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Solvent Effects in Square Planar Complexes: Kinetics of Substitution at [1-(2-Hydroxyphenyl)-3,5-diphenylformazanato]palladium(II) Complexes

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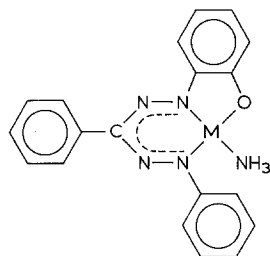
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Summary

A kinetic study is reported on the substitutions: $\text{FoPdX} + \text{Y} \rightarrow \text{FoPdY} + \text{X}$ ($\text{H}_2\text{Fo} = 1\text{-}(2\text{-hydroxyphenyl})\text{-}3,5\text{-diphenylformazan}$) with $\text{X} = \text{NH}_3$ and py and $\text{Y} = \text{thiourea}$, tetramethylthiourea, triphenylphosphine and the thiocyanate ion, in seven nonaqueous pure solvents. Under pseudo first-order conditions a two-term rate-law is obeyed: $k(\text{obs}) = k_1 + k_2 [\text{Y}]$. The results in terms of reactivity pattern and solvent effects on initial and transition states are very similar to the ones found for the analogous substitutions at platinum(II). The rate of solvolysis (k_1) is determined by the donor number of the solvent and is not related to the transfer free energy of solvation of the substrate. Nonspecific solvation effects dominate. The entropy of activation for the direct nucleophilic displacement, $\text{FoPdNH}_3 + \text{Ph}_3\text{P}$, is found to lie between -110 and $-20 \text{ JK}^{-1} \text{ mol}^{-1}$, indicating the associative character of the substitutions. The named reaction exhibits an isokinetic relationship in the various solvents. In spite of that, an initial state – transition state – final state comparison shows the position of the transition state on the reaction coordinate to be solvent dependent. The importance of charge transfer from the donor solvent to the metal ion in determining the Gibbs free energy of the transition state is emphasized.

Introduction

Substitutions at square planar metal complexes of the dibasic tridentate ligand 1-(2-hydroxyphenyl)-3,5-diphenylformazan (H_2Fo) present an interesting case for mechanistic study^(1,2). The formula (1) for the ammine complex is given as an example of the structure of these complexes.



Advantages in using these complexes are as follows. In the first place the rigidity of the substrate hinders the formation of a relatively stable five-coordinate intermediate, thereby giving substitutions at palladium(II)⁽¹⁾ and platinum(II)⁽²⁾ an unusually high degree of synchronicity^(3,4). It further fixes the geometry of the transition state so that it will not undergo a drastic change on varying the solvent. Another interesting point is the possibility of steric hindrance in the reactions of triphenylphosphine as entering ligand. Steric hindrance could

also be a determining factor for electronic effects operative in the transition state for reactions at FoMpy ($\text{py} = \text{pyridine}$) complexes⁽²⁾. Solvent variation has indicated the dominance of general solvation effects, equalizing the transfer functions of initial and transition states. Exceptions are encountered in solvents with strong donor properties where charge transfer to the metal centre destabilizes the transition state^(1,2).

The research project described above was initiated with the palladium(II) compounds FoPdNH_3 and FoPdpy in a limited number of solvents⁽¹⁾ and was later extended to platinum(II) utilizing seven nonaqueous solvents⁽²⁾. The object of the present study is to reexamine the solvent dependence of substitutions at FoPdNH_3 and FoPdpy for the full range of solvents used for the platinum(II) compounds and thus to check the mechanism. Also a further elaboration of the mechanism was attempted, to start with in the field of steric hindrance by introducing tetramethylthiourea besides thiourea as entering ligand. Further, for one reaction, activation parameters were obtained and compared with an analysis of the reaction in terms of an initial state – transition state – final state dissection of free energy changes. The relative importance of general and specific solvation could be evaluated in the solvolysis, which however could not be observed for platinum(II). This report treats substitutions:



with $\text{X} = \text{NH}_3$ and py ; $\text{Y} = \text{tpp}$ (triphenylphosphine), tu (thiourea), tmtu (tetramethylthiourea) and the thiocyanate ion, in the pure nonaqueous solvents: Pc (propylene carbonate), MeOH (methanol), An (acetonitrile), Ac (acetone), DMSO (dimethylsulphoxide), DMF (dimethylformamide), and in Diox (1,4-dioxane) only for $\text{Y} = \text{tpp}$ and tmtu .

