Hydrogen Exchange Between Amines and Chloroform Catalysed by Palladium(II) Amine Complexes Containing a β-Diketonate Anion in the Outer Sphere

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Summary The palladium(II) complexes $[PdL_4](\beta\text{-dik})_2$ [L = a primary amine; β-dikH = β-diketone = acetylacetone (acacH) or trifluoroacetylacetone (tfacH)] and $[Pd(\beta\text{-dik})L_2]$ (β-dik) (L = a secondary amine; β-dik = acac or tfac) act as effective catalysts for the hydrogen exchange reactions between amines and chloroform; the activity parallels the basicity of the counter-anion and secondary amine complexes exchange much more quickly than those containing primary amines.

CHLOROFORM can be regarded as an acid and detritiation of C^3HCl_3 in aqueous solution by hydroxide ion[1] or amines[2] has been investigated. Dehalogenation of chloroform by ethylenediamine was also presumed to be initiated by proton abstraction from chloroform by the diamine.[3] We here report the hydrogen exchange reactions between chloroform and some amines catalysed by palladium(II) amine complexes containing a β-diketonate anion in the outer sphere.

Bis(β-diketonato)palladium(II) complexes react with an excess of amine (L) to afford $[PdL_4](\beta\text{-dik})_2$ or $[Pd(\beta\text{-dik})L_2](\beta\text{-dik})$ depending upon whether L is a primary or a secondary amine, respectively.[4]† When $[Pd(acac)(Me_2NH)_2](acac)$ is dissolved in $CDCl_3$, the n.m.r. signals due to the amine proton and the methine proton of the acetylacetonate anion in the outer sphere diminish and the peak due to $CHCl_3$ grows concurrently to attain an equilibrium in several minutes, whereas deuteriation of the methine proton of the ligated acac anion is quite slow.

A similar deuteriation of $[Pd(tfac)(Me_2NH)_2](tfac)$ in $CDCl_3$ proceeds much more slowly and takes *ca.* 10 days to attain equilibrium. The exchange reactions of $[Pd(MeNH_2)_4](\beta\text{-dik})_2$ are slower than those of the corresponding secondary amine complexes; thus it takes *ca.*

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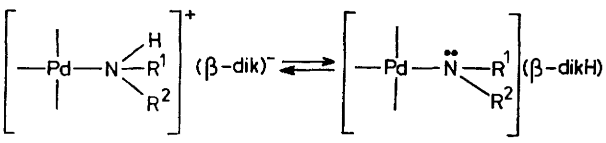
† β-dikH = β-diketone; acacH = acetylacetone; tfacH = trifluoroacetylacetone; hfacH = hexafluoroacetylacetone.

3 days when β-dik is acac and >20 days when β-dik is tfac. $[Pd(MeNH_2)_4](hfac)_2$ is not soluble enough to examine the n.m.r. spectra, but the amine and methine protons of $[Pd(Pr^nNH_2)_4](hfac)_2$ are not exchanged in $CDCl_3$. Thus the relative rate of deuteriation is in the same order as the proton affinity of the β-diketonate anions: acac>tfac>hfac.

Usually deuteriation proceeds at similar rates for the amine and methine protons, and the proton-transfer equilibrium (1) may be responsible for this behaviour.



(1)

As an extension of the above experiments the hydrogen exchange between amines and $CDCl_3$ was found to be catalysed by these palladium(II) complexes. The n.m.r. spectra of diethylamine (2·96 mmol) in $CDCl_3$ (4·93 mmol) showed no change when the solution was kept at room temperature. On dissolution of $[Pd(acac)(Et_2NH)_2](acac)$ (0·006 mmol) in this mixture, deuteriation of diethylamine attained equilibrium within 6 min. Deuteriation of n-propylamine (2·46 mmol) with $CDCl_3$ (5·50 mmol) catalysed by $[Pd(Pr^nNH_2)_4](acac)_2$ (0·062 mmol) proceeds more slowly, taking *ca.* 3 h to reach equilibrium.

In a square-planar complex ligand substitution by a primary amine is much faster than that by a bulky secondary amine.[5] Thus the rate-determining step in the catalytic reactions is not the amine exchange process but deuteriation of the co-ordinated amine molecule. Some electronic and/or steric factors seem to make equilibrium (1) more favourable with a secondary amine complex than with a primary amine complex.

Apart from $Pd(acac)_2$, which is the parent complex of the present catalytic species, other labile metal acetylacetonates can act as active catalysts. The presence of acid and base centres in the catalyst molecule is the most essential requirement, and labile metal amine complexes containing strong basic counter-anions may also catalyse the hydrogen exchange between amines and chloroform.

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