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Effect of Solvent, Leaving and Entering Ligand on Substitution Rates of Square Planar Complexes of Palladium(II) with 1-(2-Hydroxyphenyl)-3,5-diphenylformazan

S. Balt* and J. Meuldijk

Department of Inorganic Chemistry, Free University, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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Nucleophilic Substitution, Palladium(II), Formazan,1-(2-hydroxyphenyl)-3,5-diphenylformazan, Solvent Effects, Substitution Reactions

Nucleophilic substitution in different non-aqueous solvents at square planar complexes of palladium(II) with 1-(2-hydroxyphenyl)-3,5-diphenylformazan (H_2Fo) according to $FoPdX + Y \rightarrow FoPdY + X$, with X = ammonia and pyridine and Y = triphenylphosphine, thiourea and the thiocyanate ion, obeys the rate law: rate = $k_1[FoPdX] + k_2[FoPdX][Y]$. Values of k_1 and k_2 were obtained at 25.0 °C. From measured solubilities and literature values of transfer functions the transfer chemical potentials for initial and transition state were calculated. A comparison of these quantities in different solvents leads to the conclusion that non-specific solvation effects are dominant in these compounds. The mutual dependence of the effects of leaving and entering ligands and solvent on the substitution rate indicates a level of synchronicity of bond-breaking and bond-making that is unusually high for palladium(II) complexes.

Introduction

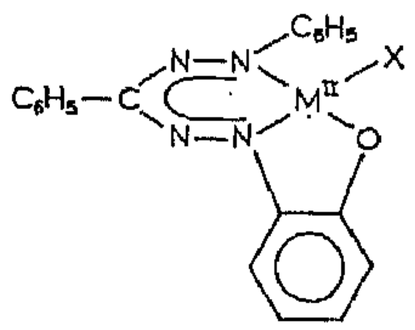
The nucleophilic displacement of ligands at platinum(II) and palladium(II) centres in square planar complexes has been intensively studied [1–5]. For the reaction

$$L_3MX + Y \rightarrow L_3MY + X \quad (1)$$

generally a two-term rate law is found [1, 2]:

$$\text{Rate} = k_1[L_3MX] + k_2[L_3MX][Y] \quad (2)$$

in which k_1 refers to a reaction path involving solvolysis, followed by a rapid substitution of solvent by Y; and k_2 is the direct displacement. The mechanism of activation for these substitution reactions is associative [1]. The considerable solubility of many of the complexes in various protic and aprotic solvents gives the possibility of studying the solvent dependence in solvent systems of widely differing properties. In spite of the considerable amount of data available, solvent effects in square planar substitutions remain difficult to interpret [4], partly because of the softness of the platinum(II) and palladium(II) centres. The correlation between reaction rates and donor properties of the solvents is therefore not straightforward [6]. As far as the solvent is concerned a distinction has been made [4] between general and specific solvation, in which the second term refers to coordination at the vacant axial positions at the metal centre. To this specific solvation effect one may add interactions between solvent acceptor sites and ligand donor atoms. As a step towards solving these and related solvent problems it seemed to be of interest to study square planar substitution reactions at a rigid substrate containing an extended organic system. To this end complexes of the weak dibasic acid 1-(2-hydroxyphenyl)-3,5-diphenylformazan (further denoted as H_2Fo) proved a good choice, as this ligand in a semiaromatic structure of its anion Fo^{2-} forms stable planar metal complexes [7, 8]:



It is possible to prepare pure complexes with M = Pd and X = NH_3, pyridine and triphenylphosphine [9]. For M = Pt up to now no sufficiently pure compounds could be obtained.

The monodentate ligand X can in the case of ammonia and pyridine easily be substituted by a ligand Y according to equation (3):

$$FoPdX + Y \rightarrow FoPdY + X \quad (3)$$

The ammine and pyridine complexes were found to give reactions going to completion with triphenyl-

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* Reprint requests to Dr. S. Balt.

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phosphine (tpp), thiourea (tu) and the thiocyanate ion. The present study of solvent dependence comprises the reactions of $FoPdNH_3$ and FoPdpy: with tpp in methanol (MeOH), acetonitrile (An) (only FoPdpy), acetone (Ac), dimethylsulphoxide (DMSO) and 1,4-dioxane (Diox); and with thiourea (tu) and the thiocyanate (SCN) ion in MeOH, Ac and DMSO. We have tried to correlate the solvent dependence of both k_1 and k_2 of equation (2) with solvent parameters as: transfer functions of both reactants [10, 11], calculated from solubilities, and the Gutmann donor and acceptor number [12].

