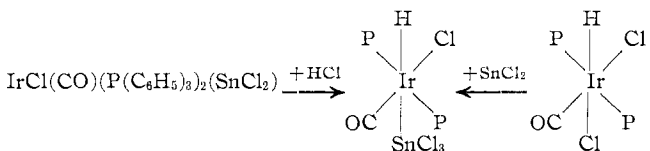


Therefore taking into account the spectroscopic data, a pentacoordinated structure may be suggested for the complexes  $\text{IrX}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SnCl}_2)$  ( $\text{X} = \text{Cl}, \text{Br}$ ). The relative steric configuration may be either a tetragonal pyramid [like  $\text{IrCl}(\text{CO})(\text{L})_2(\text{SO}_2)$ ] or a trigonal bipyramid.

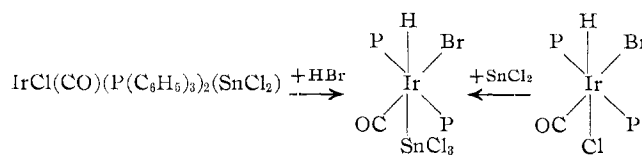
**Chemical Section.**—The complex  $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SnCl}_2)$  adds hydrogen, hydrocyanic acid, and halogen halides at room temperature, yielding stable products.<sup>13</sup> The study of the chemical behavior of the complex  $\text{IrX}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SnCl}_2)$  ( $\text{X} = \text{Cl}, \text{Br}$ ) toward the halogen hydrides gives some evidence for the pentacoordinated structure of the complex (now formulated taking into account the spectroscopic data only).

The complex  $\text{IrHCl}(\text{SnCl}_3)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  is obtained by adding  $\text{HCl}$  to  $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SnCl}_2)$  and also from  $\text{IrHCl}_2(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  by an insertion reaction of  $\text{SnCl}_2$  into the  $\text{Ir}-\text{Cl}$  bond *trans* to the hydrogen

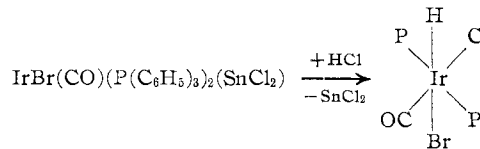


Analogous results are obtained by treating  $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SnCl}_2)$  with  $\text{HBr}$ , or  $\text{IrHBrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  with  $\text{SnCl}_2$

(13) Work in progress.



while the complex  $\text{IrBr}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SnCl}_2)$  reacts with  $\text{HCl}$  forming  $\text{IrHClBr}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$



The complex  $\text{IrHClBr}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  does not add  $\text{SnCl}_2$ .

From these results it can be concluded that (a) the  $\text{SnCl}_2$  insertion in the  $\text{Ir}-\text{Cl}$  bond *trans* to  $\text{CO}$  is not possible under the operating conditions adopted and (b) the ligand  $\text{SnCl}_2\text{Br}^-$  is not obtained by the  $\text{SnCl}_2$  insertion into the  $\text{Ir}-\text{Br}$  bond *trans* to hydrogen. These considerations exclude the possibility of obtaining a tetracoordinated complex by adding  $\text{SnCl}_2$  to  $\text{IrX}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and confirm the proposed pentacoordinated structure of the  $\text{IrX}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2(\text{SnCl}_2)$ .

**Acknowledgments.**—We thank Professor P. Corradini of Naples University for a useful discussion and Dr. G. Fagherazzi of G. Donegani Research Institute for the anticipated communication of the X-ray determinations.

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## The Reaction of Imides with Some Zerovalent Platinum and Palladium Complexes<sup>1</sup>

By D. M. ROUNDHILL

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The reaction of some imides with tetrakis(triphenylphosphine)platinum, tetrakis(triphenylarsine)platinum, and tetrakis(triphenylphosphine)palladium has been studied. With the platinum complexes, imide hydride complexes of the type  $\text{L}_2\text{Pt}(\text{H})(\text{imide})$  have been prepared using succinimide, phthalimide, saccharin, and parabanic acid. The structure of these complexes was confirmed by ir spectra and also by the presence of a high-field line in the  $^1\text{H}$  nmr spectra. Tetrakis(triphenylphosphine)palladium reacted with succinimide but a complex of stoichiometry  $(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{Pd}(\text{succinimide})_2$  was formed rather than a hydride. Maleimide readily reacted with all three complexes to give compounds which still showed an  $\text{N}-\text{H}$  stretch in the ir spectrum and were of stoichiometry  $\text{L}_2\text{M}(\text{maleimide})$ , with the imide coordinated *via* the olefinic double bond.

