Intermolecular Imine Formation: Condensation of Organic Molecules with Hexammine Ru^{III} and Pt^{IV} Ions

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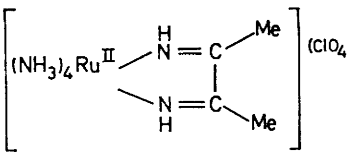
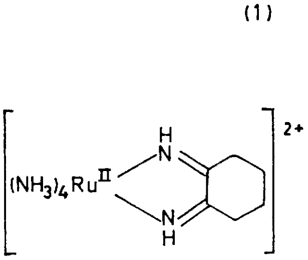
Summary $M(NH_3)_6{}^{n+}$ ($M = Ru^{III}$ and Pt^{IV}) ions condense with dicarbonyl compounds to give chelates where the co-ordinated nucleophile is the effective agent in the reaction and the resulting, normally unstable, organic group is stabilised.

Several intramolecular reactions have been described recently[1] where condensation has occurred between carbonyl centres and co-ordinated nucleophiles to give chelated organic molecules sometimes of surprising complexity and specificity. In one instance two co-ordinated OH^- groups have been shown to capture the carbonyl centres on acetylacetone[2] and this could also occur with co-ordinated NH_2^- if the concentration of the nucleophile can be made reasonably high. Using metal hexammine complexes, $M(NH_3)_6{}^{n+}$, of suitable acidity it should be possible to generate $M(NH_3)_5NH_2{}^{(n-1)+}$ ions in substantial concentration in basic solution. Condensation of such species with a carbonyl group followed by deprotonation of another co-ordinated ammonia and the capture of another carbonyl centre can stabilise imines difficult or impossible to synthesise by more traditional routes.



(1)



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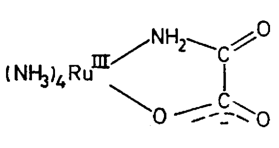
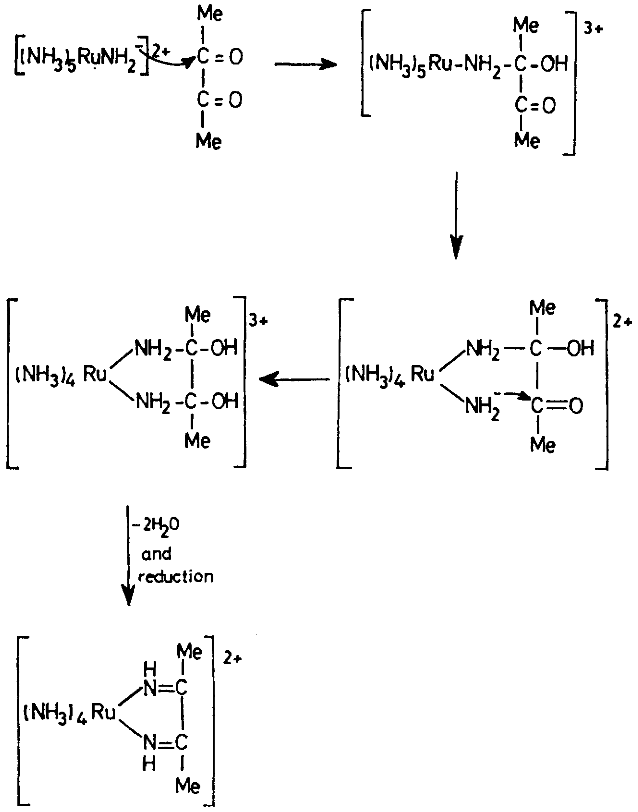


(3)