Experimental

Chemicals

The preparation of the palladium complexes will be described elsewhere [9]. The remaining chemicals were purchased in reagent grade and subjected to further purification in the following way:

Triphenylphosphine, thiourea and sodium thiocyanate were recrystallized from ethanol and vacuum dried over phosphorus pentoxide. The solvents used were dried and purified according to the usual procedures [13].

Kinetics

Kinetic runs were performed at 25.0 ± 0.1 °C using two types of stopped-flow spectrophotometers depending on the reaction rates, as described previously [8]. The concentration of the palladium complexes was circa 10^{-4} mol dm^{-3}. Only in the case of thiocyanate as entering group a constant ionic strength of 0.10 mol dm^{-3} was employed by adding sodium perchlorate, to eliminate changes in the degree of ion-association. For each substitution reaction the concentration of the entering ligand was chosen so high in excess that the backward reaction was negligible and pseudo first-order conditions were secured.

The reaction was monitored in the wavelength region of maximum change, 16,000 to 25,000 cm^{-1}, and was found to be independent of the wavenumber. The variation of the reaction rate on varying the concentration of the incoming ligand (minimum of 8 concentrations over at least one order of magnitude) was found to obey equation (2). The experimental rates were fitted to this equation using a computerized least-squares procedure. The experimental values are available on request.

Results of the kinetic studies of the substitution reactions in terms of the two rate constants k_1 and k_2 of equation (2) are summarized in Table I. The standard deviation is given in parentheses in terms of the last decimal of the rate constant.

Solubilities

The solubilities of the palladium(II) complexes and the entering ligands triphenylphosphine and thiourea in the solvents used were determined by

Table I. Kinetic parameters k_1 (in s^{-1}) and k_2 (in s^{-1} mol^{-1} dm^3) and transfer functions (in kJ mol^{-1}) for the reactions between FoPdX and Y, at 25.0 °C in different solvents*.

$X = NH_3$									
Y = tpp	MeOH	Ac	DMSO	Diox					
$10^2 \times k_1$	1.4(2)	0.76(6)	4.2(2)	0.15(15)					
k_2	6.2(3)	3.63(5)	0.17(9)	3.35(7)					
$\delta_m \mu^{\neq}$	0	—12.23	— 3.76	—14.54					
$\Sigma \delta_m \mu^{\theta}$ (R)	0	—13.56	—12.67	—16.06					
X = py									
Y = tpp	MeOH	An	Ac	DMSO	Diox				
k_1	0.092(6)	0.47(4)	0.066(6)	2.23(3)	0.028(4)				
k_2	15.8(8)	22.6(4)	15(1)	7.2(5)	13.9(4)				
$\delta_m \mu^{\neq}$	0	—7.27	—12.71	—12.46	—15.83				
$\Sigma \delta_m \mu^{\theta}$ (R)	0	—6.38	—12.85	—14.41	—16.15				
$X = NH_3$						X = py			
Y = tu	MeOH	Ac	DMSO			Y = tu	MeOH	Ac	DMSO
$10 \times k_1$	0.14(3)	0.02(5)	0.36(3)				0.90(6)	0.6(1)	21.2(3)
k_2	6.1(1)	5.4(2)	1.94(4)				59(2)	600(35)	11(1)
$\delta_m \mu^{\neq}$	0	—3.84	— 7.42				0	—9.19	— 7.83
$\Sigma \delta_m \mu^{\theta}$ (R)	0	—4.14	—10.26				0	—3.43	—12.00
$X = NH_3$						X = py			
Y = SCN	MeOH	Ac	DMSO			Y = SCN	MeOH	Ac	DMSO
$10 \times k_1$	0.147(4)	0.02(5)	0.36(1)				0.95(3)	1.0(2)	21.7(3)
k_2	0.184(5)	0.188(6)	0.10(2)				0.97(4)	13.9(6)	8.9(5)
$\delta_m \mu^{\neq}$	0	—2.21	—3.48				0	—8.05	—12.22
$\Sigma \delta_m \mu^{\theta}$ (R)	0	—2.15	—4.99				0	—1.45	— 6.73

* MeOH = methanol; An = acetonitrile; Ac = acetone; DMSO = dimethylsulphoxide; Diox = 1,4-dioxane; tpp = triphenylphosphine; py = pyridine; tu = thiourea; SCN = SCN^-.

equilibrating at 25.0 ± 0.1 °C up to a reproducible constant concentration (obtained after 3 h). The concentration of the palladium complexes followed from spectrophotometric measurement. The amount of triphenylphosphine was determined by precipitation of the compound by the addition of water to the saturated solution. For thiourea the concentration was determined by a conductometric titration with mercury(II) chloride [14]. The solubilities are given in Table II. The accuracy of the data is 2%.