Results and Discussion

Under pseudo first-order conditions (a more than 10-fold excess concentration of entering ligand, $[\text{Y}]$) the observed rate constant for reaction (1) obeys the usual two-term rate-law for square planar substitution^(5,6), as found before^(1,2):

$$k(\text{obs}) = k_1 + k_2 [\text{Y}] \quad (2)$$

The results of a least-squares analysis of the rate at varying $[\text{Y}]$ (generally eight concentrations varied over one order of magnitude) are summarized in terms of k_1 and k_2 in Table 1 (The full set of kinetic data is available on request). Utilizing the transfer functions calculated from measured solubilities, an i.s. (initial state) – t.s. (transition state) dissection^(7,8) was performed on k_2 as described⁽¹⁾. Transfer chemical potentials for initial $[\sum \delta_m \mu^\ominus(\text{R})]$ and transition states ($\delta_m \mu^\ddagger$) for the direct displacement (k_2) are displayed in Figure 1. Pc is the reference solvent. In this Figure, broken lines are introduced

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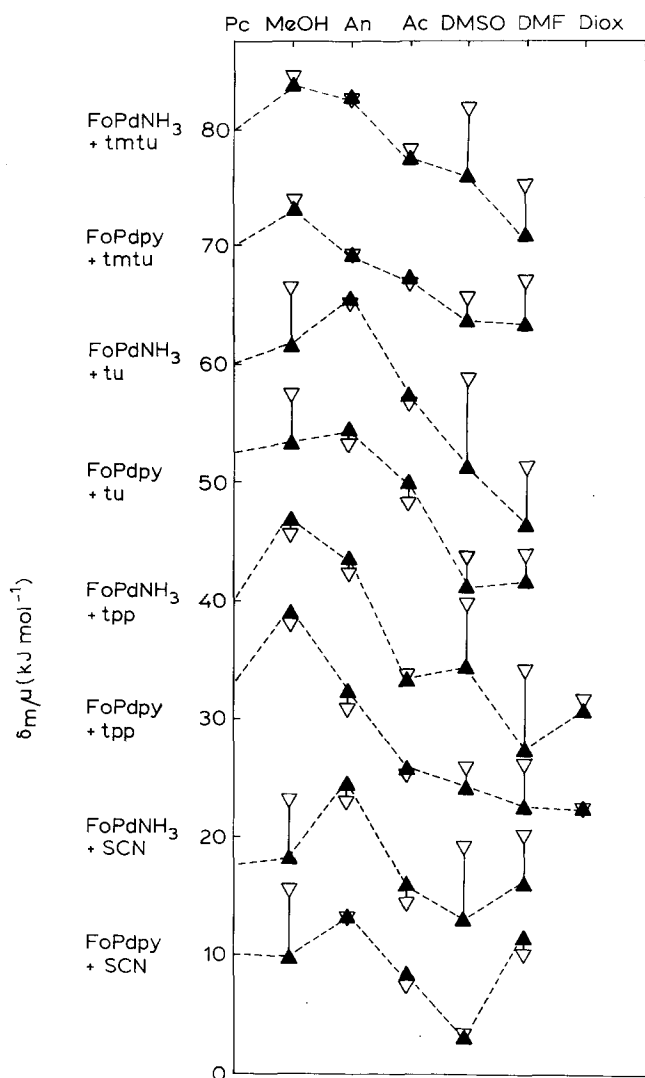


Figure 1. Variation of transfer chemical potential of reactants (▲) and transition state (▽) for the reactions between FoPdX and Y, with propylene carbonate as reference solvent, at 25.0°. The reference potential ($\mu = 0$) is vertically displaced. Values of corresponding states are connected.

