobenzene solution than required for a 1:1 electrolyte; the value rose to that required when excess triphenylphosphine was added to the solution (Table III).

This can be explained by an equilibrium such as



This equilibrium might be due to the strong *trans* effect of hydrogen, established kinetically;<sup>14</sup> it is clearly a function of the nucleophilic power of the anion and of the solvent.

In order to investigate the effect of the solvent, the reaction between zerovalent platinum compounds and acid was examined in the case of HCl. Here both covalent and ionic derivatives, [PtHCl((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>2</sub>] and [PtH((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>3</sub>]Cl, are known and can be isolated without trouble. The ionic hydride was found to be the product when donor solvents, such as ethanol, were used, even when excess dilute hydrochloric acid was used. The covalent hydride was the product when nonpolar solvents, such as benzene, were used; the reaction time was longer here than before. In either case, excess hydrogen chloride and long reaction time afford a platinum(IV) derivative, according to the equation



(14) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).

TABLE II  
ANALYTICAL AND SOLUBILITY DATA

Compd <sup>a</sup>	Mp, °C	% C	% H	% P	% Pt	% N	Mol wt <sup>b</sup>	Soluble <sup>d</sup> in
		Calcd Found	Calcd Found	Calcd Found	Calcd Found	Calcd Found	Calcd Found	
1 [PtHL <sub>3</sub> ]Cl	110-112	63.68 64.29	4.52 4.75	9.14 8.95	19.16 19.17	...	...	A
2 [PtHL <sub>3</sub> ]ClO <sub>4</sub> <sup>e</sup>	270-290 (dec)	59.92 59.60	4.25 4.28	8.60 8.63	18.03 17.16	...	...	E
3 [PtHL <sub>3</sub> ]BF <sub>4</sub>	203-205	60.62 60.99	4.30 4.57	...	...	...	...	E
4 [PtHL <sub>3</sub> ]NO <sub>3</sub>	125-127	62.06 62.08	4.41 4.35	8.90 8.92	18.67 20.1	1.34 1.35	...	A
5 [PtHL <sub>3</sub> ]CH <sub>3</sub> OSO <sub>3</sub>	163-165	60.38 59.98	4.48 4.54	...	...	...	...	A
6 [PtHL <sub>3</sub> ]HSO <sub>4</sub>	167-170	60.05 59.90	4.35 4.68	8.61 8.63	18.07 18.10	...	...	A D
7 [PtHL <sub>3</sub> ]((C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> B)	176-178	72.55 72.38	5.12 5.07	7.21 7.22	15.11 15.00	...	...	C D
8 [PtHClL <sub>2</sub> ] <sup>13</sup>	215-218	57.18 56.85	4.10 4.25	...	25.81 25.80	...	...	B C
9 [PtH(CN)L <sub>2</sub> ]	224-227	59.52 60.04	4.15 4.33	...	...	1.88 1.85	746 725 <sup>c</sup>	B C
10 [PtH(NCS)L <sub>2</sub> ]	195-197	57.07 56.51	3.98 4.17	...	...	1.80 1.74	778 770	B C
11 [PtHCl((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> As) <sub>2</sub> ]	296-297	51.23 51.10	3.68 3.48	...	...	...	843 920 <sup>c</sup>	B C
12 [PtH <sub>2</sub> Cl <sub>2</sub> L <sub>2</sub> ]	...	54.55 55.70	4.04 4.15	7.82 8.28	...	...	...	...
13 [Pd(H <sub>2</sub> O)L <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>f</sup>	230-232	58.41 58.73	4.24 4.24	8.38 8.30	...	...	...	E
14 [Pd(H <sub>2</sub> O)L <sub>3</sub> ](BF <sub>4</sub> ) <sub>2</sub> <sup>f</sup>	210-214	59.78 59.41	4.33 4.30	...	...	...	...	C D
15 [PdCl <sub>2</sub> L <sub>2</sub> ]	288-290	61.61 61.67	4.28 4.10	...	...	...	701 680	C
16 [Pd(NO <sub>3</sub> ) <sub>2</sub> L <sub>2</sub> ] <sup>f</sup>	170-172	57.26 56.79	3.97 3.78	...	...	3.71 3.48	754 772	C D
17 [Pd(SO <sub>4</sub> )L <sub>2</sub> ]	155	59.47 59.50	4.12 4.14	...	...	...	726 742	C
18 [PtL' <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	305	52.44 51.80	4.03 3.87	...	...	...	...	E
19 [PtL' <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	300-308	56.65 55.21	4.36 4.54	...	...	...	...	E
20 [NiL' <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>f,h</sup>	248	59.22 58.59	4.55 4.76	...	5.57 <sup>g</sup> 5.60 <sup>g</sup>	...	...	D