Table II. Solubilities (in units 10^{-2} mol dm^{-3}) of palladium(II) formazan complexes and entering ligands at 25.0 °C in different solvents.

Compound	MeOH	An	Ac	DMSO	Diox
F_oPdNH_3	0.40	–	5.5	8.3	10.0
F_oPdpy	0.017	0.060	0.176	0.71	0.44
F_oPdtpp	0.036	0.57	0.34	2.23	14.3
tu	132	–	51	400	–
tpp	8.6	32	149	69	225

Transfer functions

Solubilities and rate parameters provide a basis for the calculation of transfer chemical potentials [10, 11]. These quantities will be designed here by $\delta_m\mu$, in which δ_m is the solvent operator [15]. Methanol was chosen as the reference solvent, because it is the solvent common to all systems studied. The symbol $\delta_m\mu^0$ stands for the transfer chemical potential of the different compounds studied in the standard state (a concentration of 1 mol dm^{-3} [16]). For the uncharged species $\delta_m\mu^0$ follows from the solubilities assuming that no change in the solid phase in contact with the different solvents takes place [17]. Then:

$$\delta_m\mu_S^0(A) = RT \ln\left(\frac{S_{RS}(A)}{S_S(A)}\right) \quad (4)$$

in which $S_S(A)$ and $S_{RS}(A)$ are the solubilities (in moldm^{-3}) of compound A in solvent S and the reference solvent RS respectively.

Transfer free energy values for ions have been tabulated (Table 14-4 of reference [18]) containing values for the thiocyanate ion in MeOH and An. We could calculate [17, 19] the $\delta_m\mu^0$ difference between Ac and An from the solubility products of silver(I) thiocyanate:

$$\Delta\delta_m\mu^0(SCN) = RT \ln\left(\frac{P_{S1}(AgSCN)}{P_{S2}(AgSCN)}\right) - \Delta\delta_m\mu^0(Ag^+) \quad (5)$$

in which P(AgSCN) denotes the solubility product in the solvents. In this calculation we used extrapolated P values of Barraqué *et al.* [20] and recent transfer values for the silver(I) ion [21]. $\mu^{\neq}$ refers to the chemical potential of the transition state; the corresponding transfer function was calculated from:

$$\delta_m\mu^{\neq} = \Sigma\delta_m\mu^0(R) + \delta_m\Delta G^{\neq} \quad (6)$$

Here the summation is over the reactants and the activation Gibbs function follows from:

$$\delta_m\Delta G^{\neq} = RT \ln\left(\frac{k_{RS}}{k_S}\right) \quad (7)$$

where k is the rate constant, measured in the reference solvent: k_{RS} and the other solvents: k_S.

Transfer chemical potentials of reactants and transition state are listed in Table I. Figures 1 and 2 exhibit the transfer chemical potential of palladium complexes and entering ligands respectively. In these and following figures the order of the solvents is arbitrarily chosen as following the most common decrease in chemical potential found for the palladium complexes. Broken lines are introduced for clarity and do not indicate any functional relation.