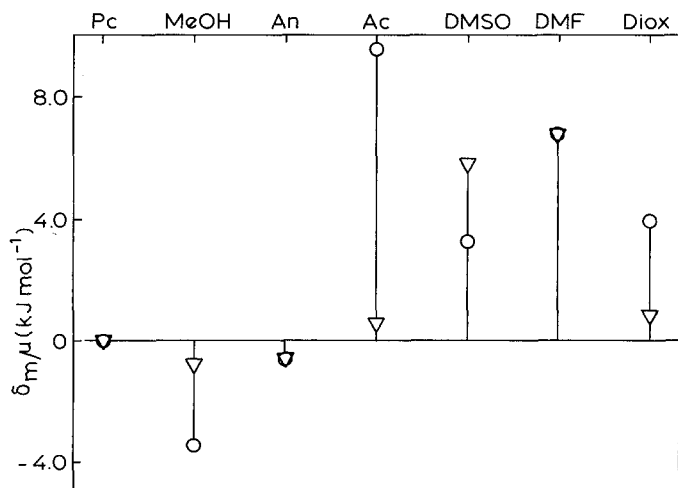


Figure 2. Position of transfer chemical potential of transition (▽) of final (○) state relative to the initial state for the reaction FoPdNH₃ + tpp. Values at 25.0°. Reference solvent propylene carbonate.

for clarity; no functional relation is implied. For the reaction FoPdNH₃ + tpp a further survey of i.s.-t.s.-f.s. (final state)⁽²⁾ is displayed in Figure 2.

The solvent dependence of the rate constants k_1 and k_2 will now be treated separately.

Rate constant k_1

k_1 refers to the rate-determining solvolysis of X in FoPdX, followed by a rapid interchange of solvent and entering group Y^(4,5). The k_1 values in Table 1 show a higher reactivity of FoPdpy to solvolysis compared to FoPdNH₃. A similar reactivity dependence on the leaving group is found for the direct displacement in the present formazan complexes of palladium(II) (*vide infra*) and of platinum(II)⁽²⁾ and is in line with the order of base strength⁽⁶⁾. Solvolysis rates may be related to the donor capacities of the solvent as entering ligand. To look into this relation we plotted the transfer Gibbs free energy of activation $\delta_m \Delta G^\ddagger$ for k_1 as a function of the Gutmann donor number⁽⁹⁾ (Figure 3). Although no perfect linear relation is present, there is a significant correlation (correlation coefficient -0.92) between $\delta_m \Delta G^\ddagger$ and ΔDN for the entire ensemble of ammine and pyridine displacements, with the exception of the reactions in acetonitrile. It is remarkable that in spite of the noted difference in reactivity between FoPdNH₃ and FoPdpy no significant difference in behaviour of the transfer functions is observed. The exceptional solvolysis rate in acetonitrile may be due to its π -acceptor capacity and/or the smallness of the solvent molecule, which minimizes steric hindrance. This kind of behaviour is more often met for acetonitrile as solvent, as exemplified by the isolation of acetonitrile complexes⁽⁴⁾.

In contrast to the donor number, the transfer chemical potential of the substrate (Figure 4) shows no relation with $\delta_m \Delta G^\ddagger(k_1)$: correlation coefficient = -0.02 for FoPdNH₃ and -0.53 for FoPdpy. As deduced before⁽¹⁾ from a much more limited amount of data, this means that the donor number is a much better measure for specific solvent coordination, operative in the solvolysis reaction, than the overall free energy of solvation, which is consequently dominated by non-specific (general⁽⁴⁾) solvational effects.

For one reaction, FoPdNH₃ + tpp, activation parameters were obtained for five of the solvents studied (Table 2). The

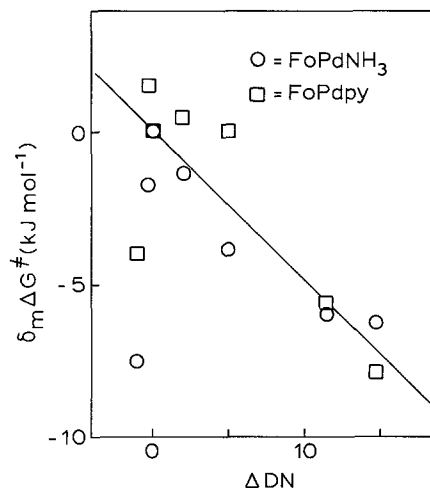


Figure 3. Relation between the transfer Gibbs free energy of activation (relative to propylene carbonate) for the solvolysis rate constant k_1 , and the Gutmann donor number DN.

