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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

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

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:

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

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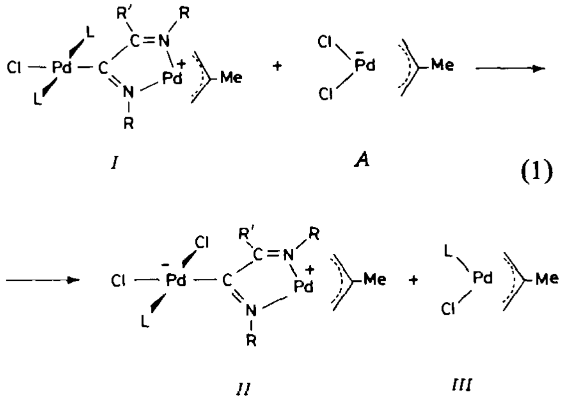
We have studied the mechanism of the following transfer of ligands between Pd(II) metal centers of different complex moieties:



(1)

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

at various temperatures and ionic strengths in different solvents.

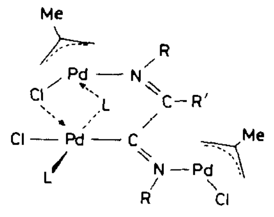
The pseudo-first order rate constants for the disappearance of *I* fit the complex rate law (2):

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

indicating a formal mechanism of the type (3):

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

The pre-equilibrium step (K_e) is shown by ^1H 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 slow, rate-determining migration (k_2) of ligands L and Cl^-. For this step we propose a trinuclear transition state which requires opening of the five-membered ring.



The k_1 path implies a slow intramolecular rearrangement of *I*, *via* either L dissociation of α-diimine chelate ring opening, yielding a reactive intermediate *I*. The latter reacts rapidly with *A* to give the final products. An increasing polarity of solvents, on going from 1,2-dichloroethane to acetone, produces a marked increase of both K_e and k_2. The pre-equilibrium constant K_e is also strongly depressed by increasing ionic strength.

Influence of the Nature and Presence of the Solvent on H Atom Abstraction by O_2 and Electron Transfer $O_2 \rightarrow O_2^{\cdot-}$ during the Aerobic Oxidation of Electron-rich Fe(I) Sandwiches

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We have recently designed organometallic electron reservoirs η^5-$C_5R_5Fe(I)\eta^6$-$C_6R'_6$ to serve as powerful electron-transfer reagents in stoichiometric (activation of C–H bonds by O_2) and catalytic (redox catalysis of $NO_3^- \rightarrow NH_3$) processes [1, 2].

We wish to emphasize here the dramatic roles of the nature and presence of the solvent on the reactions of $CpFe(I)C_6R_6$ with O_2 (Cp = C_5H_5 or C_5Me_5, R = H, Me or Et). In pentane, $CpFe(I)C_6Me_6$ reacts instantaneously with air at 20 °C with the loss of a H atom from a CH_3 group according to eqn. 1:

$$CpFe(I)\eta^6\text{-}C_6Me_6 + \tfrac{1}{4}O_2 \rightarrow CpFe\eta^5C_6Me_5CH_2 + \tfrac{1}{2}H_2O \qquad (1)$$

In DME, however, simple electron transfer proceeds, according to eqn. 2:

$$CpFe(I)\eta^6\text{-}C_6Me_6 + O_2 \rightarrow CpFe^+(II)\eta^6\text{-}C_6Me_6O_2^{\cdot-} \qquad (2)$$

Evidence is given as eqn. 2 being the first step of eqn. 1, so that the H atom abstraction is an electron transfer to O_2 followed by deprotonation by superoxide radical anion $O_2^{\cdot-}$.

In the solid state, aerobic oxidation occurs according to eqn. 1 at the surface of mono or polycrystalline samples with complete lattice rearrangement.

$CpFe(I)C_6H_{6-n}Me_n$ (n = 1 to 5) react with O_2 in pentane (or without O_2 in the solid state) without H atom abstraction nor even electron transfer to O_2 despite the large difference (1 volt) between the organometallic redox potential and that of $O_2/O_2^{\cdot-}$. Instead, dimerization is observed (eqn. 3) whereas in DME electron transfer proceeds as in eqn. 2.

$$CpFe(I)\eta^6\text{-}C_6H_{6-n}Me_n \rightarrow \tfrac{1}{2}[CpFe(II)\eta^5\text{-}C_6H_{6-n}Me_n]_2 \qquad (3)$$

The Mössbauer spectra of the Fe(I) sandwiches and of those of the various oxidized Fe(II) forms afford following the aerobic process in the solid state. This helps delineating the role of the solvent in sandwich–sandwich and sandwich–O_2 interactions.

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