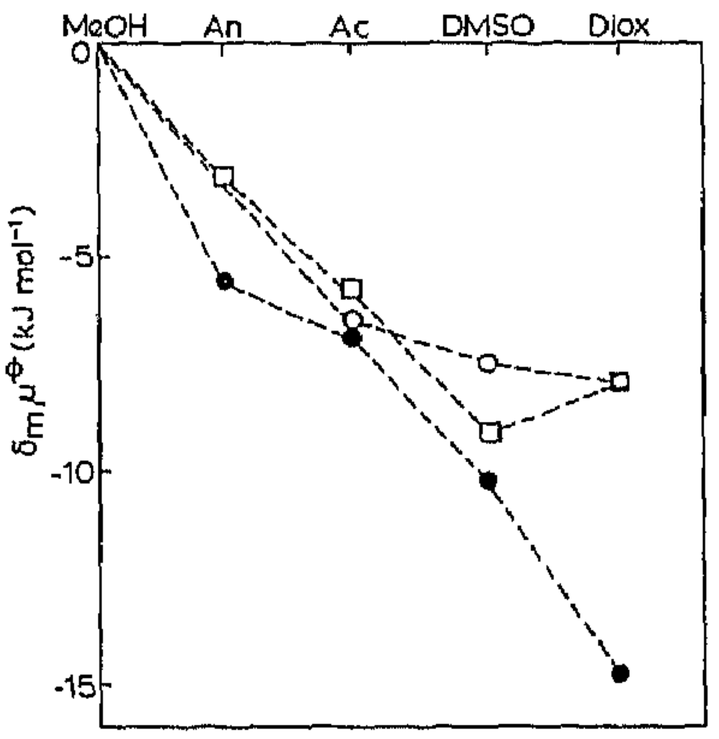

Fig. 1. Variation of transfer chemical potential with solvent of the palladium(II) formazan complexes: $FoPdNH_3$, O; FoPdpy, □ and FoPdtpp, ●. Values at 25.0 °C. Reference solvent methanol.

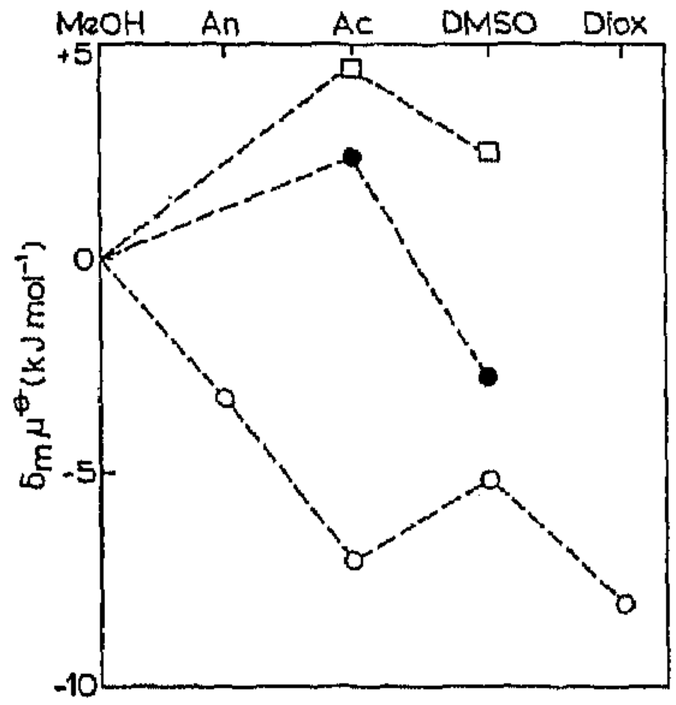

Fig. 2. Variation of transfer chemical potential of the entering ligands with solvent: tpp, O; SCN^-, □ and tu, ●. Values at 25.0 °C. Reference solvent methanol.

Results and Discussion

Rate constant k_1

In this discussion we adopt the generally accepted [1, 3, 4] interpretation of k_1 as referring to a rate-

determining displacement of the leaving group by a solvent molecule (solvolysis) followed by a fast introduction of the entering group in place of the solvent molecule. Indeed within the experimental error k_1 for one substrate is independent of the entering group (Table I) as expected for the postulated mechanism. It is then reasonable to assume that specific coordination of a solvent molecule to a vacant coordination site of Pd^{2+}, above or under the complex plane, will be a first step in the displacement of the leaving group.

The dependence of k_1 on solvent properties will therefore give information on the fact whether specific coordination as described above or general (non-specific) solvation is dominant in the different solvent parameters. To consider this issue we plotted (Figure 3) the transfer Gibbs function