Table 1. Rate parameters k_1 (10^{-2}s^{-1}) and k_2 ($\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$) and transfer chemical potentials (kJ mol^{-1}) for the reaction between FoPdX and Y, at 25.0°C .

X; Y	Solvent Pc	MeOH	An	Ac	DMSO	DMF	Diox
NH_3 ; tu	0.4(6)		5.9(8)	0.2(5)		2.8(2)	
	48(1)		46(1)	54(2) ^b		5.6(1)	
	0		5.60	-2.58		-13.34	
	0		5.71	-2.87		-8.01	
NH_3 ; tmtu	0.3(4)	1.5(1)	7.3(3)	0.7(1)	3.5(3)	3.6(2)	1.0(1)
	0.91(4)	0.78(2)	1.11(7)	0.77(2)	0.089(8)	0.14(2)	1.53(4)
	0	3.67	2.78	-2.75	-3.97	-9.30	
	0	4.05	2.28	-2.34	1.80	-4.66	
NH_3 ; tpp	0.18(9)		6.1(4)		4.2(2) ^b	3.4(1)	
	4.5(1)		5.7(4)		0.45(3) ^b	0.3(1)	
	0		3.47		-5.73	-12.52	
	0		2.89		-0.02	-5.80	
NH_3 ; SCN^-	0(1)		4.9(2)	0.2(5)		3.1(1)	
	1.28(3)		1.61(4)	1.88(6) ^b		0.28(3)	
	0		6.9	-1.6		-1.2	
	0		6.4	-2.6		2.6	
py; tu	14(6)		20(20)		212(3)	81(9)	
	336(7)		447(7)		108(14) ^b	141(4)	
	0		1.91		-11.23	-10.68	
	0		1.20		-8.41	-8.53	
py; tmtu	6(2)	9.0(8)	43(1)	7.3(8)	202(2)	68(3)	6.7(6)
	9.1(3)	7.3(1)	9.3(2)	11.0(2)	4.1(2)	3.1(2)	20.0(3)
	0	2.88	-0.92	-2.85	-6.49	-6.65	
	0	3.42	-0.97	-3.32	-4.52	-3.97	
py; tpp	0(2)					80(2)	
	14.0(6)					4.6(3)	
	0					-9.87	
	0					-7.11	
py; SCN^-	15(2)		44(2)			109(5)	
	10.1(2)		9.9(3)			15.4(3)	
	0		3.3			1.5	
	0		3.3			0.5	

a) For each combination of X; Y and solvent the entries are: $\begin{cases} k_1 \\ k_2 \\ \delta_{\text{m}}^{\text{tr}} = \sum \delta_{\text{m}}^{\text{tr}}(\text{R}) \\ \delta_{\text{m}}^{\text{tr}}(k_2) \end{cases}$

The standard deviation is given in parentheses in terms of the last figure of the rate constant; ^b) Redetermination of values reported in ref. 1.

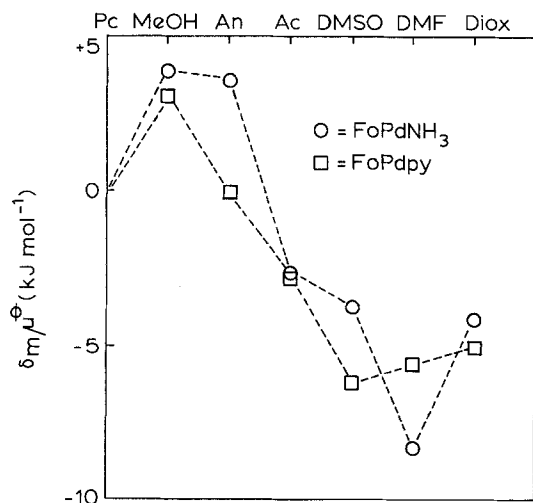


Figure 4. Variation of transfer chemical potential with solvent for the palladium(II)-formazan complexes. Values at 25.0°C . Reference solvent propylene carbonate.