<sup>a</sup> L = (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P, L' = (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. All of the compounds listed are colorless, unless stated otherwise, and diamagnetic in the solid state. Some of them were found to be electrolytes; the relevant data are given in Table III. <sup>b</sup> By osmometry in chloroform, unless otherwise stated. <sup>c</sup> In benzene. <sup>d</sup> Solubility in alcohol (A), benzene (B), chloroform (C), or dichloromethane (D); E means that the compound does not dissolve in common organic solvents. <sup>e</sup> Variable amount of water of crystallization is present sometimes. <sup>f</sup> Yellow. <sup>g</sup> Nickel. <sup>h</sup> The same compound was obtained from nickel(II) perchlorate and the ligand in ethanol.

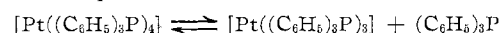
TABLE III

Compd	Molar conductivities, Λ <sub>M</sub> , ohm <sup>-1</sup> cm <sup>2</sup>	
	a	b
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]ClO <sub>4</sub>	17.8	18.2
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]BF <sub>4</sub>	24.06	24.15
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>	15.3	15.7
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]CH <sub>3</sub> OSO <sub>3</sub>	20.05	20.00
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]HSO <sub>4</sub>	21.8	21.8
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]Cl	12.05	24.4
[PtH((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>3</sub> ]NO <sub>3</sub>	18.7	24.6
[PtHCl((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>2</sub> ]	nc	24.1
[PtH(CN)((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>2</sub> ]	nc	nc
[PtH(SCN)((C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P) <sub>2</sub> ]	nc	nc

<sup>a</sup> Solutions 10<sup>-3</sup> M in nitrobenzene at 25 ± 0.5°. <sup>b</sup> Solutions as in a with excess of triphenylphosphine, (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P:compound = 10:1.

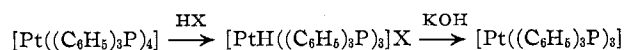
The compound, dihydridodichlorobis(triphenylphosphine)platinum(IV) loses HCl slowly in the solid state but quickly in solution.

Instead of [Pt((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>3</sub>], [Pt((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>4</sub>] can be used with the same results. This can be explained, as the latter complex dissociates in solution according to



The existence of this equilibrium was confirmed by measuring the molecular weight in benzene solution.<sup>9</sup>

Acid addition is reversible. [Pt((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>3</sub>] can be obtained by treating an ionic hydride with alcoholic KOH or NaOH, under nitrogen. Therefore, it is possible to prepare [Pt((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>3</sub>] from [Pt((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>-P)<sub>4</sub>] in nearly quantitative yields as follows.

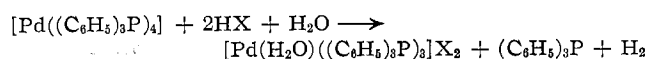


The previously published method<sup>9</sup> is not as convenient as this one since a low yield is obtained by reduction of  $[\text{PtI}_2((\text{C}_6\text{H}_5)_3\text{P})_2]$  with hydrazine and, moreover, the reaction product may contain some  $[\text{PtHI}((\text{C}_6\text{H}_5)_3\text{P})_2]$ .<sup>15</sup>

When  $[\text{Pt}((\text{C}_6\text{H}_5)_3\text{As})_4]$  was used, only  $[\text{PtHCl}((\text{C}_6\text{H}_5)_3\text{As})_2]$  was isolated; with other acids, only oily products were formed and these did not show any Pt-H stretching frequency. Surprisingly, a  $[\text{PtHCl}((\text{C}_6\text{H}_5)_3\text{As})_2]$  solution in nitrobenzene was nonconducting, even when excess  $(\text{C}_6\text{H}_5)_3\text{As}$  was added.

