Studies on Metal Ion Coordination in Solution

VI. The Complex Formation of Diphenylphosphinobenzene-*m*-sulphonate with Palladium(II) and Platinum(II)

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Complex formation between diphenylphosphinobenzene-*m*-sulphonate (Dpm) and palladium(II) tetraaqua and platinum(II) diaquadiammine ions was studied in 1 M perchloric acid at 25°C. Solutions in equilibrium were studied with a mercury electrode, using the mercury(II)-phosphine system, previously studied, as an indicator system. In this way formation curves could be obtained for the exchange of the four water molecules in the Pd(II) aqua ion with Dpm as well as for the exchange of the two water molecules in the *cis*- and *trans*-diaquadiammine Pt(II) complexes. The formation curve for Pd(Dpm)$_4$$^{2+}$ showed a pronounced stop for $\bar{n} = 2$, and evidence was given that it is the *cis*-diaquadiphosphine palladium complex which is dominating in the equilibrium. The following values for the consecutive stability constants 1 mol^{-1} were obtained: Pd(II), $K_1 10^{10.2}$, $K_2 10^{9.8}$, $K_3 10^{6.3}$, $K_4 10^{4.9}$; Pt(II) *cis*, $K_1 10^{11.5}$, $K_2 10^{11.1}$, and Pt(II) *trans*, $K_1 10^{11.5}$, $K_2 10^{10.5}$.

The rates of formation of the Pd(II) and Pt(II) complexes were studied by spectrophotometric and stopped-flow measurements. The Pd(II)-phosphine complexes are formed nearly instantaneously, while the equilibria in the platinum systems are established relatively slowly. The second order rate constants k_1 and k_2 (M^{-1} sec^{-1}) for the uptake of the first and second phosphine for the *cis*-diammine were found to be 25 and < 10, respectively, and for the *trans*-diammine 300 and $\lesssim 5 \times 10^6$, respectively, in agreement with a very large *trans* effect.

In 1958 Ahrland *et al.* prepared a water-soluble sodium salt of a tertiary aromatic phosphine anion, diphenylphosphinobenzene-*m*-sulphonate (abbreviated Dpm), and determined the stability constants of its complexes with silver(I) and cadmium(II).[1] This work was continued by Bjerrum and coworkers, who determined the stability constants of several other metal-ion complexes of this phosphine.[2-5] In this paper, complex formation studies with Dpm have been extended to palladium(II) and platinum(II). Solutions of tetraaquapalladium(II) ion were prepared by dissolving PdSO$_4$ in perchloric acid.[6] As solutions of tetraaquaplatinum(II) ions probably cannot be prepared,[7]

solutions of the *cis* and *trans*-diaquadiammineplatinum(II) ions were chosen for this study. All measurements were made in 1 M perchloric acid at 25°C.

Preliminary experiments were attempts to measure the aqua palladium ion concentration with a palladium electrode. Templeton *et al.*[8] have with some success used a specially prepared spongy palladium electrode in acid chloride-containing solutions, but it was found by us that palladium electrodes were poisoned in phosphine containing solutions. Instead a mercury electrode was employed, using the earlier studied mercury(II) phosphine system[2] as an indicator system. Such a mercury indicator electrode was found to be useful for the determination of the formation curve for both the palladium(II) and platinum(II) phosphine systems.

The equilibria in the palladium phosphine system were established nearly instantaneously. Stopped-flow measurements gave only lower limits for the rate constants. The equilibria in the diammine platinum(II) phosphine systems were established more slowly, and the kinetics were here studied by classical spectrophotometry and stopped-flow measurements.

EXPERIMENTAL

Materials. Sodium diphenylphosphinobenzene-*m*-sulphate dihydrate was prepared by the method of Ahrland *et al.*[1,2] (Found: C 53.81; H 4.02; S 8.16; H_2O 8.96. Calc. for $C_{18}H_{14}O_3PSNa.2H_2O$: C 54.0; H 4.52; S 8.01; H_2O 9.00.)

Palladium sulfate was prepared by the method of Rasmussen and Jørgensen.[6] (Found: Pd 40.01; H_2O 23.51. Calc. for $PdSO_4.3\frac{1}{2}H_2O$: Pd 40.08; H_2O 23.75.)

cis- and *trans*-Dinitratodiammineplatinum(II) were prepared by the method of King[9] from *cis*- and *trans*-dichlorodiammineplatinum(II), respectively, these latter compounds being prepared by standard methods from potassium hexachloroplatinate(IV).[10] (Found for the *cis* isomer: Pt 55.56; N 15.76; H 1.62. Found for the *trans* isomer: Pt 55.78; N 15.78; H 1.89. Calc. for $[Pt(NO_3)_2(NH_3)_2]$: Pt 55.24; N 15.86; H 1.71.)
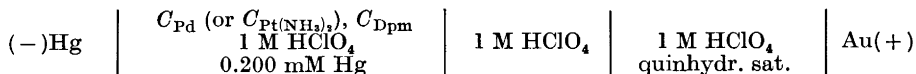
Solutions of *cis*- and *trans*-diaquadiammineplatinum(II) were prepared by dissolving *cis*- and *trans*-$[Pt(NO_3)_2(NH_3)_2]$, respectively, in 1 M perchloric acid and allowing the solutions to stand overnight at room temperature.[9,11]

All other chemicals were of reagent grade.