markedly negative value of the entropy of activation (-80 to $-120 \text{ JK}^{-1} \text{ mol}^{-1}$) and the relatively small value of the enthalpy (45 to 60 JK mol^{-1}) are an indication of the expected associative mode of activation^(4,5,6). The activation parameters for k_1 of Table 2 display an isokinetic relation with an isokinetic temperature of 423 K . This so-called compensatory effect on changing the solvent will be met again for k_2 (*vide infra*).

Table 2. Activation parameters for the reaction: $\text{FoPdNH}_3 + \text{tpp}$

Solvent	$\Delta H^\ddagger(k_1)$ (kJ mol^{-1})	$\Delta S^\ddagger(k_1)$ ($\text{JK}^{-1} \text{ mol}^{-1}$)	$\Delta H^\ddagger(k_2)$ (kJ mol^{-1})	$\Delta S^\ddagger(k_2)$ ($\text{JK}^{-1} \text{ mol}^{-1}$)
Pc	60	-80	38	-106
MeOH	59	-81	45	-77
An	45	-116	41	-90
Ac	59	-86	40	-100
DMSO	53	-95	69	-19

Rate constant k_2

Without repeating previous discussions⁽²⁾ the following interesting features of the reactivity pattern displayed by the FoPdX reactions and analogous to the one found for the FoPtX reactions are summarized: a) The weaker base pyridine is a better leaving group than ammonia; b) The apparent nucleophilicity of the entering group is dependent on both solvent and substrate (Table 1), possibly indicating⁽²⁾ a high degree of synchronicity^(3,4) of bond-forming and bond-breaking in the transition state; c) The exceptionally high reactivity of tpp as entering ligand^(6,10) is not reproduced for the formazan complexes. The cause of this fact may be a high degree of π -acceptor ability in the substrate or steric hindrance due to the rigidity of the substrate^(1,2). For the only charged entering ligand, the thiocyanate ion, the reaction with FoPdpy in Pc and DMF was studied as a function of the ionic strength (I) by varying I between 0.1 and 2 mol dm⁻³. No influence on the observed rate was found. In addition the reactions in acetonitrile were repeated under addition of kryptofix 222 in order to sequester Na⁺, so that all thiocyanate is present as the free ion. Under these conditions the measured rates increased by 10 to 20%. This means that the reactivity of the thiocyanate ion and ion-pair (NaSCN) are similar. This similarity has been noted before for square-planar d⁸ systems⁽¹¹⁾.

Activation parameters are available for the direct displacement in the reaction: FoPdNH₃ + tpp (Table 2). The negative values of the entropy of activation are indicative of the expected associative mode of activation^(4-6,10). For the entries in Table 2 there is a linear relation between ΔH^\ddagger and ΔS^\ddagger for k_2 (correlation coefficient 0.99) with an isokinetic temperature of 364 K. This compensatory effect of ΔH^\ddagger and ΔS^\ddagger is characteristic for many sets of reactions, in which solvational changes are important. The isokinetic temperature in such cases lies between 300 and 400 K⁽¹²⁾, as it does here. An isokinetic relationship does not have to imply that the position of the t.s. on the reaction coordinate relative to the i.s. and the f.s. is solvent independent. Following the procedure for the platinum(II) reactions⁽²⁾ we calculated the transfer chemical potential of the f.s. for the reaction: FoPdNH₃ + tpp, the only reaction of the present set for which this is possible. In Figure 2 the transfer chemical potential $\delta_{m\mu}$ of t.s. and f.s. relative to the i.s. is displayed as a function of the solvent. From this Figure it is clear that, similar to the pattern obtained for the analogous platinum(II) reaction, the position of the t.s. on the reaction coordinate is solvent dependent, or, in other words, no linear free energy relation (LFER) is observed. This means that the solvent dependence of the rate is not only determined by the primary interaction between solvent and substrate. In the following argument, indications as to the operation of electronic effects on the effective charge of the metal ion on changing the solvent will be presented. A dissection^(7,8) of solvent effects on i.s. and t.s. chemical potential for the direct displacement reactions studied is shown in Figure 1.

