$6\pi + 2\sigma \rightarrow 8\pi$ electrocyclic reactions probably amounts to at least 18–20 kcal/mol, a figure substantially larger than the previously suggested minimum value of 11–12 kcal/mol.[5,25]

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(25) It is possible that the transformation to the "nonallowed" system (ref 5) actually occurs *via* allowed hydrogen shifts from *all-cis*-2,4,6,8-decatetraene. We acknowledge a stimulating discussion with Professor W. R. Roth concerning this point.

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Reaction between Azide Ion and $[Ru(bipy)_2(NO)Cl]^{2+}$

Sir:

The preparation of a series of cis complexes $[Ru(AA)_2(NO)X]^{3+}$ {AA = 2,2′-bipyridine and 1,10-phenanthroline; X = Cl^-, Br^-, NO_2^-, and pyridine} was reported recently.[1,2] In the complexes, coordinated nitrosyl behaves chemically as NO^+ since reaction with hydroxide ion gives the corresponding nitro complexes.

$$[Ru(AA)_2(NO)X]^{3+} + 2OH^- \longrightarrow [Ru(AA)_2(NO_2)X]^+ + H_2O \quad (1)$$

We find that the reactivity of the nitrosyl as NO^+ extends to a variety of nitrogen bases, including azide ion. In aqueous solution, a stoichiometric amount of N_3^- (3×10^{-3} *M*) reacts with $[Ru(bipy)_2(NO)Cl]^{2+}$ (3×10^{-3} *M*) according to

$$H_2O + Ru(bipy)_2(NO)Cl^{2+} + N_3^- \longrightarrow Ru(bipy)_2(OH_2)Cl^+ + N_2 + N_2O \quad (2)$$

The aquo complex has been identified spectrophotometrically, and nitrogen and nitrous oxide have been identified by mass spectrometry. The reaction of N_3^- with HNO_2 apparently involves the formation of a nitrosyl azide intermediate, N_4O,[3] but no evidence for the existence of $[Ru(bipy)_2(N_4O)Cl]^+$, $[Ru(bipy)_2(N_2O)Cl]^+$, or $[Ru(bipy)_2(N_2)Cl]^+$ has yet been obtained.

The rate law for the reaction in solutions containing either excess acid or excess azide ion is

$$\frac{-d[Ru(bipy)_2(NO)Cl^{2+}]}{dt} = k[Ru(bipy)_2(NO)Cl^{2+}][N_3^-]$$

At 25.0° in 0.5 *M* lithium chloride, k is 32 ± 4 M^{-1} sec^{-1}. $Ru(bipy)_2Cl_2$ is *not* observed as a product of the reaction in 0.5 *M* LiCl.

Reaction 2 is analogous in the opposite sense to the nitrosation of azidopentaamminecobalt(III) studied by Haim and Taube[4] (reaction 3), since the nitrosating group is coordinated, and N_3^- free.

$$H_2O + Co(NH_3)_5N_3^{2+} + NO^+ \text{ (or } H_2NO_2^+) \longrightarrow Co(NH_3)_5OH_2^{3+} + N_2 + N_2O \quad (3)$$

When carried out in nonaqueous solvents using $NO^+ClO_4^-$ as the nitrosating agent, reaction 3 has led to labile solvent complexes $Co(NH_3)_5S^{3+}$ {S = triethyl phosphate, sulfolane, etc.} which have proven useful as synthetic intermediates.[4-7]

Reaction 2 can also be carried out in nonaqueous solvents, and it appears to be as synthetically useful for the ruthenium complexes as reaction 3 is for the cobalt complexes. A stoichiometric amount of sodium azide suspended in acetonitrile rapidly converts $[Ru(bipy)_2(NO)Cl]^{2+}$ into the acetonitrile complex with gas evolution

$$CH_3CN + Ru(bipy)_2(NO)Cl^{2+} + N_3^- \longrightarrow Ru(bipy)_2(NCCH_3)Cl^+ + N_2 + N_2O \quad (4)$$

The complex has also been prepared by refluxing $Ru(bipy)_2Cl_2$ in acetonitrile.[8] The same reaction in acetone apparently gives the acetone complex, $[Ru(bipy)_2(OC(CH_3)_2)Cl]^+$ [λ_{max} 511 ($\epsilon \sim 7250$) and 359 nm ($\epsilon \sim 7850$)]. The coordinated acetone molecule is labile and addition of excess chloride ion, pyridine, or water gives $Ru(bipy)_2Cl_2$, $[Ru(bipy)_2(py)Cl]^+$, and $[Ru(bipy)_2(OH_2)Cl]^+$, respectively, within a few minutes at room temperature.

Reactions analogous to (2) and (4) also occur for $[Ru(bipy)_2(NO)NO_2]^{2+}$, and several complexes of the type $[Ru(bipy)_2(NO_2)X]$ have been isolated. Initial experiments indicate that the entire series of complexes $[Ru(AA)_2(NO)X]^{3+}$ behave chemically as a controlled source of nitrosonium ion.

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A Novel Synthesis of 3-Substituted Pyridines from Pyridine

Sir:

While a wide variety of 3-substituted pyridines and their derivatives find many important applications, *e.g.*, in biological studies,[1] insecticide,[2] and anticorrosion formulations,[3] as intermediates in organic and pharmaceutical synthesis, and in mechanistic investigations,[4] the preparation of these compounds has been a problem. The direct alkylation, aralkylation, or arylation at the 3 or 5 position of the pyridine ring has been particularly difficult.[4,5] Thus, the alkylation

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