

N-FORMYLATION OF PIPERIDINE DURING THE REACTION OF RHODIUM
TRICHLORIDE WITH PIPERIDINE IN ETHANOL

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In a recent paper⁽¹⁾ we reported the slow stepwise hydrogenation of the pyridine ligands of $[\text{RhCl}_2(\text{BH}_4)(\text{py})_2(\text{dmf})]$, leading ultimately to an unstable rhodium hydride approximating to a composition: $[\text{Rh}_n(\text{C}_5\text{H}_{11}\text{NHC1})_3]$. Since this type of product is apparently active as a catalyst for hydrogenation of pyridine or quinoline⁽²⁾ we examined the possibility of a more direct synthesis from rhodium trichloride and piperidine.

Rhodium trichloride trihydrate (Engelhard) with excess piperidine (ca. 6 molar equivalents) in ethanol solution was heated under reflux (1 hr.), the precipitated metal filtered, and the filtrate evaporated in vacuo. After washing with hot water the residue was extracted and crystallised from chloroform. In the mass spectrometer the product gave an ion of mass $113.0832 = \text{C}_6\text{H}_{11}\text{NO}$ with a fragmentation pattern identical to that of an authentic sample of N-formylpiperidine. Elemental analysis indicated the complex to be $[\text{RhCl}_3(\text{C}_6\text{H}_{11}\text{NO})_3]$ (Found: C, 39.3%; H, 5.9%; N, 7.6%; Cl, 19.2%; $\text{C}_{18}\text{H}_{33}\text{N}_3\text{O}_3$ RhCl_3 requires: C, 39.4%; H, 6.1%; N, 7.7%; Cl, 19.4%) and the infrared and n.m.r. spectra were consistent with co-ordinated N-formylpiperidine although the formyl proton could not be observed.

Decomposition of the complex with triphenylphosphine or with sodium borohydride gave N-formylpiperidine with infrared, n.m.r. and mass spectra identical to those of an authentic sample.

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The reaction proved too slow to follow by n.m.r. using a solution of rhodium trichloride, piperidine and ethanol (1:6:3 molar ratio) in CDCl_3 at 25° . However, the crude product from this reaction showed in the infrared ν_{CO} bands at 1950 (s) and 2080 cm^{-1} (m) characteristic of a rhodium carbonyl, in addition to bands attributable to N-formyl piperidine. From this crude material $[\text{RhCl}_3(\text{C}_5\text{H}_{10}\text{NCHO})_3]$ could be isolated.

Formation of N-formyl piperidine clearly exemplifies the well known⁽³⁾ base catalysed transition metal oxidation of ethanol via acetaldehyde which by decarbonylation forms a rhodium carbonyl which in turn carbonylates the amine.

Tris(N-formylpiperidine)trichlororhodium in dimethyl formamide solution proved highly active as a catalyst for hydrogenation of oct-1-ene, cyclohexene, cholestenone and testosterone, and of nitrobenzene to aniline.

References

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