Transition metal hydrides have been prepared using strong reducing agents, such as sodium borohydride and hydrazine,<sup>2</sup> and by oxidative addition reactions.<sup>3</sup> These latter reactions are usually carried out with strong mineral acids, and in the case of tetrakis(triphenylphosphine)platinum it was found that two types of

hydride were formed, depending on the coordinating ability of the anion. Weakly coordinating anions ( $\bar{\text{X}}$ ) gave ionic hydride complexes of the type  $[\text{PtH}(\text{P}(\text{C}_6\text{H}_5)_3)_3]\bar{\text{X}}$ , whereas ones with strong coordinating ability ( $\bar{\text{Y}}$ ) gave covalent complexes,  $\text{PtHY}(\text{P}(\text{C}_6\text{H}_5)_3)_2$ .<sup>4</sup>

The preparation of hydrides from weak acids has however received little study, although recent publications have described their preparation from  $\text{HCN}$ .<sup>4,5</sup>

(1) D. M. Roundhill, *Chem. Commun.*, 567 (1969).

(2) B. L. Shaw, "Inorganic Hydrides," Pergamon Press, Ltd., Oxford, 1967, p 82.

(3) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).

(4) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, 5, 1128 (1966).

(5) H. Singer and G. Wilkinson, *J. Chem. Soc., A*, 2516 (1968).

TABLE I  
 MICROANALYTICAL DATA FOR THE COMPLEXES

Compound	No.	% calcd				% found				Yield, %	Mp, <sup>a</sup> °C
		C	H	N	Mol wt	C	H	N	Mol wt		
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(succinimide)	I	58.7	4.31	1.71	819	58.1	4.14	1.40	853	84	220-233
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(phthalimide)	II	61.0	4.07	1.62	867	61.4	4.24	1.81	923	91	194-215
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(saccharin)	III	57.2	3.91	1.55	903	56.7	3.90	1.68	887	98	197-205
(As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(saccharin)	IV	52.1	3.56	1.41	942	52.0	3.55	1.38	991	74	186-193
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(parabanic acid)	V	56.2	3.87	3.36	834	56.3	3.99	3.32	773	68	226-233
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pd(succinimide) <sub>2</sub> <sup>c</sup>	VI	63.8	4.62	3.38	<i>b</i>	64.1	4.72	3.08	<i>b</i>	99	257-261
						61.8	4.38	1.66			
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(maleimide)C <sub>6</sub> H <sub>6</sub>	VII	61.7	4.39	1.56	<i>b</i>	61.6		1.69	<i>b</i>	96	250-255
(As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(maleimide)	VIII	53.1	3.68	1.55	<i>b</i>	54.0	3.80	1.49	<i>b</i>	50	245-255
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pd(maleimide)	IX	66.0	4.54	1.92	<i>b</i>	65.4	4.57	1.90	<i>b</i>	98	160-163

<sup>a</sup> The complexes melt with decomposition to red liquids; the first temperature shown is that at which decomposition initially occurs, and the second is that at which the solid completely melts. <sup>b</sup> Insoluble in benzene. <sup>c</sup> This complex is yellow whereas all the others are colorless.

 TABLE II  
 SPECTROSCOPIC DATA FOR THE N-BONDED COMPLEXES

	Ir				Nmr			
	$\nu_{\text{SO}_2}$ , cm <sup>-1</sup>	$\nu_{\text{CO}}$ , cm <sup>-1</sup>	$\nu_{\text{PtH}}$ , cm <sup>-1</sup>	$\nu_{\text{NH}}$ , cm <sup>-1</sup>	$\tau_{\text{phenyl}}$ , ppm	$\tau_{\text{PtH}}$ , <sup>a</sup> ppm	$J_{\text{PH}}$ , cps	$\tau_{\text{CH}_3}$ , ppm
Succinimide	...	1728 <sup>b</sup>	...	...	...	...	...	7.08
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(succinimide)	...	1635	2190	...	2.47	24.1	<i>b</i>	8.47
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(phthalimide)	...	1650	2200	...	2.57	24.0	12.3	...
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(saccharin)	1155	1680	2230	...	2.50	25.7	12.8	...
	1175							
(As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(saccharin)	1150	1670	2185	...	2.47	28.0	...	...
	1165	1660						
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(parabanic acid)	...	1750	2210	3150	2.43	24.6	<i>b</i>	...
		1790						
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pd(succinimide) <sub>2</sub>	...	1645	...	...	2.33	...	...	8.57

<sup>a</sup> This value represents the center of the multiplet. <sup>b</sup> Triplet only poorly resolved. <sup>c</sup> Data taken from T. Matsuo, *Bull. Chem. Soc. Japan*, **37**, 1844 (1964).

and 1-ethynylcyclohexanol<sup>6</sup> to give cyano and acetylide hydrides, respectively. The preparation from imides was attempted in order to try and develop a useful synthesis of metal hydrides without involving strong-acid media or reducing agents.