The general picture is similar to the pattern observed for the analogous platinum(II) reactions⁽²⁾: in spite of the presence of a considerable solvent effect on the transfer chemical potential of the substrate (Figure 4) and the erratic behaviour of the potentials of the entering and leaving ligands (only NH₃ is available) (Figure 3 of ref 2), the transfer chemical potentials of i.s. and t.s. stay close together. From this pattern of behaviour again the conclusion must be drawn that nonspecific or general solvation effects dominate the free energy changes connected with the change of solvent, in line with the similar

conclusion drawn from the solvent dependence of the solvolysis rate constant k_1 .

The exceptions to the general picture outlined above occur exactly where they did for the platinum(II) reactions. Following the discussion on the platinum(II) reactions, we may then put down the exceptions with MeOH as solvent to an i.s. stabilization of the entering ligands tu and SCN⁻ (see Figure 3 of ref. 2) in the protic solvent MeOH. This acceptor stabilization by the solvent is then partially lost on forming the t.s..

This behaviour distinguishes protic from dipolar aprotic solvents⁽¹³⁾, but is generally not unambiguously present for the substitutions at square planar d⁸ systems^(14,15). The effect is not observed for tpp and tmtu, which do not show a stabilization in MeOH, compared to the reference solvent Pc (Figure 3 of ref. 2 and Table 3).

Table 3. Solubilities S (mol dm⁻³)^{a)} of palladium(II)-formazan complexes and one ligand at 25.0°.

Compound	Solvent					
	Pc	MeOH	An	Ac	DMSO	DMF
FoPdNH ₃	-3.96		-5.43			-0.62
FoPdpy	-7.44					-5.17
FoPdtp	-4.28		-5.69	-5.17		-2.32
tmtu	0.64	0.72	0.99	0.69	0.77	1.05

^{a)} The entries are in lnS.

The lack of reactivity of all FoPdNH₃ reactions in DMF and DMSO is hardly noticed in the FoPdpy reactions. If, like the methanol exceptions, the explanation is a stabilization of the i.s., caused by interaction of the substrate with strongly donating solvents, which is partially lost on activation, as advanced by Belluco⁽¹⁵⁾, it should be mimicked in a comparable stabilization of the chemical potential of FoPdNH₃ compared to FoPdpy in both DMSO and DMF. This effect is clearly absent (Figure 4). Therefore the decrease in rate noted on going to the powerful donor solvents, DMSO and DMF, must stem from a t.s. labilization. The most obvious cause is then the increased negative charge on Pd²⁺ in the t.s., transferred to the metal by the donor solvents. Indeed for the expected associative mode of activation increased charge on the metal means a labilization of the t.s.. This effect, which also occurs for FoPtNH₃⁽²⁾, could be due to weak (as to free energy of solvation) direct specific coordination to the vacant axial positions of Pd²⁺ by a solvent molecule. However the main free energy of solvation would come from general solvation and not from this specific interaction (otherwise an i.s. effect would operate). The effect should then only occur for FoPdNH₃ and being prevented sterically in FoPdpy. This explanation becomes less probable for the platinum(II) system, when the solvent dependence of ¹⁹⁵Pt n.m.r. chemical shifts is taken into account⁽²⁾.

This report presents additional arguments against charge transfer by axial coordination of the solvent to Pd²⁺ as the dominant explanation for the t.s. labilizations in DMSO and DMF:

a) On going down the group: nickel(II), palladium(II) and platinum(II), the ease of additional axial bonding, as exemplified by a preference for octahedral over square planar coordination, decreases. This is also evident from the fact that for platinum(II) the solvolysis rate constant k_1 of Equation(2) is much less important than for palladium(II). Now the general picture of i.s. – t.s. transfer chemical potential in our case is

not changed on going from palladium (Figure 1) to platinum (Figure 2 of ref. 2);

b) A similar argument can be based on the fact that solvent acetonitrile shows an exceptionally large solvolysis rate (Figure 3), which must be due to the ease of bonding of An to Pd²⁺, but which is not reproduced as an exceptional position in the t.s. values in Figure 1;

c) Also the set of tmtu reactions are revealing in this respect. This incoming ligand is expected to show steric constraint and indeed direct substitution rates for this ligand are 10 to 50 times slower than the tu reactions. Now this ligand tmtu shows exceptional behaviour in its transfer chemical potential in DMSO and DMF like tu does, which is contrary to expectation, since steric hindrance should be an important factor in determining this pattern.