Zerovalent palladium and nickel compounds were also allowed to react with acids, in order to study their electrophilic reactivity. No stable hydride formation was likely here.<sup>16</sup>

In ethanol, acid attack on  $[\text{Pd}((\text{C}_6\text{H}_5)_3\text{P})_4]$ , which is extensively dissociated in solution,<sup>11</sup> was very rapid; hydrogen was evolved and Pd(II) phosphine complexes (Table II) were formed, at temperatures as low as  $-50^\circ$  and with different acids. With aqueous  $\text{HClO}_4$  or  $\text{HBF}_4$  uni-bivalent electrolytes<sup>17</sup> were isolated, according to



where  $\text{X}^- = \text{BF}_4^-, \text{ClO}_4^-$ . One molecule of hydrogen per mole of palladium was evolved. Excess  $(\text{C}_6\text{H}_5)_3\text{P}$  did not displace the coordinated water, even in refluxing methanol. When  $[\text{Pd}(\text{H}_2\text{O})((\text{C}_6\text{H}_5)_3\text{P})_3](\text{ClO}_4)_2$  and excess  $(\text{C}_6\text{H}_5)_3\text{P}$  were melted together, the latter was oxidized to  $(\text{C}_6\text{H}_5)_3\text{PO}$  and  $[\text{PdCl}_2((\text{C}_6\text{H}_5)_3\text{P})_2]$  was formed. With  $\text{HCl}$  or  $\text{HNO}_3$ , nonionic  $[\text{PdX}_2((\text{C}_6\text{H}_5)_3\text{P})_2]$  complexes were formed; sulfuric acid gave  $[\text{Pd}(\text{SO}_4)((\text{C}_6\text{H}_5)_3\text{P})_2]$  where the  $\text{SO}_4^{2-}$  anion is chelating, as shown by the infrared spectrum (Table I).

$[\text{Ni}((\text{C}_6\text{H}_5)_3\text{P})_4]$ <sup>18</sup> was attacked by acids, the reaction product being always the corresponding hydrated nickel(II) salts.

Since Ni(0), Pd(0), and Pt(0) complexes with chelating diphosphines such as 1,2-bis(diphenylphosphino)ethane are known,<sup>10,12</sup> the investigation was extended to these complexes. While  $(\text{C}_6\text{H}_5)_3\text{P}$  complexes of Ni(II) and Pd(II) show a different behavior from those of Pt(II), the reaction with  $\text{HClO}_4$  gave always  $[\text{ML}'_2](\text{ClO}_4)_2$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ;  $\text{L}' = 1,2$ -bis(diphenylphosphino)ethane). Other inorganic acids gave similar  $[\text{ML}'_2]^{2+}$  complexes ( $\text{M} = \text{Pt}, \text{Pd}$ ), while the same reactions on  $[\text{Ni}((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_2]$  gave hydrated nickel(II) salts.

**Infrared Spectra.**—All ionic platinum(II) hydrides show an infrared adsorption band of medium strength between 2100 and 2120  $\text{cm}^{-1}$  (Pt-H stretching) and another less intense one between 830 and 800  $\text{cm}^{-1}$  (Pt-H bending). If  $\nu_{\text{Pt-H}}$  in the series  $\text{trans-}[\text{PtHX}((\text{C}_6\text{H}_5)_3\text{P})_2]$  and  $[\text{PtH}((\text{C}_6\text{H}_5)_3\text{P})_3]^+$  is considered (Table

I) according to the criteria given by Chatt,<sup>13</sup> it can be seen that the values are in agreement with the *trans* effect of  $(\text{C}_6\text{H}_5)_3\text{P}$ , which is between cyanide ion (strong *trans* effect) and chloride ion (not so strong as  $\text{CN}^-$ ).