## Results and Discussion

(1) **N-Bonded Complexes.**—The preparation of the hydrides has been carried out using four different imides—succinimide, phthalimide, saccharin, and parabanic acid—which have  $pK_a$ 's ranging from 6.1 to 11.7. In each case the reaction product from (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Pt<sup>0</sup> is the platinum(II) imide hydride complex. The analytical data for all the complexes which have been prepared are shown in Table I, and the spectral data for the hydrides are shown in Table II. The molecular weight data, which were obtained in benzene in order to avoid any possible side reactions with chlorinated solvents, show that the complexes are monomeric. In each case the ir spectrum shows strong bands which can be assigned to the platinum hydride stretch and to the carbonyl group of the imide, although it is not possible to assign bands unambiguously for the Pt-H bend. The position of the hydride stretch is at the expected frequency,<sup>7</sup> with the band occurring at a signifi-

cantly lower wavelength for the triphenylarsine complex than for the analogous triphenylphosphine one.

The position and multiplicity of the carbonyl stretch are considerably different in the complexes from those found in the free ligand. The free imides show two bands in the 1700-1800-cm<sup>-1</sup> range separated by 30-40 cm<sup>-1</sup>,<sup>8</sup> the low-frequency band being usually strong with the high-frequency band being considerably weaker. The succinimide complexes however show only one band which is found between 1635 and 1650 cm<sup>-1</sup>, representing a lowering in frequency of about 100 cm<sup>-1</sup> from the position of the low-frequency band found in the spectrum of the free ligand.

A recent publication<sup>9</sup> describes the preparation of some complexes of succinimide and phthalimide with titanium and tin tetrachlorides. These complexes were considered to contain an imide bonded to the metal *via* an oxygen atom. This mode of coordination was deduced by consideration of the change in the ir carbonyl frequency in the imide on coordination, which was found to be lowered by about 50 cm<sup>-1</sup>. In the platinum complexes which have now been prepared, the lowering in frequency of the carbonyl stretching mode is not considered to be indicative of oxygen bonding to the platinum but is believed to be caused by the bis-(triphenylphosphine)platinum group being more effec-

(6) D. M. Roundhill and H. B. Jonassen, *Chem. Commun.*, 1233 (1968).

(7) P. W. Atkins, J. C. Green, and M. L. H. Green, *J. Chem. Soc., A*, 2275 (1968).

(8) T. Matsuo, *Bull. Chem. Soc. Japan*, **37**, 1844 (1964).

(9) S. C. Jain and R. Rivest, *J. Inorg. Nucl. Chem.*, **31**, 399 (1969).

tive in reducing the electron density at the N atom than is a hydrogen atom, thereby causing a drift of electrons away from the carbonyl group as shown in Figure 1.

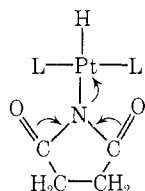


Figure 1.—Electron-withdrawing effect of  $L_2Pt$  on the imide.

The phthalimide complex shows the carbonyl stretch at a similarly lowered frequency, although in this case the band is a multiplet rather than simply a singlet.

The proposed structure for these complexes (Figure 2) is further confirmed by the  $^1H$  nmr spectra. These

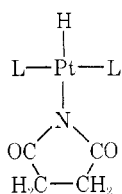


Figure 2.—Structure of the imide hydride complexes. Complexes I-V ( $L = P(C_6H_5)_3, As(C_6H_5)_3$ ).

show a broad unresolvable peak at low field due to the phenyl protons, a high-field line due to the hydride, and, in the case of the succinimide complexes, a singlet for the methylene protons. In the case of the saccharin complex the high-field line resolves into a triplet which is caused by the  $^{31}P$  coupling to the hydride protons, and the value of  $J_{P-H}$  is similar to that previously found for phosphine platinum hydrides.<sup>10</sup> Since the *trans* coupling has always been found to be larger than the *cis*,<sup>11</sup> a triplet can only arise by coupling of the hydride proton to two equivalent  $^{31}P$  nuclei, which can only occur when the hydrogen atom is *cis* to each of the triphenylphosphines, making the phosphines *trans* to each other. The satellite peaks caused by  $^{195}Pt-^1H$  coupling could not be seen because of the rather limited solubility of the complexes.