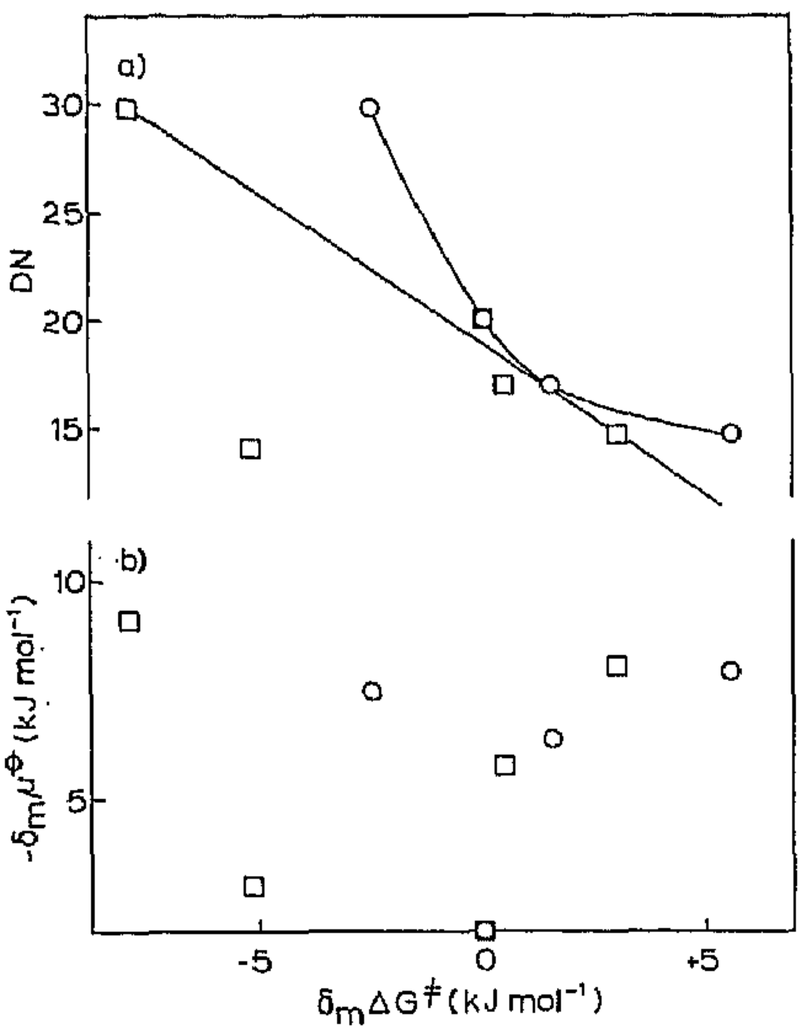

Fig. 3. Relation between transfer Gibbs free energy of activation (relative to methanol) of the solvolysis rate constant k_1 and a) the Gutmann donor number (DN) and b) the transfer chemical potential of the palladium(II) complexes: $FoPdNH_3$, ○ and FoPdpy, □. Values at 25.0 °C.

$\delta_m\Delta G^\neq$ as a function of a) the Gutmann donor number [12] and b) the transfer chemical potential $\delta_m\mu^\theta$ of the palladium complexes for the different solvents. It is clear that in spite of the softness of the substrate [6] the donor number referring to specific donor-acceptor interaction at the palladium centre for both $FoPdNH_3$ and FoPdpy is a much better criterium (with only the unexplainable exception of the solvolysis of FoPdpy in An) for the reaction rate than the total solvation of the complex measured by the transfer chemical potential $\delta_m\mu^\theta$(FoPdX). From this the important conclusion can be drawn that non-specific solvation, inactive in the mechanism of solvolysis, comprises a large part of the total solvation of the palladium(II) complexes. This conclusion will also have a consequence for the interpretation of the rate constant of the second term in the rate law of equation (2).

Rate constant k_2

The rate constant k_2 for the direct displacement of the leaving ligand by the entering one shows a very complicated pattern of mutual dependence in the effects of leaving group, entering group and solvent, as summarized in Table III. The higher activity of the pyridine complex is a well known consequence of its lower base-strength [2].

Table III. Effect of leaving group on the rate for different substrates and solvents.

	$FoPdNH_3$	FoPdpy
MeOH	tu $\simeq$ tpp $>$ SCN	tu $>$ tpp $>$ SCN
Ac	tu $\simeq$ tpp $>$ SCN	tu $\gg$ tpp $\simeq$ SCN
DMSO	tu $>$ tpp $\simeq$ SCN	tu $\simeq$ tpp $\simeq$ SCN