*trans-}[\text{PtH}(\text{NCS})((\text{C}\_6\text{H}\_5)\_3\text{P})\_2] has a remarkable value since  $\nu_{\text{Pt-H}}$  is found at 2247  $\text{cm}^{-1}$ , higher than  $\nu_{\text{Pt-H}}$  for *trans-}[\text{PtHCl}((\text{C}\_6\text{H}\_5)\_3\text{P})\_2]. On the contrary, *trans-}[\text{PtH}(\text{NCS})((\text{C}\_2\text{H}\_5)\_3\text{P})\_2] displays a Pt-H stretching (2195  $\text{cm}^{-1}$ )<sup>13</sup> very near that of *trans-}[\text{PtHCl}((\text{C}\_2\text{H}\_5)\_3\text{P})\_2] (2183  $\text{cm}^{-1}$ ).<sup>13</sup> The surprisingly high value found for *trans-}[\text{PtH}(\text{NCS})((\text{C}\_6\text{H}\_5)\_3\text{P})\_2] cannot be due to the presence of a Pt-SCN instead of a Pt-NCS linkage: in this case, according to Powell and Shaw,<sup>19</sup>  $\nu_{\text{Pt-H}}$  should be lower than the value found for the corresponding chloride. Further, a doublet (872 and 822  $\text{cm}^{-1}$ ) was found: one of these two (perhaps the higher one) can be assigned to  $\nu_{\text{C-S}}$ , showing that the NCS group is bound to the metal through nitrogen.<sup>20</sup>*****

The frequency shift found here may be due to different  $\pi$ -acceptor properties of triphenylphosphine compared with those of triethylphosphine. Further, since  $(\text{C}_6\text{H}_5)_3\text{P}$  has more  $\pi$ -accepting power than  $(\text{C}_2\text{H}_5)_3\text{P}$ , less negative charge is left on the metal and so back donation from nonbonding d orbitals of platinum to the NCS group is reduced, and polarity of the Pt-H bond is increased.<sup>19</sup> This view is confirmed by the shift of  $\nu_{\text{Pt-H}}$  from 2183  $\text{cm}^{-1}$  for *trans-}[\text{PtHCl}((\text{C}\_2\text{H}\_5)\_3\text{P})\_2] to 2210  $\text{cm}^{-1}$  for *trans-}[\text{PtHCl}((\text{C}\_6\text{H}\_5)\_3\text{P})\_2].**

The infrared spectra (Table I) give additional support to the ionic structure of many compounds, since the number and type of infrared bands for the anions are in agreement with those expected for noncoordinated ions. When the anion is bound covalently to the metal, as in  $[\text{Pd}(\text{NO}_3)_2((\text{C}_6\text{H}_5)_3\text{P})_2]$  or  $[\text{Pd}(\text{SO}_4)((\text{C}_6\text{H}_5)_3\text{P})_2]$ , there are more bands than before as required by the lowering of the symmetry of the anion due to coordination (Table I).

### Conclusion

Some conclusions can be drawn from the easy electrophilic attack by a proton on d<sup>10</sup> atoms, such as those present in zerovalent Ni, Pd, and Pt compounds with phosphines and diphosphines.

The d<sup>10</sup> configuration alone would not be expected to have basic properties, on the ground of the high first ionization potential, especially for Pd and Pt.<sup>21</sup> However, medium strength  $\pi$ -acceptor ligands as phosphines enhance the negative charge on the metal. It is known that some zerovalent platinum carbonyl derivatives with phosphines are stable.<sup>9</sup> Besides, tricoordinated platinum(0) complexes are stable in the solid state, as if there were some electrostatic repulsion working against the formation of a fourth  $\sigma$  bond, though this might be explained also in terms of steric hindrance. All this evidence is in favor of the existence of an excess of negative charge on the metal owing to phosphine coordination. This excess of negative charge might be completely delocalized into the molecular orbitals

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formed from  $(n + 1)s$  and  $(n + 1)p$  atomic orbitals and  $\sigma$ -type ligand orbitals, but it might also be strongly localized along the  $z$  axis normal to the plane of the three phosphorus atoms. Indeed, according to some authors<sup>22</sup> a tricoordinated, trigonal structure gives rise to a better  $\pi$ -bonding distribution than in a tetrahedral structure, not so much as far as the number of possible  $\pi$  bonds<sup>23</sup> is concerned, but certainly as far as the strength of such bonds is concerned.

