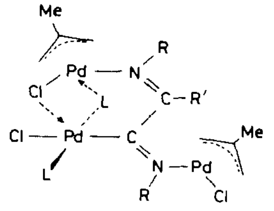
slow, rate-determining migration (k_2) of ligands L and Cl^-. For this step we propose a trinuclear transition state which requires opening of the five-member-



ed 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 $O_2 \rightarrow O_2^{\overline{\cdot}}$ during the Aerobic Oxidation of Electron-rich Fe(I) Sandwiches

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We have recently designed organometallic electron reservoirs $\eta^5\text{-}C_5R_5Fe(I)\eta^6\text{-}C_6R'_6$ 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:

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

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 $O_2^{\overline{\cdot}}$.

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 $O_2/O_2^{\overline{\cdot}}$. 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.

References

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