Analytical methods. Palladium was analyzed gravimetrically as the dimethylglyoxime complex,[12] and platinum was analyzed spectrophotometrically by the method of Ayres and coworkers.[13] The water content of the compounds was determined by thermal analysis, and we are indebted to cand. scient. Erik Pedersen, who carried out these determinations. Carbon, hydrogen, nitrogen, and sulfur were determined by microanalysis by Mr. Preben Hansen in the Department of Organic Chemistry.

Spectrophotometric measurements. All visible and ultraviolet absorption spectra were measured on a Cary 14 recording spectrophotometer, using matched silica cells and 1 M $HClO_4$ as solvent, also in the reference cell.

Potential measurements. The following cell arrangement was used:

| $(-)$Hg | C_{Pd} (or $C_{Pt(NH_3)_2}$), C_{Dpm}
 1 M $HClO_4$
 0.200 mM Hg | 1 M $HClO_4$ | 1 M $HClO_4$
 quinhydr. sat. | Au$(+)$ |

The whole cell arrangement was placed in a water thermostat at 25°C. The mercury potential of the mixed complex solution in 1 M $HClO_4$ containing 0.200 mM mercury ions was measured with a mercury electrode of the J-tube described before.[3] The measuring instrument was a French AOJP P-12 potentiometer equipped with spot galvanometer and Weston cell. The reference electrode, which was a bright gold foil in 1 M perchloric acid saturated with quinhydrone, was connected by a syphon bridge to the main electrode

vessel. Tests of several such reference electrodes against each other showed that their potentials were reproducible and stable for $2-3$ h within ± 0.1 mV.

The potential of the mercury electrode in the 0.200 mM mercury(I), mercury(II) equilibrium solution with $C_{\mathrm{Dpm}} = 0$ was measured several times and found to be -22 mV relative to the quinhydrone electrode.

The cylinder nitrogen used to deaerate the complex solutions was purified for oxygen by passing through a Meyer-Ronge apparatus.[14]

Rate measurements. The rates of formation of the complexes were estimated spectrophotometrically on the Cary 14 recording spectrophotometer. For the more rapid reactions the absorbance of the reacting solutions was recorded continuously at a selected wavelength in 2 or 5 cm cells in the thermostated cell compartment. Attempts were made to measure a few nearly instantaneous reactions by a stopped-flow technique. The stopped-flow apparatus used was constructed by Tranter and Nord.[15]
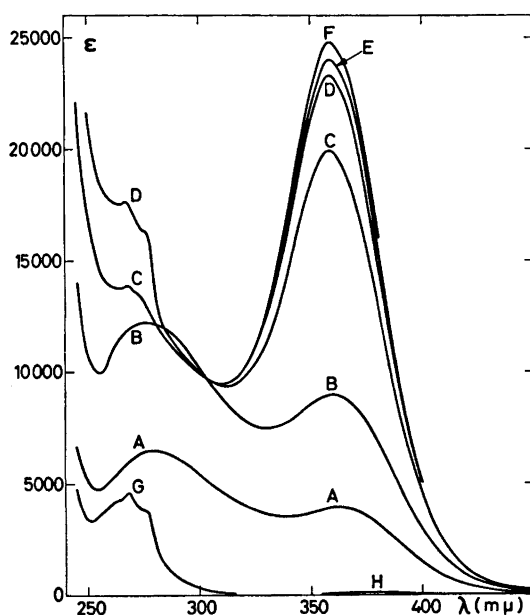

Fig. 1. Absorption spectra of Pd(II)-Dpm mixtures in 1 M HClO$_4$.

	$C_{\mathrm{Pd}} \times 10^5$	$C_{\mathrm{Dpm}} \times 10^5$	
A	5.0	5.0	1:1
B	2.5	5.0	1:2
C	1.25	3.75	1:3
D	1.25	5.0	1:4
E	1.25	6.25	1:5
F	1.25	12.5	1:10
G	—	5.0	Dpm
H	500	—	$\mathrm{Pd(H_2O)_4^{2+}}$

Molar absorptivities ε (M^{-1}cm^{-1}) are based upon C_{Pd}, except for the ligand itself.

PHOSPHINE COMPLEX FORMATION WITH Pd(II)