It is well established [3, 4] that for substitution reactions at platinum(II) the nature of the replaceable ligand X (equation (1)) influences the reactivity, but not the discrimination of the substrate among the entering nucleophiles. As a consequence the entering ligands can be arranged in a self-consistent sequence of nucleophilicity resulting in a quantitative (n-$^{0}_{Pt}$) scale. Unfortunately no extended studies of these effects exist for palladium complexes, in contrast to the large quantity of data available for the platinum(II) complexes. However a conclusion can be drawn as to the intimate mechanism [22] of the substitution reactions of the palladium(II) formazan complexes. Starting from the familiar two-maxima curve of the reaction profile [1, 2] it has been argued [4, 22] that for platinum(II) complexes the fact that effects of leaving and entering ligand are largely mutually independent is an indication that the two stages in the process of substitution, bond-breaking with the leaving group and bond-making to the incoming group, are relatively independent of each other, which means that the Gibbs free energy of the five-

coordinated intermediate differs from that of the transition states. On the other hand analogous reactions of square planar gold(III) complexes do show a mutual dependence of the effects of entering and leaving groups suggesting a higher degree of synchronicity of bond-breaking and bond-making [4, 22]. In this connection it was pointed out that the available information on palladium(II) complexes could indicate an increase in the stability of the intermediate corresponding to a decrease of synchronicity compared to platinum(II), fitting in the synchronicity order:

$$\mathrm{Rh(I)} < \mathrm{Pd(II)} < \mathrm{Pt(II)} < \mathrm{Au(III)} \qquad (8)$$

It also proved possible recently [23] to draw up a $n\text{-}^{\mathrm{o}}_{\mathrm{Pd}}$ scale for nucleophilicity of the incoming group for a limited number of palladium(II) complexes, where the $n\text{-}^{\mathrm{o}}_{\mathrm{Pd}}$ sequence was found to resemble the one established for the platinum substitutions. This conclusion has been confirmed for palladium(II) complexes of 3-azapentane-1,5-diamine [24].

The present series of substitution reactions at palladium(II) shows effects of mutual dependence of incoming and leaving groups as discussed above. These are indications of an increase in synchronicity in the substitution reactions compared to the general picture of the substitution at platinum(II), contrary to equation (8). This fact most probably must be explained from the rigidity of the palladium-formazan moiety, which is expected to decrease the stability of the postulated five-coordinated intermediate. In this discussion one must regret that up to now we have not been able to prepare the analogous platinum(II) formazan complexes in a sufficiently pure form. Concluding this part of the discussion it must be emphasized that the synchronicity arguments presented here are questioned [25].

A further interesting point is that the high nucleophilicity of tpp as entering ligand [2, 3] is not reproduced for the present reactions: tpp and tu are of comparable reactivity, whereas generally for platinum(II) substitution reactions rates increase more than one order of magnitude on going from tu to tpp as incoming group. The reason for this discrepancy again must be sought in the rigidity of the substrate resulting in extra steric hindrance for the bulky tpp ligand, but probably also in the availability of a high degree of π-acceptor ability in the formazan system, so that extra stabilization by tpp as π-acceptor in the transition state plays a less important role. The last mentioned argument would be reinforced if it could be demonstrated that the systems under study show larger reaction rates than usually found for palladium(II) substitution reactions. Regrettably this point is difficult to establish because substitution rates for palladium complexes vary widely and a saturated analogue for our system could not be located. However the larger rate of substitutions at unsaturated substrates compared to saturated ones is well established for platinum(II) [26].

Influence of solvent; transfer quantities

The transfer chemical potentials (Fig. 1) of both complexes, $\mathrm{FoPdNH_3}$ and FoPdpy, follow each other closely in different solvents, which means that differences in reaction rate between the two substrates cannot be explained from ground state solvent effects.

We found that the transfer chemical potentials of the two palladium compounds cannot be fitted as a linear function of the differences (compared to the reference solvent methanol) in the Gutmann donor number [12], referring to specific solvation of the Pd^{2+} centre. It is especially noteworthy that an exceptional solvational stability in DMSO with its high donor number (29.8) is not present. Because the complexes have both donor and acceptor sites we also tried to fit the transfer functions to a linear combination of donor and acceptor terms [27, 28], but this fit unrealistically gave a positive coefficient for the acceptor term meaning a destabilization, besides the expected negative donor contribution. This picture reinforces the conclusions drawn in the previous section when discussing k_1.

In Fig. 4 we have schematically displayed the relative change in chemical potential of the reactants and the transition state. For the thiocyanate ion no corrections were applied for a change in ion-association or activity coefficient between the solvents.

With a few exceptions to which we shall come back later the entries for ground and transition state stay close together. From this the conclusion must be drawn that the changes in chemical potential are largely due to general solvation effects that do not change on activation, as special interactions between either Pd^{2+} and solvent donor sites

or ligand donor atoms and solvent acceptor sites would.