The platinum succinimide complex also shows a peak in the nmr spectrum at  $\tau$  8.47 due to the methylenic protons. The relative integration of the phenyl:methylene protons shows that there are two triphenylphosphine groups for each succinimide, thereby verifying that the complex is a platinum(II) hydride formed by oxidative addition of only one molecule of the imide to the platinum. This resembles the reaction found with HCN<sup>4</sup> but differs from the reaction with 1-ethynylcyclohexanol where two molecules of ligand add to give a platinum(IV) hydride complex.<sup>6</sup>

The relative integration of the phenyl:methylene protons in the nmr spectrum of the succinimide pal-

(10) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 141 (1965).

(11) E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Commun.*, 860 (1967).

ladium complex shows that one molecule of the imide is present for every molecule of triphenylphosphine, which confirms that two molecules of succinimide have added to the bis(triphenylphosphine)palladium group. The complex however shows no band in the ir spectrum due to a palladium hydride, and the stoichiometry confirms that the structure is four-coordinate with two triphenylphosphine and two succinimide groups bonded to the palladium as shown in Figure 3.

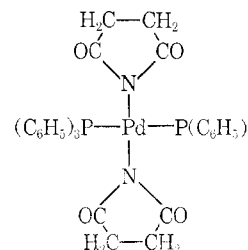


Figure 3.—Structure of the palladium succinimide complex.

Coordination of the nitrogen atom of succinimide strongly influences the chemical shift of the methylene protons. The free imide shows a resonance at  $\tau$  7.08, whereas in the complexes the methylene protons are shielded and are now found at  $\tau$  8.47 and 8.57 for the platinum and palladium complexes, respectively.

The confirmation of this reaction led to a study of the reaction of  $(P(C_6H_5)_3)_4Pt$  with parabanic acid, which is a diimide having the structure shown in Figure 4. The

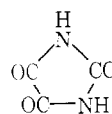


Figure 4.—Parabanic acid.

ligand reacted readily to give a complex whose ir spectrum showed bands due to the presence of both N-H and Pt-H groups. The stoichiometry agrees with the spectral results, thereby confirming that the structure consists of one imide molecule bonded to each platinum as shown in Figure 5. This complex still

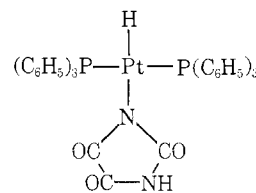


Figure 5.—Structure of the hydride obtained with parabanic acid.

contains an uncoordinated imide N-H group, but no complex has been isolated with both N atoms coordinated and the ligand acting as a bridging group across two  $(P(C_6H_5)_3)_2Pt$  groups.

(2) **Olefin-Bonded Complexes.**—The preparation of hydrides in this manner led to a study of the reaction with maleimide. This olefinic imide has several possible modes of coordination to the metal. Complexes anal-

ogous to the imide hydrides may be formed by oxidative addition, or 2 mol of imide may add as was found with the palladium complex. A further possibility is that the imide coordinates *via* a metal-olefin bond or that coordination occurs by two of these ways simultaneously to two different metal atoms. The stability of the metal-olefin bond would be enhanced by the carbonyl groups since electron-withdrawing substituents on an olefin allow a stronger metal-olefin bond to be formed because of enhanced back-donation.<sup>12</sup>

The complexes formed show no band in the ir spectrum due to a metal hydride, but whereas in the N-bonded complexes the N-H stretch was absent, in the maleimide complexes this band occurs in the 3170-3180-cm<sup>-1</sup> region. The presence of the N-H stretch in the ir spectrum of the complex shows that maleimide must be coordinated through the olefinic double bond rather than bonded directly through the nitrogen. The stoichiometry of the complex shows it to contain one molecule of imide for each (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Pt, (As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Pt, or (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Pd group, which is consistent with the structure shown in Figure 6.

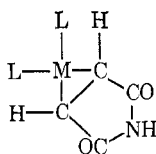


Figure 6.—Olefin-bonded complexes (M = Pt, Pd; L = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>).