Spectra. Solutions of $PdSO_4$ in 1 M $HClO_4$ were found to have an absorption maximum at 380 mμ ($\varepsilon_{max} = 83.8$ M^{-1} cm^{-1}). This is in good agreement with that other authors [6,16,17] find for the $Pd(H_2O)_4^{2+}$ ion. When solutions of $PdSO_4$ and Dpm are mixed, the phosphine complex formation causes a very large increase in the molar absorbancy (up to 25 000), and the absorption maximum of $Pd(H_2O)_4^{2+}$ is gradually shifted from 380 mμ towards lower wavelengths with increasing phosphine concentration until 358 mμ when the molar ratio of Dpm to Pd is $\gtrsim 4$ (Fig. 1). The ligand does not absorb in this wavelength range, and it will be seen from the figure that the peak at 358 mμ increases only slightly when the ratio C_{Dpm}/C_{Pd} passes 4 for increasing ligand concentration. This shows that a tetraphosphine complex is formed which must be very stable considering the very low palladium concentration $C_{Pd} \sim 10^{-5}$ M. The phosphine complexes are formed nearly instantaneously, but they undergo secondary changes. The absorbance decreased in time especially for very dilute solutions with $C_{Dpm}/C_{Pd} > 4$ probably because of a palladium catalyzed oxidation of the free phosphine in equilibrium with the complexes. The decreases in absorbance were lower when the experiments were made in a nitrogen atmosphere where oxygen was removed by red-hot copper in a Meyer-Ronge apparatus, as mentioned in the experimental section. Only traces of oxygen could have been present but, as it seems, enough to oxidize the very dilute palladium phosphine solutions. After some days, the spectra resembled the $Pd(H_2O)_4^{2+}$ spectrum in the visible region, while the ultraviolet spectra changed towards the spectrum of the phosphine oxide.

Hg-electrode measurements. Fig. 1 gives information about the spectra for selected values of $\bar{n} \sim C_{Dpm}/C_{Pd}$, but no information about the very small concentration of free ligand present in the solutions. This concentration cannot be estimated from pH measurements because of the aprotic character of the aromatic phosphine.[3] Some preliminary experiments showed further that the Pd-electrode cannot be used in phosphine containing solutions. Therefore, the only possibility left to obtain information about the stability of the complexes was to introduce another metal phosphine system as an indicator system. Such a system should have a stability comparable to that of the palladium system, and it should be possible to measure the metal ion concentration with an electrode. The only possible choice in our case was the previously studied mercury-phosphine system,[2] and the use of this system was found to work better than could be expected considering that palladium is a little more noble than mercury. The standard potential for the $(PdH_2O)_4^{2+}$, Pd couple is given [17] as 0.92 V compared to 0.854 V for the $Hg(H_2O)_4^{2+}$, Hg couple, and when a perchloric acidic $Pd(H_2O)_4^{2+}$ solution is shaken with mercury, a black precipitate of palladium is formed after some time. However, it was fortunate that palladium phosphine solutions react so sluggishly with metallic mercury that potential measurements could be performed with only little interference by the mercury reduction. The procedure was as follows. A weighed amount of $PdSO_4 \cdot 3\frac{1}{2}H_2O$ was dissolved in 1 M $HClO_4$ (through which a stream of purified nitrogen had been passed for 1 h) containing 2 ml of a 0.01 M $(HgClO_4)_2$ in 1 M $HClO_4$ so as to give 100 ml of a solution 0.200 mM in Hg^{2+}. The nitrogen

flow was then continued for 20 min after which a weighed amount of the phosphine salt was added to the solution. When the phosphine was dissolved, the solution was transferred under nitrogen into the electrode vessel for measurement of the Hg-potential against a saturated quinhydrone reference electrode as mentioned in the experimental section. The dissolving of the phosphine and the transfer of solution took less than 2 min, and potential measurements began 5 min after the ligand was added and were continued at 5 min intervals. The potential usually reached the most negative value in 10 min after which the potential became slightly less negative, the new value being stable to within $1-3$ mV for $10-20$ min after which the potential dropped to even less negative values. The stable potential rather than the most negative potential was used for the calculation of $-\log[\text{Dpm}]$ and the ligand number $\bar{n}_{\text{Pd}}$. It was observed that, when the ratio $C_{\text{Dpm}}/C_{\text{M}} < 1.3$, where $C_{\text{M}} = C_{\text{Pd}} + C_{\text{Hg}}$, corresponding to a value of $\bar{n}_{\text{Pd}} \lesssim 1$, no stable potentials could be obtained. In these cases the potential 30 min after adding the phosphine was tentatively chosen since, in other cases, the stable potentials were reached at $25-35$ min after adding the ligand.

Calculation of data. The data for a series of measurements with $C_{\text{Pd}} \simeq 0.5 \times 10^{-3}$ are given in Table 1. The numerical difference between the measured

Table 1. Estimation of ligand exponent $-\log[\text{Dpm}]$ and average ligand number $\bar{n}_{\text{Pd}}$ from measurements of Hg-electrode potentials in mixed Hg(II), Pd(II)-phosphine solutions with $C_{\text{Hg}} = 0.200$ mM in 1 M HClO$_4$ at 25°C.

$C_{\text{Pd}} \times 10^3$	$C_{\text{Dpm}} \times 10^3$	$E_{\text{M}}{}'$	$\bar{n}_{\text{Hg}}$	$-\log[\text{Dpm}]$	$\bar{n}_{\text{Pd}}$
0.495	0.500	67.8	1.412	10.402	0.440
0.498	0.506	67.9	1.414	10.399	0.448
0.498	0.749	86.3	1.646	9.993	0.843
0.499	0.757	79.4	1.566	10.138	0.889
0.506	0.877	95.9	1.742	9.800	1.04
0.498	0.878	89.4	1.680	9.930	1.09
0.502	0.999	101.8	1.788	9.679	1.28
0.499	1.12	103.8	1.802	9.649	1.53
0.495	1.25	123.8	1.904	9.280	1.76
0.497	1.37	209.6	1.998	7.809	1.96
0.494	1.50	250.6	2.007	7.134	2.22
0.504	1.63	297.6	2.048	6.338	2.42
0.503	1.68	298.2	2.049	6.331	2.51
0.505	1.75	298.0	2.049	6.330	2.65
0.498	1.88	341.1	2.200	5.642	2.87
0.482	1.94	348.6	2.247	5.529	3.06
0.508	2.00	337.3	2.180	5.699	3.06
0.501	2.13	366.5	2.375	5.264	3.25
0.501	2.25	376.0	2.450	5.131	3.43