This hypothesis is supported by the results of kinetic study of CO exchange in nickel carbonyl: here the activation energy for the  $S_N1$  process was found to be lower than the energy found for the Ni-C bond.<sup>24</sup> In the case of  $[\text{Pt}((\text{C}_6\text{H}_5)_3\text{P})_3]$  there should be directional back-donating bonds, formed from hybrid  $6p_z$ ,  $5d_{z^2}$ , and  $5d_{yz}$  platinum orbitals and  $3d$  phosphorus orbitals.

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Such bonds, however, are not very strong, since phosphorus is not a strong  $\pi$  acceptor, so that a  $6p_z$  orbital is engaged only slightly in these bonds and is able to hybridize with the  $5d_{z^2}$  orbital, in which there is a non-bonding electron pair; charge is then mainly directed along the  $z$  axis. The amount of energy required for  $d^{10} \rightarrow d^9p^1$  promotion is a good deal lower than  $d^{10} \rightarrow d^9$  ionization energy;<sup>21</sup> this amount of energy is a good measure of the possibility of  $(n + 1)p$  and  $nd$  hybridization and could be taken as a rough measure of the activation energy for protonation reaction.

Using this picture, tricoordinated compounds appear with structures like those of bases of group V-B with a strong density of directional negative charge.

In any case the results of this research confirm that basic properties of coordination compounds are enhanced when the ligands are poor  $\pi$  acceptors as cyclopentadienyls<sup>2,3</sup> and phosphines.<sup>5</sup>

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## Kinetics of the Reaction of Nickel(II) with Ethylenediaminetetraacetatocobaltate(II)

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Kinetics of the reaction of nickel(II) with ethylenediaminetetraacetatocobaltate(II) is investigated in detail in the pH range 3 to 4.5. The reaction is found to proceed through three independent paths, and the rate constants for each path are determined. The rates of nickel ion attack of normal and protonated cobalt-EDTA complexes are consistent with the binuclear intermediate model proposed by Bydalek and Margerum.

The kinetics of displacement reactions involving metal-ethylenediaminetetraacetato (EDTA,  $L^{4-}$ ) complexes have been studied by several workers,<sup>1-5</sup> and the reaction rates for acid-dependent and acid-independent paths have been measured for some metal-EDTA complex systems. Recently Bydalek and Margerum<sup>6</sup> proposed that the acid-independent path proceeds through a binuclear reaction intermediate, MLM', where the multidentate ligand is partially unwrapped and the iminodiacetate segment is partly or completely coordinated to the attacking ion prior to the rate-determining step, and the stability of this species greatly influences the exchange rate. These authors have shown that the exchange rates in Ni-L-Cu<sup>7</sup> and Ni-L-Zn<sup>8</sup> systems can be satisfactorily explained on the basis of this mechanism. In the present

study the kinetics of  $\text{Ni}^{2+}$  attack of Co-EDTA was investigated in detail mainly to check the applicability of the "binuclear reaction intermediate" mechanism to this system.

### Experimental Section

The experimental procedure for the preparation of metal perchlorates, purification of EDTA, standardization, etc., have been described earlier.<sup>9</sup> Temperature was maintained at the desired value with variation of  $\pm 0.1^\circ$ , and ionic strength was kept at  $\mu = 0.5$  by addition of sodium perchlorate. No buffer was used in order to avoid its possible influence on the exchange rate, and all pH adjustments were made by addition of either perchloric acid or sodium hydroxide. pH measurements were made with a Beckman Model G pH meter using glass-calomel electrodes. All spectral readings were taken with a Beckman DU spectrophotometer using quartz cells. The exchange reaction was followed spectrophotometrically by measuring the absorbance at  $980 \text{ m}\mu$ , which corresponds to the spectral peak of the nickel complex.

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