A second and more plausible reason for the DMSO-DMF discrepancy is a specific donor interaction of already bound solvent (*vide supra*) with the H-atoms of the coordinated NH₃ in FoPdNH₃, also resulting in transfer of electronic charge to the metal ion.

If the labilization of the t.s. is put down to an increase of negative charge on the metal atom, the transfer chemical potential of the t.s. will not only be determined by changes in the primary interaction between solvent and substrate. This means that the position of the t.s. on the reaction coordinate will be solvent dependent, exactly as found and discussed above (Figure 2). From this Figure it is also evident that the pattern changes when a reverse reaction such as FoPdtp + NH₃ is considered. However, this example gives a much more complicated picture. The paucity of data on the reverse reactions, especially the absence of data on py as entering ligand, prohibits a more detailed elaboration of the mechanism. In the case noted, the complication may arise out of t.s. steric hindrance for tpp and i.s. stabilization effects.

Empirical solvent parameters

The importance of donor and acceptor interactions in determining the chemical potentials of i.s. and t.s. for the present set of reactions makes it interesting to subject the data to a least-squares fitting on the basis of a two-parameter equation⁽²⁾:

$$\delta_m \Delta G^\ddagger = p_0 + p_1 \cdot \Delta DN + p_2 \cdot \Delta AN \quad (3)$$

Here we use the Gutmann donor numbers⁽⁹⁾ DN and the Gutmann-Mayer acceptor numbers⁽¹⁶⁾ AN with Pc as reference solvent. The results are summarized in Table 4 together with the comparable p values for the platinum(II) reactions. The closeness of the correlation coefficient to unity is impressive. The p values in Table 4 emphasize the importance of donor interactions at FoPdNH₃ compared to FoPdpy and the similarity between the palladium(II) and the platinum(II) set on a more quantitative basis than Figure 1. Consequently the conclusions drawn above for palladium on the basis of the solvent dependence of k₁, the isokinetic relations and the importance of axial coordination, are also applicable for the platinum(II)-formazan substitutions.

Table 4. Regression parameters (kJ mol⁻¹) for the rate constant k₂ of the direct displacement.

Substate	Ligand	p ₁ (Pd)	p ₁ (Pt) ^{a)}	p ₂ (Pd)	p ₂ (Pt) ^{a)}	multiple corr. coeff. (Pd)
FoPdNH ₃	tpp	0.47	0.40	-0.12	-0.11	0.97
	tu	0.51	0.63	0.12	0.11	0.99
	tmtu	0.43		-0.04		0.98
	SCN ⁻	0.42	0.49	0.15	0.19	0.99
FoPdpy	tpp	0.19	0.20	-0.04	-0.07	0.90
	tu	0.23	0.17	0.16	0.16	0.99
	tmtu	0.21		0.02		0.87
	SCN ⁻	-0.02	0	0.25	-0.14	0.99

a) From ref 2.

Experimental

The preparation of the palladium(II) formazan complexes⁽¹⁷⁾ and the purification of ligands used^(1, 2), the stopped-flow technique for monitoring the reaction⁽¹⁾ and the procedure used to obtain solubilities and transfer functions^(1, 2) have been described previously. All solvents were purified prior to use by way of conventional methods⁽¹⁸⁾. The reactions were monitored in the region of maximal spectral change of the complexes: 16000 to 25000 cm⁻¹, and were found to be wavelength independent in that region. Reactions were followed up to more than 90% completion and obeyed a first-order rate-law under conditions of an excess of entering ligand. Every single rate constant employed in the calculations had a standard deviation smaller than 2%. The temperature accuracy was ± 0.1°.

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