negative potential of each run, E, and the Hg(I),Hg(II) equilibrium potential of a solution without ligand (-22 mV, see Experimental) is denoted $E_{\text{M}}{}'$ by Salvesen and Bjerrum[2] and given in the 3rd column of the table. The ligand exponent $-\log[\text{Dpm}]$ and also $\bar{n}_{\text{Hg}}$ is a direct function of this potential, and

consequently can be calculated when the stability constants and $K_0 = [Hg_2^{2+}]/$ $[Hg^{2+}]$ are known. Such a calculation corresponding to values of $E_M{}'$, from 2 to 600 mV in 2 mV intervals, was performed by O. Mønsted using a computer program, applying the refined stability constants of the Hg(II)-phosphine system.[4] The values for $\bar{n}_{Hg}$ and $-\log[Dpm]$ in the 4th and 5th columns of Table 1 are interpolated from these data under the reasonable assumption that these constants, $K_1 = 10^{-14.5}$, $\beta_2 = 10^{-24.7}$, $\beta_3 = 10^{-29.8}$, $\beta_4 = 10^{-32.4}$ and $K_0 \sim 100$ determined in 1 M KNO_3 with sufficient accuracy, are valid also in 1 M $HClO_4$. In 1 M $HClO_4$ was found $K_0 = 107$. The last column gives finally $\bar{n}_{Pd}$, the average number of phosphine ligands bound to the palladium ion. This ligand number is directly calculated from the expression:

$$\bar{n}_{Pd} = \frac{C_{Dpm} - \bar{n}_{Hg}C_{Hg} - [Dpm] - [DpmH^+]}{C_{Pd}}$$

where according to spectrophotometric measurements of Wright and Bjerrum [3]

$$[DpmH^+] = 4.3[Dpm] \text{ in 1 M } HClO_4$$

The formation curve $\bar{n}_{Pd}$ *versus* $-\log[Dpm]$ is shown in Fig. 2. The data from Table 1 are plotted as ○ points, and another series of measurements
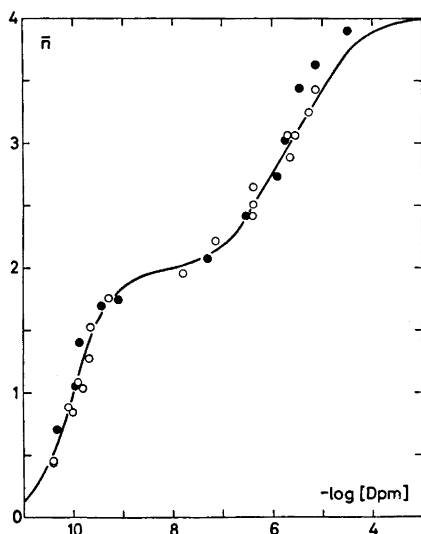

Fig. 2. The complex formation curve of palladium(II) tetraaqua ions and diphenyl-phosphinebenzene-*m*-sulphonate (Dpm) in 1 M $HClO_4$ at 25°C. ○ Experimental points with $C_{Pd} = 0.5$ mM, $C_{Hg} = 0.2$ mM. ● Experimental points with $C_{Pd} = 0.3$ mM, $C_{Hg} = 0.2$ mM. The full curve is calculated from the consecutive stability constants $\log K_1 = 10.16$, $\log K_2 = 9.84$, $\log K_3 = 6.33$, $\log K_4 = 4.92$.

with $C_{Pd} = 0.3$ mM and $C_{Hg} = 0.2$ mM are plotted as ● points. It will be seen that there is a pronounced stop in the curve at $\bar{n}_{Pd} = 2$. The stability constants, therefore, could be evaluated by dividing the formation curve into two parts, from $\bar{n} = 0$ to $\bar{n} = 2$, and from $\bar{n} = 2$ to $\bar{n} = 4$, using the method of Bjerrum. The middle part of the curve from $\bar{n} \sim 1$ to $\bar{n} \sim 3$ is best determined and was used in the calculation, and the full curve in the figure shows how the constants found reproduce all of the experimental points.

It is interesting that Rasmussen and Jørgensen [6] also found a distinct but somewhat smaller stop at $\bar{n} = 2$ in the Pd(II)-ammonia system showing that the affinity for the two ligands first taken up in both systems are somewhat higher than for the two following ones. The logarithms of the consecutive stability constants are given in Table 3.