The maleimide complexes show quite different solubility characteristics from the imide hydride complexes; whereas the hydrides are quite soluble in benzene and chloroform, these olefin-bonded complexes are about insoluble. Also with this ligand, the palladium complex forms a compound which is structurally analogous to the ones obtained with platinum, which is not the case with the N-bonded succinimide. The ir spectrum of maleimide itself is only very poorly resolvable but shows two peaks at 1737 and 1770 cm<sup>-1</sup>,<sup>8</sup> with the high-frequency peak being very weak. Both the platinum and palladium complexes however show two strong peaks of about equal intensity, which are very well resolved. The position of these bands again occurs at markedly lower frequencies than is observed for the free ligand, as was found for the N-bonded complexes. It seems therefore that whereas coordination of the metal to the N atom of the imide suppresses the intensity of the high-frequency band of the carbonyl group of the imide, coordination to the olefinic double bond enhances its ir intensity.

Detailed consideration of the bonding in the maleimide complexes is made difficult because of the low solubility of the compound. The ir spectra of the complexes show no band which can be assigned to the olefinic C=C stretch, but the triphenylarsineplatinum complex is sufficiently soluble in CDCl<sub>3</sub> to obtain an nmr spectrum. This shows two peaks—a resonance at

$\tau$  2.73 which is due to the triphenylarsine and a further resonance at  $\tau$  6.27. Maleimide itself shows a doublet ( $J \approx 1$  cps) centered at  $\tau$  3.3 due to the olefinic protons, and the upfield peak in the spectrum of the complex can only be assigned to the protons on the coordinated olefin. This means that the position of the olefinic protons has shifted upfield by 2.97 ppm on coordination, although neither the magnitude nor the direction of this shift is unusual for olefin coordination. This value closely compares to that found for the (maleic anhydride)Fe(CO)<sub>4</sub> complex. The nmr of the free ligand shows a resonance at  $\tau$  2.87 due to the olefinic protons, but on coordination this resonance is shifted to  $\tau$  5.93 representing an upfield shift of 3.06 ppm,<sup>13</sup> which is very similar to the 2.97 ppm found with this (As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Pt(maleimide) complex. The bonding is probably best described as two  $\sigma$  bonds by analogy with the (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Pd(maleic anhydride) complex, in which this mode of bonding was deduced by a study of the nmr spectrum.<sup>14</sup> The ir and nmr spectra of maleimide and the three complexes are shown in Table III.

TABLE III  
SPECTROSCOPIC DATA FOR THE  
OLEFIN-BONDED COMPLEXES

	$\nu_{\text{CO}}$ , cm <sup>-1</sup>	$\nu_{\text{NH}}$ , cm <sup>-1</sup>	$\tau_{\text{-CH}}$ , ppm
Maleimide	1770 1737 <sup>a</sup>	3190	2.87
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(maleimide)C <sub>6</sub> H <sub>6</sub>	1680 1725	3170	
(As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pt(maleimide)	1677 1728	3180	5.93
(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ) <sub>2</sub> Pd(maleimide)	1680 1730	3180	

<sup>a</sup> Data taken from ref 8.

Whereas the imide hydride complexes have the usual *trans* stereochemistry for the triphenylphosphines, the stereochemistry of the olefin-coordinated complexes must of necessity be *cis*, and this difference in stereochemistry could readily account for the solubility differences between the two types of complexes.

The preparation of the maleimide complex was repeated, but this time 2 mol of (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>4</sub>Pt was used for each mole of maleimide. The reaction gives good yields of (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Pt(maleimide) and unchanged (P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)<sub>3</sub>Pt but no complex containing the double bond of the imide coordinated to one Pt and the nitrogen atom coordinated to a second one.

### Experimental Section

The preparation of all complexes was carried out under a nitrogen atmosphere, but the subsequent work-up was carried out in the air. Succinimide, phthalimide, saccharin, maleimide, and parabanic acid were commercially available samples and used without prior purification. The solvent was removed from

(13) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 47 (1965).

(14) P. Fitton and J. E. McKeon, *Chem. Commun.*, **4** (1968).

(12) R. Jones, *Chem. Rev.*, **68**, 785 (1968).

the crude product by means of a rotary evaporator. Melting points were determined on a hot-stage microscope and are uncorrected. Benzene was dried over sodium and calcium hydride prior to use. Molecular weights were determined on a Hitachi Perkin-Elmer Model 115 osmometer as benzene solutions at 40.5°. Microanalyses were performed by Chemalytics Inc., Tempe, Ariz. Infrared spectra were obtained as Nujol or hexachlorobutadiene mulls on a Perkin-Elmer Model 700 spectrometer. Nuclear magnetic resonance spectra were obtained as solutions in  $\text{CDCl}_3$  on Varian A-60 or DP 60 spectrometers.

