either the five-coordinate Fe(III) in $ClFe(Et_2dtc)_2$[16] (0.50 mm/s, 100 K vs. Fe) or the five-coordinate Fe(II) in the $[Fe(Et_2dtc)_2]_2$ dimer[16] (0.90 mm/s, 100 K vs Fe).

The voltammetry of I in DMF[17] shows both a reduction wave at −1.2 V and an oxidation wave at −0.07 V. Quantitative studies of these waves by chronoamperometry show both the oxidation and the reduction to be diffusion controlled over the range of 20 ms–1 s. The current functions $i_ct^{1/2}/C$ and $i_at^{1/2}/C$ for the reduction and oxidation, respectively, correspond to one-electron processes. The reduction wave shows no associated anodic wave, and the reduction product appears completely unstable. The oxidation wave is accompanied by a small cathodic wave. The i_c/i_a ratio in double potential step chronoamperometry shows the oxidation product to be stable for about 100 ms. A significant decline in this ratio is observed at longer potential steps ($i_c/i_a = 0.16$, $t = 1$ s).

The $[Fe_4S_4L_4]^{2-}$ clusters generally undergo reversible one-electron reductions. The apparently different redox properties of I must be attributed mainly to the Et_2dtc^- ligand. The latter is known to stabilize highly oxidized states in simple $M(Et_2dtc)_n$ complexes.[13] The effects of terminal ligand coordination characteristics in the redox properties of the $[Fe_4S_4L_4]^{n-}$ clusters at present are not well understood. A systematic study of the molecular and electronic structures and redox properties of various "mixed" terminal ligand clusters is under way in our laboratory.

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Registry No. I, 83692-59-5; $(Ph_4P)_2[Fe_4S_4(SPh)_2Cl_2]$, 80939-30-6; $(Ph_4P)_2[Fe_4S_4(SPh)_4]$, 80765-13-5.

Supplementary Material Available: Tables of structure factors and positional and thermal parameters (26 pages). Ordering information is given on any current masthead page.

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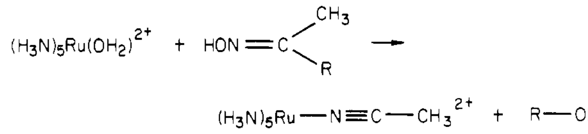
Spontaneous Carbon–Carbon Bond Cleavage of Some Ruthenium(II)-Bound α-Substituted Ketoximes

Sir:

We report the first example of C–C bond cleavage in a ligand attached to ruthenium(II) that is not accompanied by an oxidation–reduction reaction.[1]

The reaction, which occurs when $(H_3N)_5RuOH_2^{2+}$ is generated[2] in the presence of a ketoxime containing an α-keto or α-hydroxy group, has the overall stoichiometry

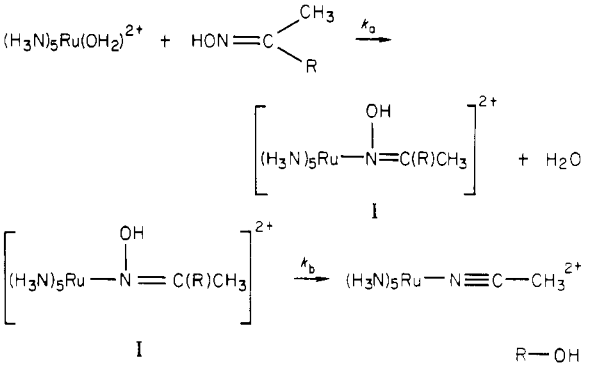


$$(H_3N)_5Ru(OH_2)^{2+} + HON{=}C(CH_3)R \longrightarrow (H_3N)_5Ru{-}N{\equiv}C{-}CH_3^{2+} + R{-}OH \quad (1)$$

where R is $-C(O)CH_3$, $-C(O)C_6H_5$, or $-CH(OH)C_6H_5$.

The ruthenium(II)–nitrile products were isolated as the perchlorate salts and identified by comparison of their UV–vis and IR spectra with those of authentic samples.[3] Benzoic acid was recovered and identified (proton NMR and IR spectra and melting point) in the R = $C(O)C_6H_5$ case, and benzaldehyde was identified (proton NMR) in the R = $CH(OH)C_6H_5$ case.

Since these oximes do not normally decompose in aqueous solutions and ligand substitution for H_2O in $(H_3N)_5Ru{-}OH_2^{2+}$ is rapid,[4] the reaction must involve the two steps shown in eq 2.



$$(H_3N)_5Ru(OH_2)^{2+} + HON{=}C(CH_3)R \xrightarrow{k_a} \left[(H_3N)_5Ru{-}\overset{OH}{\overset{|}{N}}{=}C(R)CH_3\right]^{2+} + H_2O \quad (2a)$$

I

$$\left[(H_3N)_5Ru{-}\overset{OH}{\overset{|}{N}}{=}C(R)CH_3\right]^{2+} \xrightarrow{k_b} (H_3N)_5Ru{-}N{\equiv}C{-}CH_3^{2+} + R{-}OH \quad (2b)$$

I

Attempts to isolate or detect the presence of the proposed ruthenium(II)–oxime intermediate, I, were unsuccessful, suggesting that the rate of disappearance of I is fast compared to its rate of formation. This remarkable increase in the reactivity of the oxime ligand in the absence of a concurrent redox change provides unambiguous evidence for the ability of Ru(II) to promote increased unsaturation on bonded nitrogen atoms, a phenomenon generally attributed to strong back-bonding from the filled 4d orbitals on Ru(II) to the empty π* orbitals on sp^2- or sp-hybridized nitrogen.[5]

Reactions were carried out at about 25 °C in dilute solution (~0.01 M in Ru and ~0.02 M in oxime).

A lower limit of 0.020 s^{-1} can be estimated for k_b if it is assumed (a) that $[I] < [Ru_{total}]/10$, (b) that k_a is similar to that for other sp^2-hybridized ligands[4] (average of seven neutral unhindered ligands 0.10 $M^{-1}\ s^{-1}$, range 0.05–0.20 $M^{-1}\ s^{-1}$), and (c) that reaction 2b is first order.

Related studies on aldoximes and unsubstituted oximes will be reported elsewhere.

Acknowledgment. This research was supported in part by the Metal Loan Program of Johnson Matthey, Inc.

Registry No. $(H_3N)_5Ru(OH_2)^{2+}$, 21393-88-4; $HON{=}C(CH_3)C(O)CH_3$, 57-71-6; $HON{=}C(CH_3)C(O)C_6H_5$, 119-51-7; $HON{=}C(CH_3)CH(OH)C_6H_5$, 26226-58-4; $(H_3N)_5RuN{\equiv}CCH_3^{2+}$, 26540-31-8; HOAc, 64-19-7; benzoic acid, 65-85-0; benzaldehyde, 100-52-7.

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(2) $(H_3N)RuOH_2^{2+}(aq)$ is prepared from $[(H_3N)_5RuCl]Cl_2$ (A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967)) by treatment with $Ag^+(aq)$ or $OH^-(aq)$ followed by amalgamated zinc.

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(4) R. E. Sheperd and H. Taube, *Inorg. Chem.*, **12**, 1392–401 (1973).

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