PHOSPHINE COMPLEX FORMATION WITH THE ISOMERIC DIAQUADIAMMINE Pt(II) IONS

The techniques applied to the palladium complexes were also used to study the phosphine complex formation with the *cis*- and *trans*-diaquadiammineplatinum(II) ions. The aquaammine ions were selected since solutions of tetraaquaplatinum(II) ions cannot be prepared,[7] and because they do not isomerize during the phosphine complex formation. A study with these ions
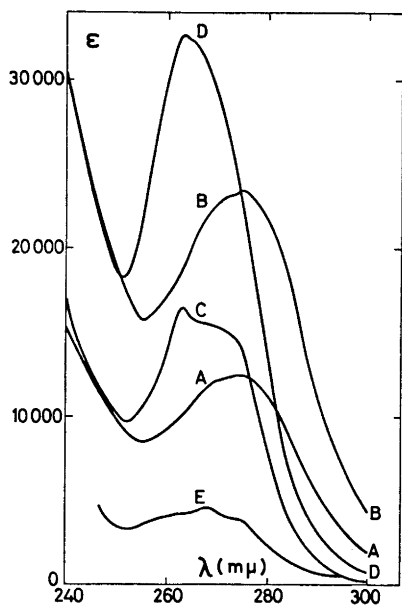
Fig. 3. Absorption spectra of *cis*- and *trans*-diammineplatinum(II)-Dpm mixtures in 1 M HClO₄.

	$C_{Pt} \times 10^5$	$C_{Dpm} \times 10^5$
A *cis*-Pt(NH₃)₂	1.0	1.0
B *cis*-Pt(NH₃)₂	1.0	2.0
C *trans*-Pt(NH₃)₂	1.0	1.0
D *trans*-Pt(NH₃)₂	1.0	2.0
E Dpm	—	5.0

Molar absorptivities ε (M⁻¹ cm⁻¹) are based upon C_{Pt}, except for the ligand itself.
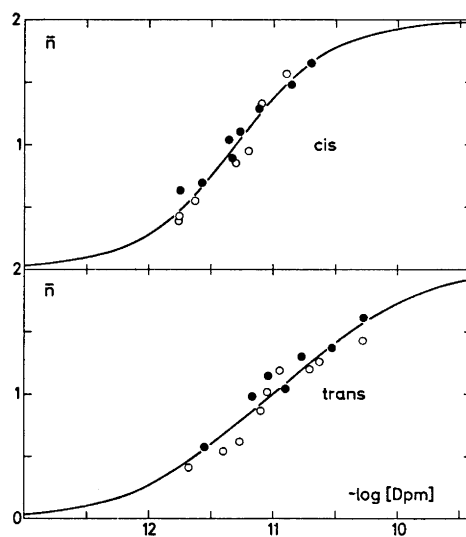
Fig. 4. The complex formation curves of the isomeric diaquadiammineplatinum(II) ions and diphenylphosphinebenzene-*m*-sulphonate (Dpm) in 1 M HClO₄ at 25°C. ○ Experimental points with $C_{Pt} = 0.5$ mM, $C_{Hg} = 0.2$ mM. ● Experimental points with $C_{Pt} = 0.3$ mM, $C_{Hg} = 0.2$ mM. The full curve for the *cis* complexes is calculated with $\log K_1 = 11.46$, $\log K_2 = 11.14$, and for the *trans* complexes with $\log K_1 = 11.53$, $\log K_2 = 10.47$.

has the additional advantage that the mercury potentials can be measured without interference form the platinum complexes. Solutions of the *cis*- and *trans*-diaquadiammineplatinum(II) ions in 1 M $HClO_4$ were prepared as described in Experimental. These ions have no light absorption maximum above 260 mμ, and the molar absorptivities between 240 and 260 mμ are very low (less than 100 M^{-1} cm^{-1}). However, when the diaqua ions and Dpm were mixed, there was a large increase in the absorbancies. The increase was not instantaneous as in the palladium system, but equilibrium was established in a few hours depending on the concentrations of the reactants. Owing to the high absorptivities it was necessary to measure solutions with C_{Pt} as low as $\sim 10^{-5}$ M, but they were made up from 20 times stronger solutions before measurements. The secondary changes due to oxidation of the phosphine were slower than in the palladium system and, in agreement with the stoichiometry, it was found that the molar absorptivities reached a limiting value when the ratio C_{Dpm}/C_{Pt} exceeded two. The spectra of the *cis* and *trans* complexes for $\bar{n} = 1$ and 2 are shown in Fig. 3.

When mercury(II) ions were present to compete for the phosphine, the equilibria were established more slowly. Therefore in each measurement, a solution saturated with nitrogen and containing the Pt(II)-phosphine mixture was left standing to equilibrate before the mercury(II) ions were added. This solution was then transferred to the electrode vessel and the mercury potential followed in time. By this technique, stable potentials within less than 1 mV were obtained in 30 min to several hours, depending on the phosphine concentration.

Table 2. Estimation of ligand exponent $-\log[\text{Dpm}]$ and average ligand number $\bar{n}_{Pt}$ from measurements of Hg-electrode potentials in mixed Hg(II), Pt(NH$_3$)$_2$-phosphine equilibrium solutions with $C_{Hg} = 0.200$ mM in 1 M $HClO_4$ at 25°.