**Method A.**—Tetrakis(triphenylphosphine)platinum (415 mg) was dissolved in benzene (~20 ml) and succinimide (35 mg) was added. The yellow solution was refluxed for 24 hr and then allowed to stand for a further 24 hr, after which time it had become colorless. The solvent was removed and ether (~20 ml) was added. The suspension was stirred magnetically for several hours, filtered, washed with ether, and dried *in vacuo* to give the colorless complex; yield 230 mg.

A similar procedure was used for the preparation of complex II except that in this case phthalimide was used instead of succinimide.

**Method B.**—Tetrakis(triphenylphosphine)platinum (250 mg) was dissolved in benzene (~20 ml) and saccharin (52 mg) was added. Within a few minutes the color of the solution changed to a very pale yellow. The solvent was removed, and ether (30 ml) was added. The colorless precipitate was stirred for several hours, filtered, washed with ether, and dried *in vacuo* to give the colorless complex; yield 178 mg.

A similar procedure was used to prepare complex V, using parabanic acid instead of saccharin, although with this preparation it was several hours before the solution became pale yellow.

**Method C.**—Tetrakis(triphenylphosphine)platinum (325 mg) was dissolved in benzene (25 ml) and maleimide (29 mg) was added. The solution rapidly became pale yellow, and a microcrystalline precipitate slowly formed. After 12 hr the solid was filtered, washed with benzene, and dried *in vacuo* to give the complex; yield 224 mg.

A similar procedure was used for the preparation of complex VIII using tetrakis(triphenylarsine)platinum, complex IX using tetrakis(triphenylphosphine)palladium, and complex VI using tetrakis(triphenylphosphine)palladium and succinimide.

**Method D.**—Tetrakis(triphenylarsine)platinum (773 mg) as a suspension in benzene (~30 ml) was stirred with saccharin (104 mg) for 24 hr. The suspension was filtered to remove unchanged starting material and the solvent was removed from the solution of the complex. Ether was added and the resulting suspension was stirred for 2 hr. The solid was then filtered, washed with ether, and dried *in vacuo* to give the complex; yield 398 mg.

Complexes I-V can be recrystallized from a mixed chloroform-ether solvent.

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## Kinetics of Ligand Substitution Reactions for Platinum Complexes. Relative Influence of *cis*-Triethylphosphine and Amine Ligands upon the Isotopic Exchange between Chloride and Bromide Ions and the Halo Ligands<sup>1</sup>

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The kinetics of exchange for chloride and bromide ions with the corresponding halide ligands have been measured in methanol at 25 and 35° for the complexes *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)(NH<sub>3</sub>)Cl<sub>2</sub>, *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)(N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>)Cl<sub>2</sub>, *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>, and *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)(NH<sub>3</sub>)Br<sub>2</sub>. For each complex the rate law was found to be: rate = [Pt](*k*<sub>1</sub> + *k*<sub>2</sub>[halide]), where *k*<sub>1</sub> can be considered to characterize a solvation step. Exchange in the bromide systems is more rapid than for the corresponding chloride complexes. No systematic difference was evident between a phosphine or an amine in the *cis* position. However, in view of the trends observed the *trans*-Pt(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> proved exceptionally inert.

### Introduction

Kinetics studies on the large variety of substitution-inert square-planar complexes of platinum(II) have provided much information about the mechanisms for the ligand substitution processes. Reviews of the relevant literature<sup>2,3</sup> have summarized the evidence for a *normal* type of mechanism which is believed to involve an associative type of process with a five-coordinate (approximately trigonal-bipyramidal) configuration. Also, in many instances the direct replacement of a

ligand, X, by an entering group, Y, must compete with replacement of X by solvent. Although sometimes the intermediate may be characterized, frequently the solvent is rapidly displaced by Y. The result is a first-order term characterized by the rate constant *k*<sub>1</sub> in the rate law for substitution, *i.e.*

$$\text{rate} = [\text{Pt}](k_1 + k_2[\text{Y}]) \quad (1)$$

Evidence has been summarized<sup>4</sup> for a number of halide-exchange studies<sup>5</sup> in which an alternative mechanism must be operative. Also, it has been pointed out that some influences upon the kinetics which have

(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2565.

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