driving force for the change may be the relief of strain associated with the lessening of the $\pi-\pi$ repulsion of the overlapping aromatic rings.

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Ligand-Bridged Ruthenium Complexes

Sir:

Creutz and Taube[1] have characterized the pyrazine bridged dimer, compound **1**, and its oxidized forms


1


2


3

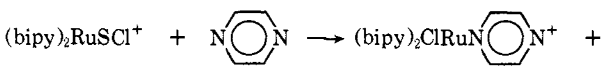
compounds **2** and **3** (see above). We have developed a general synthetic route to ligand bridged bis(2,2'-bipyridine)ruthenium complexes. The syntheses are based on our earlier work on reactions of NO and NO_2^- coordinated to ruthenium. It appears that with an appropriate combination of reactions, long-chain molecules can be obtained with synthetic control at each step. We report here cases of two, three, and four ruthenium atoms linked by bridging ligands. We have also investigated the oxidation–reduction properties of these complexes electrochemically.

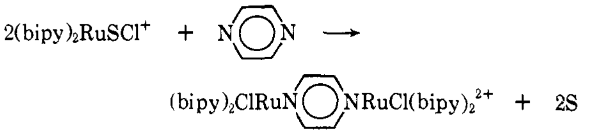
Azide ion reacts with $Ru(bipy)_2(NO)X^{2+}$ (X = Cl, NO_2)[2,3] in water or nonaqueous solvents giving solvent complexes.

$$Ru(bipy)_2(NO)X^{2+} + N_3^- + S \longrightarrow Ru(bipy)_2SX^{+} + N_2 + N_2O \quad (1)$$

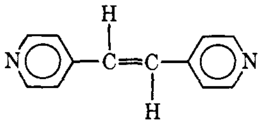
$$S = H_2O,\ CH_3CN,\ CH_3OH,\ (CH_3)_2CO$$

The acetone and methanol complexes are useful synthetic intermediates because of the lability of the coordinated solvent molecule.[3] With dibasic ligands both 1:1 and 2:1 complexes can be isolated. We have used reactions 2 and 3 to prepare 1:1 and 2:1


(2)


(3)

complexes with pyrazine (pyz), 4,4'-bipyridine (4,4'-bipy), and *trans*-1,2-bis(4-pyridyl)ethylene (BPE). The


BPE

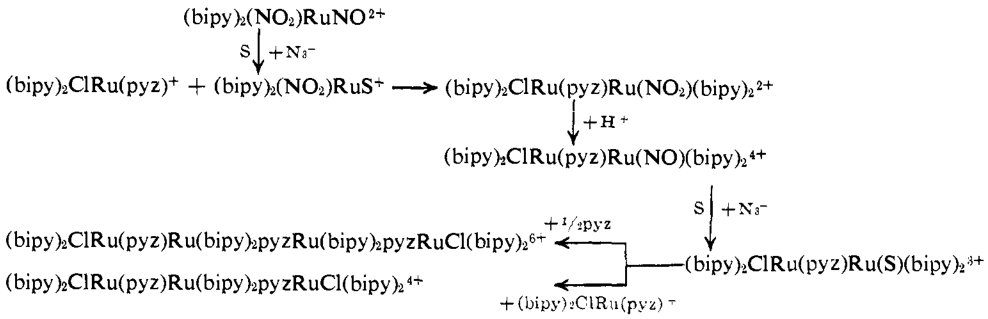
coordination at the ruthenium in all cases is presumably cis.[3,4]

The bipyridine complexes are remarkably versatile synthetically. Coordinated nitrite is converted into nitrosyl by acids,[4,5] *e.g.*

$$Ru(bipy)_2NO_2Cl + 2H^+ \longrightarrow Ru(bipy)_2(NO)Cl^{2+} + H_2O \quad (4)$$

By combining reactions like 1, 2, 3, and 4, we have prepared more highly linked systems (S is acetone or methanol; pyz is pyrazine) (Scheme I). With the exception of the solvent complexes, all of the intermediates and products have been isolated as PF_6^- salts and characterized by elemental analyses. Examples follow. *Anal.* Calcd for $[(bipy)_2ClRu(pyz)RuCl(bipy)_2](PF_6)_2\cdot 2H_2O$: C, 40.53; H, 3.10; N, 10.74; Cl, 5.44; F, 17.49; Found: C, 40.43; H, 2.91; N, 10.27; Cl, 5.68; F, 17.74. Calcd for $[(bipy)_2ClRu(pyz)Ru(bipy)_2(pyz)RuCl(bipy)_2](PF_6)_4\cdot 3H_2O$: C, 38.78; H, 2.94; N, 10.64; Cl, 3.37. Found: C, 38.38; H, 2.76; N, 10.80; Cl, 3.25. We are currently extending the uses of these reactions synthetically in the preparation of higher polymers, mixed metal polymers, and of polymers with mixed ligand bridges.