$C_{Pt} \times 10^3$	$C_{Dpm} \times 10^3$	$E_M{}'$	$\bar{n}_{Hg}$	$-\log[\text{Dpm}]$	$\bar{n}_{Pt}$
Data with *cis*-diaquadiammineplatinum(II)					
0.499	0.370	23.3	0.862	11.759	0.397
0.501	0.381	23.3	0.862	11.759	0.416
0.501	0.457	26.6	0.909	11.633	0.549
0.501	0.632	35.9	1.016	11.305	0.857
0.501	0.684	39.2	1.051	11.199	0.947
0.501	0.878	42.2	1.083	11.104	1.32
0.499	1.01	48.3	1.153	10.919	1.57
Data with *trans*-diaquadiammineplatinum(II).					
0.499	0.379	25.4	0.893	11.678	0.403
0.501	0.467	33.0	0.985	11.405	0.540
0.499	0.515	36.9	1.026	11.274	0.621
0.499	0.648	42.3	1.084	11.101	0.865
0.499	0.729	44.0	1.103	11.048	1.02
0.499	0.822	47.2	1.140	10.952	1.19
0.501	0.849	55.7	1.245	10.710	1.20
0.499	0.888	58.9	1.288	10.625	1.26
0.499	1.01	73.0	1.488	10.280	1.43

The data for a series of measurements with the *cis* and *trans*-diaquadiammineplatinum(II) complexes are given in Table 2. The formation curves $\bar{n}_{Pt}$ *versus* $-\log[\text{Dpm}]$ are shown in Fig. 4. The data for the series with $C_{Pt(NH_3)_2}$ ~ 0.5 mM given in Table 2 are plotted as $\circ$ points, and another series of measurements with $C_{Pt(NH_3)_2}$ ~ 0.3 mM are plotted as $\bullet$ points. The logarithm of the consecutive constants corresponding to the full curves are given in Table 3. The complexity is, as could be expected, higher than for

Table 3. Estimated consecutive stability constants in 1 M perchlorate solutions at 25°C.

System	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
$Pd(H_2O)_4{}^{2+}$, NH_3	9.6	8.9	7.5	6.8
$Pd(H_2O)_4{}^{2+}$, Dpm	10.2	9.8	6.3	4.9
cis-$Pt(NH_3)_2(H_2O)_2{}^{2+}$, Dpm	11.5	11.1		
trans-$Pt(NH_3)_2(H_2O)_2{}^{2+}$, Dpm	11.5	10.5		

the palladium complexes, and though there is a relatively high uncertainty on the individual points, it will be seen that the curve for the *cis*-diaqua ion is distinctly steeper than for the *trans*-diaqua ion.

From a discussion of the absorption spectra of the palladium(II) ammine ions, Rasmussen and Jørgensen[6] suggest that the *cis*-diammine ion is dominating in the equilibrium, and their main evidence for this conclusion is that the estimated spectrum for the diammine complex is very similar to that of Pd en$(H_2O)_2{}^{2+}$. It is very likely that the diaquadiphosphine ion in the palladium system is also mainly the *cis* isomer, considering that the two first consecutive constants' ratio $(K_1/K_2 \sim 2.5)$ is very close to that of K_1/K_2 in the *cis* Pt(II) – Dpm system while the ratio $(K_1/K_2 \sim 10)$ is much higher in the *trans* Pt(11)-system. On the other hand, Chatt and Wilkins[18] have shown that for $[PtCl_2(Et_3P)_2]$ in benzene solution the *trans* complex is dominating in the equilibrium. However, after allowing for the possibly greater association of benzene with the *cis* isomer (to account for the large positive entropy change for the *cis*→*trans* isomerization), the *cis* isomer was found to be more stable than the *trans* isomer.

ON THE KINETICS OF THE Pd(II)-PHOSPHINE COMPLEX FORMATION

The substitution reactions of Pd(II) complexes reported in the literature are much faster than the analogous Pt(II) complexes;[19] therefore it was expected that the formation of the Pd(II)-phosphine complexes would be very fast. Indeed, the first step of the reaction was already too fast to be measured by our stopped-flow arrangement at 25°. An attempt was made to measure the very rapid change in absorbancy at a wavelength 363 mμ close to the main absorption maximum of the complexes (Fig. 1). However, even with concentrations of the reactants as low as 1×10^{-4} M, and a time sweep of 20 msec/div., only what seemed to be the foot of the reaction trace on the

oscilloscope could be noticed. Assuming second-order kinetics, the rate constant observed is, therefore, at least 5×10^5 M^{-1} sec^{-1}.

In case of the isomeric diammineplatinum(II) complexes the rate constants for the formation of the phosphine complexes could be estimated by classical spectrophotometry except in the case of the second step for the formation of the *trans* diphosphine complex where the rate was too fast for stopped-flow measurements.

