Facile Amido to Pyridyl Isomerization: Pentaammineruthenium(II) Walks the Nicotinamide and Isonicotinamide Rings

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The powerfully π-donating species $Os(NH_3)_5^{2+}$ preferentially binds η^2 to a C=C bond of the aromatic ring (A) of most functionalized aromatic rings instead of binding the functional group (B).[1,2] Thus reduction of the B-bonded osmium(III) results in rapid intramolecular isomerization to A-bonded osmium(II). While η^2-alkene,[3] alkyne,[3] and arene,[4] and η^2-C–O acetone species have been characterized,[5] B → A isomerization has not been encountered in the chemistry of the ruthenium congeners, the Ru–carbon bond evidently lacking the stability to drive such a rearrangement.[4] Here we report evidence for the metastability of such species in Ru(II) chemistry: When the amido-bonded ruthenium(III) complexes of both nicotinamide and isonicotinamide are reduced, the resulting ruthenium(II) complexes, $Ru^{II}(NH_3)_5(NHC(O)\text{-}3\text{-}Py)^+$ and $Ru^{II}(NH_3)_5(NHC(O)\text{-}4\text{-}Py)^+$, undergo rapid intramolecular isomerization to the pyridyl bonded forms. We believe these rearrangements proceed via A-bonded intermediates in a walk of the aromatic ring as has been found for osmium(II).

Amidoruthenium(II) complexes are unstable with respect to aquation,[6] except at very high pH and amide concentration (for binding the neutral amide, $K \sim 10^{-3}$ M^{-1}),[7] but can be studied as transients when the Ru(III) complexes[8,9] are reduced rapidly (eq 1). When R is an aromatic residue, the immediate reduction

$$(NH_3)_5Ru^{III}\text{–}NHC(O)R^{2+} + e^- \rightarrow (NH_3)_5Ru^{II}\text{–}NHC(O)R^+ \quad (1)$$

product is highly colored, with colors ranging from yellow orange (R = C_6H_5, λ_{max} 400 nm), to red orange (R = 4-C_5H_4N, λ_{max} 475 nm), to blue (R = 4-C_5H_4N–CH_3^+, λ_{max} 695 nm) as a result of low-energy Ru(II)-to-aromatic charge transfer.[7] For R = C_6H_5 and R = 4-C_5H_4N–CH_3^+, aquation results in complete bleaching of the color, with a pH-dependent rate (see Figure 1), consistent with decay of the amido complex via its conjugate acid amH (eqs 2 and 3).[10,11] (The kinetics were monitored at λ_{max}

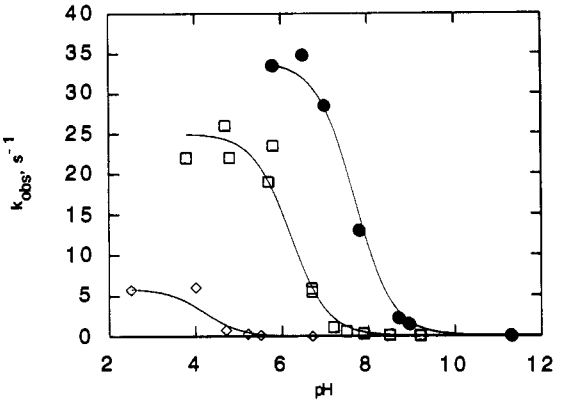


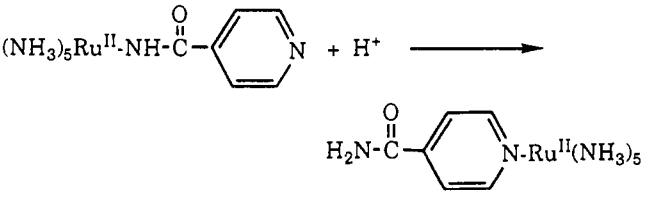
Figure 1. pH dependence of the rate constant (k_{obs}) for aquation/isomerization of the amidoruthenium(II) complex at 25.0 °C and 0.1 M ionic strength ($LiCF_3SO_3$). The curves are calculated from $k_{obs} = k_{amH}(f_{amH})$ with f_{amH} = [amH]/([am] + [amH]) calculated from the $pK_{a,amH}$: diamonds, R = 4-$PyCH_3$ ($k_{amH} = 6\ s^{-1}$, $pK_{a,amH} = 4.2$); squares, R = 4-Py ($k_{amH} = 25\ s^{-1}$, $pK_{a,amH} = 6.2$); circles, R = 4-Ph ($k_{amH} = 34\ s^{-1}$, $pK_{a,amH} = 7.7$). The reducing agent used was 5–15 mM $Na_2S_2O_4$, and buffers were 0.01 M acetate or phosphate.

$$(NH_3)_5Ru^{II}\text{–}(amH) \rightleftharpoons (NH_3)_5Ru^{II}\text{–}NHC(O)R + H^+ \quad pK_{a,amH}{}^{II} \quad (2)$$

$$(NH_3)_5Ru^{II}\text{–}(amH) + H_2O \rightarrow Ru(NH_3)_5(OH_2)^{2+} + RC(O)NH_2 \quad k_{amH} \quad (3)$$

with use of conventional syringe techniques above pH 7 and a Hi-Tech stopped-flow spectrometer at lower pH values.)

