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Solvent Effects in Substitution Reactions at Square Planar Formazan Complexes of Palladium(II) and Platinum(II)

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The kinetics of the reaction

$$\mathrm{FoMX + Y \rightarrow FoMY + X}$$

are reported. Here M = Pd, Pt; X = NH_3 and pyridine; Y = triphenylphosphine, thiourea and thiocyanate; Fo is the tridentate 1-(2-hydroxyphenyl)-3,5-diphenylformazanato ion. The reaction was studied in the solvents propylenecarbonate, methanol, acetonitrile, acetone, DMSO, DMF and 1,4-dioxane.

Generally a two-term rate-law was found:

$$\mathrm{Rate} = k_1[\mathrm{FoMX}] + k_2[\mathrm{FoMX}][\mathrm{Y}]$$

Activation parameters for one system in different solvents were related in an isokinetic relationship, indicating a similar intrinsic mechanism in all solvents studied. A thorough analysis was performed on the k_2 values by way of a separation of solvent effects on initial and transition states. The transfer chemical potentials of initial and transition states were found to follow each other closely, except for solvents of high Gutmann donor number (DMSO, DMF) or acceptor number (methanol). Therefore, the transfer Gibbs free energies of activation per system were tentatively fitted to the two-parameter equation:

$$\delta_m \Delta G^{\ddagger} = p_0 + p_1 \cdot \Delta DN + p_2 \cdot \Delta AN$$

In all cases the multiple correlation coefficients had a value over 0.9. This result can be interpreted as an indication for the importance of donor and acceptor interaction at the reative site in the formation of the transition state.

The model was checked by recording the ^{195}Pt NMR spectra of the $FoPtNH_3$ complex in the solvents used for the kinetics. With only one exception the systems that gave a measurable signal showed a linear correlation between chemical shift and donor number.

Solvent Effects on Ligand Exchange between Two Different Pd(II) Organometallic Complexes

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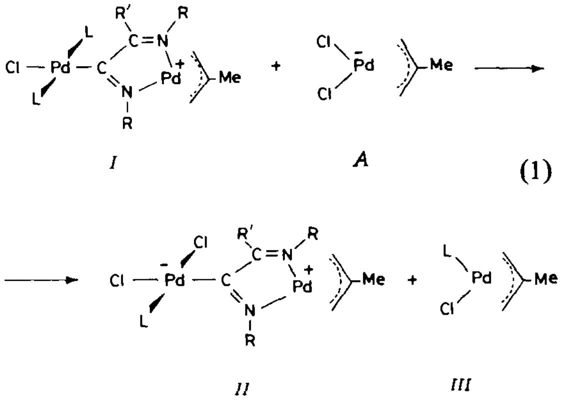
We have studied the mechanism of the following transfer of ligands between Pd(II) metal centers of different complex moieties:



(1)

($L = PPh_3, AsPh_3$; $R = p\text{-}C_6H_4OMe$; $R' = H, Me$)

at various temperatures and ionic strengths in different solvents.

The pseudo-first order rate constants for the disappearance of *I* fit the complex rate law (2):

$$k_{obs} = k_1 + \frac{k_2 K_e [A]}{1 + K_e [A]} \tag{2}$$

indicating a formal mechanism of the type (3):

$$\begin{tikzcd}
I + A \arrow[r, shift left, "K_e"] \arrow[dr, "k_1"'] & \{I \cdots A\} \arrow[l, shift left] \arrow[r, "k_2"] & II + III \\
& \{I^*\} \arrow[ur, "+A", "\text{fast}"'] &
\end{tikzcd} \tag{3}$$

The pre-equilibrium step (K_e) is shown by ^{1}H NMR and electronic spectra to be the formation of an associated species, in which a fast $\eta^3 \rightleftharpoons \eta^1$ conversion of the allyl of *I* occurs; this is followed by a