

$6\pi + 2\sigma \rightarrow 8\pi$  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.<sup>5,25</sup>

**Acknowledgment.** We are pleased to acknowledge the support of this work by the National Science Foundation. Samples of cyclooctatetraene were kindly provided by Badische Anilin-und Soda-Fabrik AG.

(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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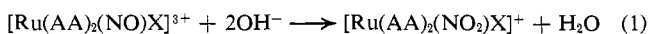
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Received January 15, 1971

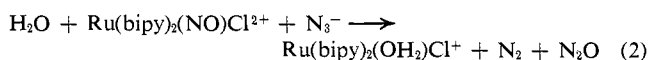
### Reaction between Azide Ion and $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}]^{2+}$

Sir:

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



We find that the reactivity of the nitrosyl as  $\text{NO}^+$  extends to a variety of nitrogen bases, including azide ion. In aqueous solution, a stoichiometric amount of  $\text{N}_3^-$  ( $3 \times 10^{-3} M$ ) reacts with  $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}]^{2+}$  ( $3 \times 10^{-3} M$ ) according to



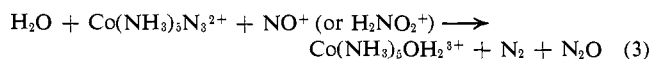
The aquo complex has been identified spectrophotometrically, and nitrogen and nitrous oxide have been identified by mass spectrometry. The reaction of  $\text{N}_3^-$  with  $\text{HNO}_2$  apparently involves the formation of a nitrosyl azide intermediate,  $\text{N}_4\text{O}$ ,<sup>3</sup> but no evidence for the existence of  $[\text{Ru}(\text{bipy})_2(\text{N}_4\text{O})\text{Cl}]^+$ ,  $[\text{Ru}(\text{bipy})_2(\text{N}_2\text{O})\text{Cl}]^+$ , or  $[\text{Ru}(\text{bipy})_2(\text{N}_2)\text{Cl}]^+$  has yet been obtained.

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

$$-\frac{d[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^{2+}]}{dt} = k[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}^{2+}][\text{N}_3^-]$$

At 25.0° in 0.5 *M* lithium chloride, *k* is  $32 \pm 4 M^{-1} \text{sec}^{-1}$ .  $\text{Ru}(\text{bipy})_2\text{Cl}_2$  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<sup>4</sup> (reaction 3), since the nitrosating



group is coordinated, and  $\text{N}_3^-$  free. When carried out in nonaqueous solvents using  $\text{NO}^+\text{ClO}_4^-$  as the nitrosating agent, reaction 3 has led to labile solvent com-

(1) T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Commun.*, 872 (1970).

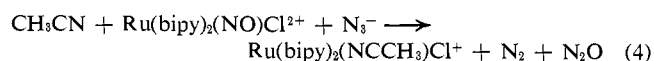
(2) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 471 (1971).

(3) See, for example, G. Stedman, *J. Chem. Soc.*, 1702 (1960).

(4) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

plexes  $\text{Co}(\text{NH}_3)_5\text{S}^{3+}$  {S = triethyl phosphate, sulfolane, etc.} which have proven useful as synthetic intermediates.<sup>4-7</sup>

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  $[\text{Ru}(\text{bipy})_2(\text{NO})\text{Cl}]^{2+}$  into the acetonitrile complex with gas evolution



The complex has also been prepared by refluxing  $\text{Ru}(\text{bipy})_2\text{Cl}_2$  in acetonitrile.<sup>8</sup> The same reaction in acetone apparently gives the acetone complex,  $[\text{Ru}(\text{bipy})_2(\text{OC}(\text{CH}_3)_2)\text{Cl}]^+$  [ $\lambda_{\text{max}}$  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  $\text{Ru}(\text{bipy})_2\text{Cl}_2$ ,  $[\text{Ru}(\text{bipy})_2(\text{py})\text{Cl}]^+$ , and  $[\text{Ru}(\text{bipy})_2(\text{OH}_2)\text{Cl}]^+$ , respectively, within a few minutes at room temperature.

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

**Acknowledgments.** Acknowledgments are made to the UNC Materials Research Center through Contract No. SD-100 with the Advanced Research Projects Agency, the University Research Council of the University of North Carolina, and the National Science Foundation through Grant No. GY-7311.

(5) R. B. Jordan, A. M. Sargeson, and H. Taube, *ibid.*, **5**, 1091 (1966).

(6) J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1174 (1968).

(7) J. L. Burmeister and N. J. De Stefano, *Inorg. Chem.*, **9**, 972 (1970).

(8) N. Winterton and T. J. Meyer, unpublished results.

(9) National Science Foundation Undergraduate Research Participant, Summer, 1970.

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Received October 29, 1970

### 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,<sup>1</sup> insecticide,<sup>2</sup> and anti-corrosion formulations,<sup>3</sup> as intermediates in organic and pharmaceutical synthesis, and in mechanistic investigations,<sup>4</sup> 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.<sup>4,5</sup> Thus, the alkylation

(1) O. Makova, L. Sindelar, and P. Vaculik, *Biol. Plant.*, **10** (5) 360 (1969).

(2) L. Goodhue, U. S. Patent 3,325,355 (1967); *cf. Chem. Abstr.*, **67**, 63301 (1967).

(3) R. Kenney, U. S. Patent 3,404,094 (1968); *cf. Chem. Abstr.*, **70**, 6146 (1969).

(4) R. A. Abramovitch and J. G. Saha, *Advan. Heterocycl. Chem.*, **6**, 229 (1966).