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COMPLEXING AND FISSION OF BENZYLIDENE ANILINES WITH Pd(II), Pt(II) AND Rh(III) CHLORIDES

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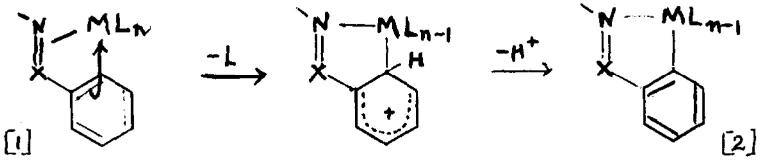
In a number of examples the structural unit [1] has been found to yield transition metal complexes of the type [2] with formation of a carbon metal σ-bond. A general reaction sequence (i) may be envisaged:



X = N, C, CH; M = Pd, Pt, Ni, Ru, Rh; L = hal, π-C_5H_5, CO etc.,

This reaction has been most fully explored with azobenzene(1), but 2-phenyl pyridine and 2-phenyl quinoline react similarly,(2) and benzylidene anilines have also been reported(3) to yield Pd(II)-derivatives of the same type. We have found, however, that Pd(II)-co-ordinated benzylidene aniline is extremely sensitive to cleavage, and that under the described conditions,(3) namely use of $(PhCN)_2PdCl_2$ in methanol, $(PhNH_2)_2PdCl_2$ constitutes the main reaction product. A related fission of azobenzene reported by Bruce, Goodall, Iqbal and Stone(4) prompts us to record the following observations.

With $PdCl_2$ in aqueous dioxan,(1b) or with $(PhCN)_2PdCl_2$ in methanol(3) at ambient temperature benzylidene aniline gave only $(PhNH_2)_2PdCl_2$, identified by analysis, the mass spectrum, which gave only an ion m/e 93 = $C_6H_5NH_2$, and by n.m.r. comparison with an authentic sample. With $(PhCN)_2PdCl_2$ in CH_2Cl_2 as solvent, however, benzylidene aniline gave a complex $(PhCH{:}NPh)_2PdCl_2$ characterised by analysis, a principal mass spectral ion m/e 181 = $C_6H_5CH{:}NC_6H_5$, and an n.m.r. signal at 1.42 τ in DMSO solution ($PhC\underline{\underline{H}}{=}NPh$). However, this product is very sensitive to

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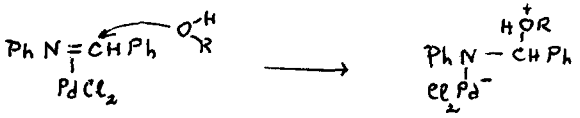
hydrolysis, or alcoholysis. Addition of methanol to a solution of $(PhCH:NPh)_2PdCl_2$ in $CDCl_3$ in an n.m.r. tube showed immediate development of a singlet signal at 0 τ characteristic of benzaldehyde. Recovery gave $(PhNH_2)_2PdCl_2$, and benzaldehyde which was identified as the 2,4-dinitrophenylhydrazone by t.l.c.. We infer that with benzylidene aniline nucleophilic addition as in (ii) is an efficient alternative to the sequence (i) above.

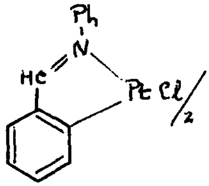
(ii)



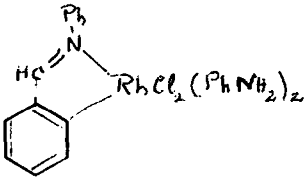
$$\longrightarrow (PhNHPdCl_2)^- \; + \; PhCH = \overset{+}{O}R \xrightarrow{H_2O} (PhNH_2)_2PdCl_2 \; + \; PhCHO \; + \; ROH$$

This conclusion is consistent with the observation that $p\text{-}NO_2C_6H_4N{=}CHC_6H_5$, which should be more susceptible to nucleophilic attack gave only $(p\text{-}NO_2C_6H_4NH_2)_2PdCl_2$ on treatment with $(PhCN)_2PdCl_2$ in $CHCl_3$ (containing the usual small amount of ethanol). The less electrophilic $p\text{-}CH_3OC_6H_4N{=}CHC_6H_5$ on the other hand, under the same conditions, gave the complex $(p\text{-}CH_3OC_6H_4N{=}CHC_6H_5)_2PdCl_2$, characterised by a mass ion m/e 211, and a singlet proton signal at 1.28 τ in DMSO.

The extent of this fission of the -N=CH- bond was found to depend on the metal used. With Na_2PtCl_4 in CH_2Cl_2, benzylidene aniline gave a product which from analysis, mass spectrum (principal ion m/e 181) and an n.m.r. singlet at 1.68 τ (DMSO) is formulated as [3]. However,



[3]



[4]

using aqueous dioxan as solvent with Na_2PtCl_4, aniline containing Pt-complexes were again found to be formed.

With $RhCl_3$ benzylidene aniline proved somewhat sensitive to hydrolysis in aqueous dioxan and gave in high yield a product regarded as [4] on the basis of analysis, mass spectral ions m/e 181 and 93, and in the n.m.r. a strong singlet signal at 1.60 τ (DMSO).

The products regarded as σ-bonded derivatives [3] and [4] are characterised by marked shielding of the =CH- proton. In DMSO benzylidene aniline shows this proton at 1.37 τ, with aromatic protons as a sharp line at 2.64 together with multiplets centred on 2.0 and 2.5 τ. In the benzylidene aniline-$PdCl_2$ complex this pattern is unchanged, but in [3] and [4] the =CH- signal is moved near to 1.6 τ and the aromatic protons appear as complex signals at 2.5 - 2.8 τ.

These observations may also offer a convenient method of fission of benzylidene anilines under very mild conditions.

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