In contrast to the simple hydrolysis reactions observed above, with R = 4-C_5H_4N, bleaching does not occur, but rather the Ru(II) spectrum shifts to longer wavelength. The final spectrum is that of the pyridyl-bonded isonicotinamide complex[12] in up to 40% yield.



(With R = 3-C_5H_4N, the yield of the pyridyl-bonded isomer[12] is 53 ± 1% at pH 5.) The isomerization is also apparent in the cyclic voltammetry: In multiple scans, the current at the amido reduction peak (–300 to –500 mV vs SCE, depending on pH) drops and peaks characteristic of $(NH_3)_5RuOH_2^{3+/2+}$ and the

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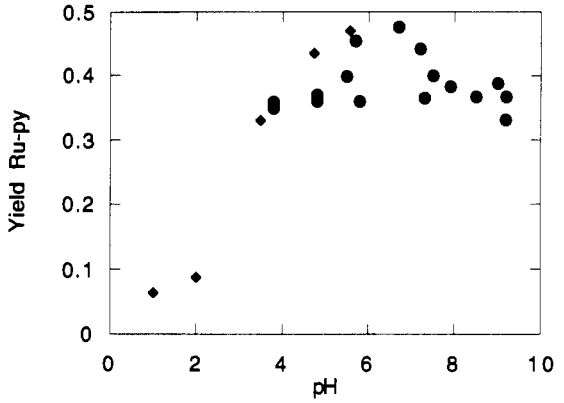
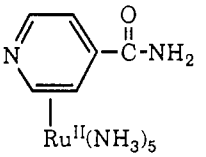


Figure 2. Yield of pyridyl-bonded Ru(II) complex obtained upon reduction of $(NH_3)_5Ru^{III}NHC(O)$-4-Py with (diamonds) V_{aq}^{2+} and (circles) $Na_2S_2O_4$ at 25 °C and 0.1 M ionic strength ($CF_3SO_3^-$) (0.01–0.1 M acetate, 0.01 M phosphate or borate buffers).

pyridyl isomer (+190 mV vs SCE) appear. The isomerization yields are independent of reducing agent ($V^{II}(aq)$, $Ru(NH_3)_6^{2+}$, amalgamated zinc, $Na_2S_2O_4$) and supporting electrolyte (0.1 M Cl^-, ClO_4^-, $CH_3CO_2^-$, or $CF_3SO_3^-$ at pH 5), but $Ru^{II}(NH_3)_5(Py)^{2+}$ forms at the expense of $Ru^{II}(NH_3)_5(OH_2)^{2+}$ when 0.1 M pyridine is present. However, the isomerization yield does drop below pH 4, as shown in Figure 2, probably because protonation of the pyridyl nitrogen (pK_a(Ru(II)) ca. 3) blocks the Ru(II)-binding site.

The composite limiting rate constant for isomerization (40%) plus hydrolysis (60%) of the protonated amide complex with R = 4-C_5H_4N is k_{obs} = 24 s^{-1} at 25 °C (Figure 1). Thus the isomerization rate constant is 0.4 × 24 = 9.6 s^{-1}. The time scale for the isomerization requires that it occur via an intramolecular pathway. Since the rate constant for substitution of isonicotinamide on $Ru^{II}(NH_3)_5(OH_2)^{2+}$ is 0.1 M^{-1} s^{-1},[13] formation of the more stable isomer via a bimolecular pathway could only take place over hours or longer under the conditions used (0.05–1 mM Ru(III) complex initially). Furthermore, the millisecond time scale for the process precludes its being a simple collapse of a $[Ru(NH_3)_5^{2+}|L]$ solvent cage (the lifetime of the latter is ≪1 ms). The isomerization rate constant (9.6 s^{-1}) is relatively high for Ru(II)[14] and more rapid than that estimated (3.5 s^{-1}) for amide N-to-O linkage isomerization in the tetraammineruthenium(II) complex of glycylglycine[15] but comparable to that found for O-to-S linkage isomerization in the DMSO complex.[16] However, in contrast to the latter, here the Ru(II) migration is not to a neighboring atom, but rather to a site six bonds away. Thus the intermediacy of A-bonded isomers is inferred.



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