ESTIMATION OF THE RATE CONSTANTS FOR THE FORMATION OF THE *cis*-DIPHOSPHINEPLATINUM COMPLEX

For the reaction of *cis*-$[Pt(H_2O)_2(NH_3)_2]^{2+}$ with Dpm, it was reasonable to expect that the rates of the two steps may not differ very much because the first phosphine is *cis* to the second leaving water molecule. Thus, in order to get a rough estimate of the first rate constant k_1 (*cis*), the initial part of the first step was treated as a simple second order reaction, assuming not much interference from the second step, and the reverse reaction was disregarded because of the large stability constant. An experiment was made as follows. The absorbance A is of a solution with the concentrations of $Pt(NH_3)_2(H_2O)_2^{2+}$, $a = 1.997 \times 10^{-5}$ M, and of Dpm, $b = 0.999 \times 10^{-5}$ M, was followed from the time of mixing the reactants, in a 2 cm cell at 275 mμ (Fig. 3). The absorbance A_∞ at $t = \infty$ was calculated from the known absorptivities and the composition of the equilibrium solution. This solution has $\bar{n} = 0.50$, and from the known stability constants we estimate that $[Dpm] = 1.86 \times 10^{-12}$ M, and that the fractions α_1 and α_2 of the mono- and diphosphine complexes are 0.341 and 0.079, respectively. This shows that a considerable amount of the bis complex exists in the equilibrium, so that probably the best approximation to the concentration x of the monophosphine complex was that calculated from the expression:

$$ x = \frac{A_t - A_0}{A_\infty - A_0} \ (\alpha_1 + \alpha_2) \ a $$

In this expression, A_0 is the absorbance at $t = 0$, and A_t at the time t. Finally, k_1 (*cis*) was calculated from the expression for second order kinetics:

$$ \frac{1}{a - b} \ \ln \frac{b(a - x)}{a(b - x)} = kt $$

The numerical data for this experiment are given in Table 4, and k_1 (*cis*) is seen to show a good constancy for a large range of the reaction. In another experiment with the concentration of $Pt(NH_3)_2(H_2O)_2^{2+}$, $a = 5 \times 10^{-5}$ M and of Dpm, $b = 1 \times 10^{-5}$ M in 1 M $HClO_4$ at 25°C, k_1(*cis*) was estimated to be about 26 decreasing from about 28 to 24 M^{-1} sec^{-1} when more than two thirds of the ligand has reacted. A less successful experiment with $a = 3 \times 10^{-5}$ M and $b = 0.52 \times 10^{-5}$ was also made. However, it is not unreasonable to assume that the reaction is at least close to being of second order, and that k_1(*cis*) has a value of about 25 M^{-1} sec^{-1}.

In order to obtain a rough estimate of the second rate constant k_2(*cis*) for the reaction of the monophosphine complex with Dpm, a run was started

Table 4. Estimation of the first rate constant k_1 in the *cis*-diammineplatinum(II)-phosphine system in 1 M $HClO_4$ at 25°C.

t(min)	A_{275}	$A_t - A_0$	$x \times 10^5$	$(a-x)10^5$	$(b-x)10^5$	$k_1(M^{-1} sec^{-1})$
0	0.090	0	0	1.997	0.999	
5	0.113	0.023	0.119	1.878	0.880	21.4
10	0.136	0.046	0.238	1.759	0.761	23.8
15	0.152	0.062	0.320	1.677	0.679	23.5
20	0.167	0.077	0.398	1.599	0.601	23.8
30	0.190	0.100	0.517	1.480	0.482	23.8
35	0.200	0.110	0.569	1.428	0.430	24.2
40	0.205	0.115	0.595	1.402	0.404	23.0
50	0.217	0.127	0.657	1.340	0.342	22.4
∞_{calc}	0.252	0.162				

from what was supposed to be an equilibrium solution with $\bar{n} \sim 1.5$. However, the data showed that the starting solution had not reached equilibrium, and the only information which could be drawn from the experiment was that k_2 (*cis*) must be smaller than 10 M^{-1} sec^{-1}.

ESTIMATION OF THE RATE CONSTANTS FOR THE FORMATION OF THE *trans*-DIPHOSPHINEPLATINUM COMPLEX

Phosphine as ligand is known to give a very strong *trans* effect. It was, therefore, to be expected that the second step in the *trans* system should be very fast. This was also confirmed in a stopped-flow experiment, where an equilibrium solution with $\bar{n} \sim 1.5$, containing mono- and diphosphine complex in a concentration of about 10^{-5} M, was mixed with the ligand in a similar concentration. The half-time of the reaction was found to be less than 20 msec and k_2 (*trans*) is, therefore, at least $1/(10^{-5} \times 2 \times 10^{-2}) = 5 \times 10^6$ M^{-1} sec^{-1}.

With a very fast second step, and a relatively slow first step, the kinetics of the reaction between *trans*-diaqua ion and Dpm can, as long as the system is far from being in equilibrium, with good approximation be treated as if the diaqua ion in one step is converted into the diphosphine complex. An experiment was made in which the initial concentrations of both the reactants, the diaqua ion and the ligand, were $a = 0.0054$ M. The rather fast reaction was studied by continuously recording the absorbance at 263 mμ after injecting an aliquot of the solution of the diaqua ion into an aliquot of the phosphine solution in a 5 cm cell in the Cary 14 cell compartment. The concentration x of the diphosphine complex was calculated from the expression

$$x = \frac{A_t - A_0}{A_\infty - A_0} \frac{a}{2}$$

where A_∞ is the calculated absorbance of a solution of the diphosphine complex in the concentration 0.5 a. According to the assumptions made, k_1 (*trans*) was calculated from the expression:

$$\frac{1}{a} \ln \frac{a-x}{a-2x} = kt$$

Table 5. Estimation of the first rate constant k_1 in the *trans*-diammineplatinum(II)-phosphine system in 1 M $HClO_4$ at 25°C.