As noted above there are a few exceptions to the general picture of solvation. To start with, the reaction $FoPdNH_3 + tpp$ in DMSO shows a considerable destabilization of the transition state compared to the other solvents. No ground state stabilization of the $FoPdNH_3$ complex is operative in this case, as discussed above. In addition the entering ligand tpp, in DMSO even shows a relative destabilization compared to changes in the chemical potentials of the complexes.

For $FoPdpy + SCN^-$ the picture in Fig. 4 suggests that in this case methanol is exceptional in a destabilization of the transition state. An alternative stabilization of the ground state as a result of the acceptor interaction of the protic solvents with the anion (Fig. 2) that subsequently would be lost in the transition state is in line with solvent effects for S_N2 reactions at saturated tetrahedral carbon, but is usually not found for substitutions at platinum(II) and palladium(II) [29]. This interpretation also does not agree with the fact that the picture for $FoPdNH_3 + SCN^-$ is normal. If the conclusion of a destabilized transition state for methanol is also accepted for the $FoPdpy + tu$ reaction, here too a destabilization of the transition state in DMSO must be assumed as an additional consequence.

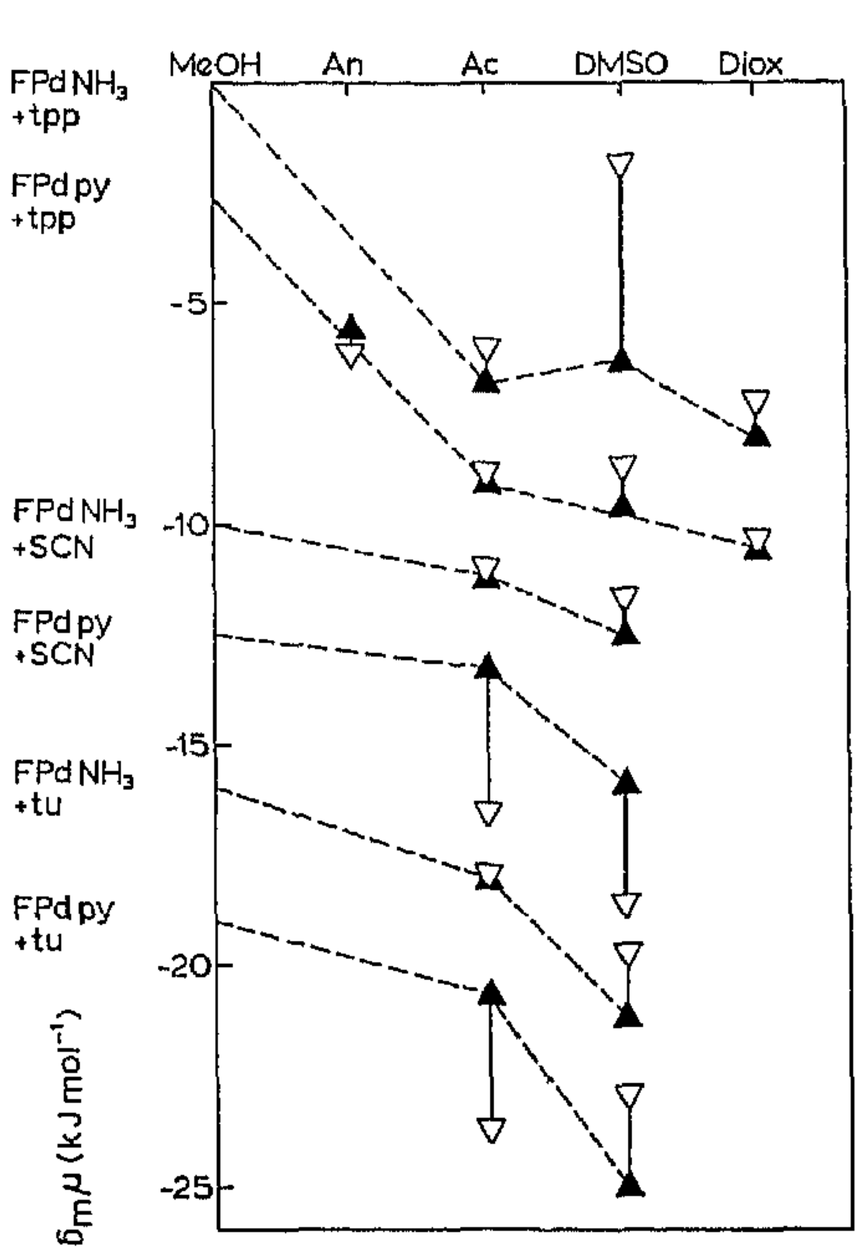

Fig. 4. Variation of transfer chemical potentials of reactants (▲) and transition state (▽) of the reactions between FoPdX and Y with methanol as reference solvent at 25.0 °C. The reference potential ($\mu = 0$) is vertically displaced. Values of corresponding states are connected.