The $Ru(NH_3)_6{}^{3+}$ ion has a pK_a of *ca.* 12·4[3] and hence substantial deprotonation of the complex could be expected in 1 M OH^-. In the presence of biacetyl and base this complex generates an intense red-brown solution from which the yellow-brown complex (**1**) was isolated [*ca.* 65% yield, characterised by elemental analysis and ^1H n.m.r. spectroscopy, δ ($[^2H_6]Me_2SO$) (rel. to Me_4Si) $-11{\cdot}83$ (2NH), $-3{\cdot}28$ ($2NH_3$), $-2{\cdot}38$ (2Me) and $-1{\cdot}67$ ($2NH_3$)]. INDOR nitrogen spectra confirm that the signals at δ $-3{\cdot}28$ and $-1{\cdot}67$ are due to co-ordinated ammonia. The electronic spectrum of the product showed the characteristic intense absorption (ϵ_{465} 7200 $M^{-1}\,cm^{-1}$ in 10^{-3} M $HClO_4$) of Ru^{II} attached to an unsaturated *N*-centre.[4] The Ru^{II} complex was readily oxidised with bromine water to the Ru^{III} ion, which was also isolated as the perchlorate salt. The redox process was reversible with $E = 0{\cdot}54$ V (IUPAC convention; established by cyclic voltammetry and AC polarography,

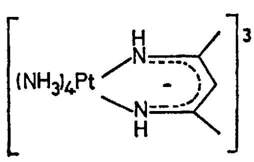
μ = 0·1 M $NaClO_4$, 22°) and the Ru^{III} ion was moderately stable in dilute acid but was reduced rapidly in base. The reduction in 1 M NaOH followed first-order kinetics with $t_{\frac{1}{2}}$ = 25 s at 25°; in 0·05 M collidine buffer at pH 7·43 the half life was *ca.* 30 s. This rapid reduction accounts for the isolation of the Ru^{II} ion from the reaction medium but the oxidised grouping has not yet been detected. In 1 M OH^- clearly H_2O could be oxidised but in the buffer at pH 7·43 another reductant is required.



Preliminary kinetics on the formation of the Ru^{II} complex in 0·05 M collidine at pH 7·36 (μ = 1·0 M in NaCl) showed a first-order dependence on biacetyl and $Ru(NH_3)_6{}^{3+}$ with a second-order rate constant of $5{\cdot}16 \times 10^{-3}$ $M^{-1}\,s^{-1}$ at 25°. For most of the kinetics, reduction was much faster than the formation process; only at high concentrations of biacetyl (> 0·5 M) was it competitive. We presume the process is initiated by attack of $Ru(NH_3)_5NH_2{}^{2+}$ at a carbonyl centre of biacetyl followed by further deprotonations, cyclisation and elimination of water as shown in the Scheme. Since deprotonation of $Ru(NH_3)_6{}^{3+}$ is fast[5] and the kinetics are first order in complex and ligand, the attack of the co-ordinated nucleophile is a feasible rate-determining step.

A substantial driving force for the reaction is the stabilisation of the Ru^{II} species by the di-imine grouping (compare the potential of the $(NH_3)_6Ru^{2+/3+}$ couple, 0·10[6]), which probably accounts also for the ease of oxidation of ethylenediamine in $Ru(en)_3{}^{2+}$ to produce the analogous di-imine complex.[4b]

There is now excellent evidence to indicate that the t_{2g} electrons in Ru^{II} species are extensively involved in bonding with such unsaturated *N*-ligands[4c,7] and are much less involved in the Ru^{III} species. The ability of Ru to stabilise such unsaturated chelate species appears to be a general one and related complexes such as (2) and (3) have been made by similar means.



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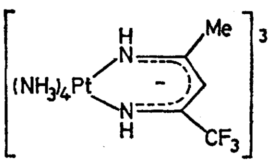

(5)

Platinum(IV)-ammine complexes may also be used and both 2,4-pentanedione and 1,1,1-trifluoro-2,4-pentanedione condense rapidly with $Pt(NH_3)_6{}^{3+}$ at pH *ca.* 9 to give the stable ring systems (**4**) and (**5**). The complexes were isolated as perchlorates and the ^1H n.m.r. spectra were consistent with the formulation. The equivalence of the methyl groups for the anionic ligand indicates complete delocalisation and the ring readily brominates at the methine centre with bromine.

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