t(sec)	A_{263}	$A_t - A_0$	$x \times 10^5$	$(a-x)10^5$	$(a-2x)10^5$	$k_1(M^{-1} sec^{-1})$
0	0.147	0	0	0.540	0.540	
20	0.165	0.018	0.0165	0.524	0.507	298
40	0.183	0.036	0.033	0.507	0.474	319
60	0.201	0.054	0.0495	0.491	0.441	333
80	0.214	0.067	0.0613	0.479	0.417	298
100	0.223	0.076	0.0695	0.471	0.401	298
120	0.236	0.089	0.0815	0.459	0.377	301
160	0.260	0.113	0.1032	0.437	0.334	313
200	0.272	0.125	0.1142	0.426	0.312	289
240	0.290	0.143	0.1309	0.409	0.278	298
$\infty_{(calc)}$	0.442	0.295	0.270			

The data for the experiment are given in Table 5. It will be seen that there is hardly any trend in the estimated constant ~ 300 M^{-1} sec^{-1} after half of the ligand has reacted, and repetition of the experiment with other initial concentrations of diaqua ion and ligand gave similar results.

DISCUSSION OF RESULTS

The outcome of the experiments on the kinetics of the phosphine complex formation, which can be considered only as preliminary results, is summarized in Table 6. The data seem to confirm that the *cis*- as well as the *trans*-di-

Table 6. Summary of estimated second order constants for the reaction of diphenylphosphinobenzene-*m*-sulphonate with Pd(II) and Pt(II) ions in 1 M $HClO_4$ at 25°C.

System		$M^{-1} sec^{-1}$
$Pd(H_2O)_4$	+ Dpm →	$k_1 \gtrsim 5 \times 10^5$
cis-$Pt(NH_3)_2(H_2O)_2$	+ Dpm →	$k_1 \sim 25$
cis-$Pt(NH_3)_2(H_2O)Dpm$	+ Dpm →	$k_2 < 10$
trans-$Pt(NH_3)_2(H_2O)_2$	+ Dpm →	$k_1 \sim 300$
trans-$Pt(NH_3)_2(H_2O)Dpm$ +	+ Dpm →	$k_2 \gtrsim 5 \times 10^6$

phosphinediammineplatinum(II) complexes are formed from the corresponding diaqua ions in two successive second order reactions, and a rough calculation with the rate constants shows that the solutions used to determine the stability constants (Table 2) cannot have been far from being in equilibrium. The *trans*-diaqua ion is seen to react more than 10 times faster with Dpm than the *cis*-diaqua ion. Further it is seen that k_2 in the *cis* system is considerably smaller than k_1. On the other hand, the opposite is very pronounced in the case of the *trans* system where the *trans* effect $k_2:k_1$ is found to be higher than 10^4. This is to be compared with a *trans* effect of about 200 for Cl^- and

about 3000 for Br^- (likewise relative to coordinated water) in the halide anation of Pt(II).[20,21]

It is the general opinion to-day [22] that the *trans* effect is nearly exclusively a kinetic effect. However, besides lowering the activation energy, it is reasonable to assume that a ligand with a strong *trans* effect also to some extent diminishes the affinity to ligands in *trans* more than in *cis* position. This conclusion is already drawn from a consideration of the estimated stability constants (Table 3), according to which the second phosphine is relatively more strongly bound in the palladium and *cis*-diammineplatinum than in the *trans*-diammineplatinum system. Let us consider instead of the diammineplatinum ions the reaction of Dpm with the unsubstituted tetraaqua Pt(II) and Pd(II) ions. The reaction starts when a phosphine *via* the penta-coordinated transition state displaces a water molecule in the square planar tetraaqua ion. Then because of the high *trans* effect the second phosphine is taken up simultaneously and nearly exclusively in the *trans* position. Therefore, when nearly all the ligand is complexly bound considering, *e.g.*, the case that $C_L \sim C_M$, much more *trans* diphosphine complex is formed than corresponding to the equilibrium. This complex is then in subsequent steps converted back into monophosphine and more stable *cis* diphosphine complex until equilibrium is established. A similar mechanism in which the complex richest in ligands during the reaction is formed to a higher degree than corresponding to the equilibrium concentration is demonstrated in other systems with high stability constants, *e.g.* in an early study of the rates of formation of Cu en_2^{2+} and Ni en_3^{2+}.[23]

In the diaquadiphosphinepalladium complex, the two remaining water molecules in the prevailing *cis* complex are both *trans* to phosphine groups and therefore very labile, but the relatively large stop in the formation curve for $\bar{n} = 2$ (Fig. 2) shows that this also involves a diminished affinity for the uptake of the third and fourth phosphine. In case of the Pd(II)-ammonia [6] and the Pt(II)-halide systems [20,21] the two last ligands taken up are also more weakly bound than the two first ligands, but not so pronouncedly as in the palladium-phosphine system. The stronger influence on the stability constants in this system may have its cause in the higher *trans* effect of the phosphine ligand, but other effects are also involved.

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