Summarizing, we find that solvation does not change on activation, with the exception of two cases of reactions in DMSO and two in methanol. This picture seems to be acceptable in view of the fact that methanol and DMSO both are structured solvents which may influence the reactivity pattern compared to other solvents [18]. Another factor of influence may be the relatively high acceptor (MeOH) or donor (DMSO) number of the two solvents. The amount of available data is insufficient to attempt a more detailed analysis of these effects in terms of intimate mechanism.

We intend to extend this study to more solvents and solvent mixtures and to the analogous nickel(II) formazan complexes that could be prepared in a pure state.

[1] C. H. Langford and H. B. Gray, Ligand Substitution Processes, Chapter 2, W. A. Benjamin, New York–Amsterdam 1965.
[2] R. G. Wilkins, The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes, Section 4.8–4.10, Allyn and Bacon Inc., Boston 1974.
[3] F. R. Hartley, The Chemistry of Platinum and Palladium, Chapter 11, Applied Science Publishers Ltd., London 1973.
[4] L. Cattalini, in MTP International Review of Science, Inorganic Chemistry, Volume 9, Series 1, Chapter 7, Butterworths London 1974.
[5] J. S. Coe, in MTP International Review of Science, Inorganic Chemistry, Volume 9, Series 2, Chapter 3, Butterworths, London 1974.
[6] U. Mayer and V. Gutmann, Adv. Inorg. Chem. Radiochem. **17,** 189 (1975).
[7] S. Balt and W. E. Renkema, J. Coord. Chem. **6,** 201 (1977).
[8] S. Balt and W. E. Renkema, Inorg. Chim. Acta **22,** 161 (1977).
[9] S. Balt, J. Meuldijk, and W. E. Renkema, in preparation.
[10] M. J. Blandamer and J. Burgess, Chem. Soc. Rev. **4,** 55 (1975).
[11] M. J. Blandamer, J. Burgess, and J. G. Chambers, J. Chem. Soc. Dalton Trans. **1977,** 60.
[12] V. Gutmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum Publishing Corp., 1978.
[13] J. A. Riddick and W. B. Bunger, Techniques of

Chemistry, Vol. II, Organic Solvents, 3rd Ed., 1970.
[14] H. L. Kies, Anal. Chim. Acta **96,** 183 (1978).
[15] J. A. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley, New York 1963.
[16] A. Ben-Naim, J. Phys. Chem. **82,** 792 (1978).
[17] H. Schneider, Topics in Current Chem. **68,** 103 (1976).
[18] J. F. Coetzee, in J. F. Coetzee and C. D. Ritchie (eds.): Solute-Solvent Interactions, Vol. 2, Chapter 14, Marcel Dekker Inc., New York 1976.
[19] B. G. Cox, A. J. Parker, and W. E. Waghorne, J. Am. Chem. Soc. **95,** 1010 (1973).
[20] C. Barraqué, J. Vedel, and B. Tremillon, Bull. Soc. Chim. Fr. **1968,** 3421.
[21] U. Mayer, Monatsh. Chem. **108,** 1479 (1977).
[22] L. Cattalini, Progress in Inorg. Chem. **13,** 263 (1970).
[23] M. Cusumano, G. Faraone, V. Ricevuto, R. Romeo, and M. Trozzi, J. Chem. Soc. Dalton Trans. **1974,** 490.
[24] L. Cattalini, M. Cusumano, V. Ricevuto, and M. Trozzi, J. Chem. Soc. Dalton Trans. **1975,** 771.
[25] J. Burgess, in: Inorganic Reaction Mechanisms, Specialist Periodical Report, Vol. 5, Chapter 2, The Chemical Society, London 1977.
[26] R. J. Mureinik and M. Bidani, Inorg. Chim. Acta **29, 37** (1978).
[27] U. Mayer, V. Gutmann, and W. Gerger, Monatsh. Chem. **106, 1235** (1975).
[28] U. Mayer, Monatsh. Chem. **109,** 421, 775 (1978).
[29] K. M. Ibne-Rasa, J. O. Edwards, and J. L. Rogers, J. Sol. Chem. **4,** 609 (1975).