Scheme I



Voltammetric and cyclic voltammetric measurements on $(bipy)_2ClRu(pyz)RuCl(bipy)_2^{2+}$ [2,2] in acetonitrile show that it also has two oxidized forms, $(bipy)_2ClRu(pyz)RuCl(bipy)_2^{3+}$ [2,3] and $(bipy)_2ClRu(pyz)RuCl(bipy)_2^{4+}$ [3,3]. The reduction potentials[6] relating the three are

$$[3,3] \xrightarrow{1.06\ V} [2,3] \xrightarrow{0.91\ V} [2,2]$$

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(1) C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, **91**, 3988 (1969).

(2) F. J. Miller and T. J. Meyer, *ibid.*, **93**, 1294 (1971).

(3) S. A. Adeyemi, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, in press.

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

(5) J. B. Godwin and T. J. Meyer, *ibid.*, **10**, 2150 (1971).

(6) All electrochemical measurements were made at platinum electrodes at 22 ± 2° using 0.1 M $(n\text{-bu})_4N^+PF_6^-$ as the supporting electrolyte. Potential values are reduction potentials *vs.* the saturated sodium chloride calomel electrode and are uncorrected for junction potentials. Ep refers to peak potentials from cyclic voltammetry measurements.

We have isolated [3,3] as the perchlorate salt by Ce(IV) oxidation of [2,2] in aqueous perchloric acid. For the [2,3] pentaammine dimer, $(NH_3)_5Ru(pyz)Ru(NH_3)_5^{5+}$, Creutz and Taube[1] reported an intense band in the near-infrared spectrum and assigned it to charge transfer between metal ions [2,3] → [3,2]*. We have not been able to observe an analogous near-infrared band for the 2,2′-bipyridine [2,3] complex.

Only one oxidation wave is observed for the 4,4′-bipy and BPE bridged complexes ($E_{1/2}$ = 0.84 and 0.82 V, respectively) indicating that the ruthenium atoms are well shielded across the longer bridging ligands. Oxidation of the [2,2] ions at >1.0 V gives $n \sim 2$ (by

$$[2,2] \xrightarrow{-2e} [3,3]$$

coulometry) showing that both rutheniums are oxidized to the +3 state. From the electrochemical measurements, K is 1 for the equilibrium

$$[2,2] + [3,3] = 2[3,3]$$

Equilibration among the three ions should be very rapid, because ruthenium polypyridine complexes are known to exchange electrons rapidly.[7] Therefore solutions containing [2,2], [2,3], and [3,3] can be prepared by partial oxidation of [2,2]. We are currently investigating the properties of the intermediate oxidation states of all three systems.

The 3:2 and 4:3 Ru-pyrazine bridged complexes, $(bipy)_2ClRu(pyz)Ru(bipy)_2pyzRuCl(bipy)_2^{4+}$ [2,2,2] and $(bipy)_2ClRu(pyz)Ru(bipy)_2pyzRu(bipy)_2pyzRuCl(bipy)_2^{6+}$ [2,2,2,2], can also be oxidized. Two oxidation waves are observed for the 3:2 complex [E_p = 0.96 V ($n \sim 2$) and E_p = 1.05 V ($n \sim 1$)] and three for the 4:3 complex (E_p = 0.96, 1.04, 1.17 V). The oxidation waves apparently correspond to the reactions

$$[2,2,2] \xrightarrow{-2e} [3,2,3] \xrightarrow{-e} [3,3,3]$$

and

$$[2,2,2,2] \xrightarrow{-2e} [3,2,2,3] \xrightarrow{-e} [3,3,2,3] \xrightarrow{-e} [3,3,3,3]$$

Acknowledgments are made to the University Research Council of the University of North Carolina and to the National Science Foundation (Grant No. GP17083) for support of this research and for a Science Development Award to the Department.

[7] J. C. Solenberger, Ph.D. Thesis, Washington University, St. Louis, Mo., June 1969.

[8] National Science Foundation Undergraduate Research Participant, summer, 1970.

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Bimolecular Homolytic Substitution with Inversion. A Stereochemical Investigation of an SH2 Reaction

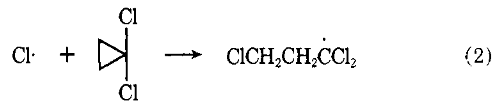
Sir:

Bimolecular homolytic substitution reactions (SH2 reactions) represent one of the most common processes available to free radicals and, as a result, have been the subject of numerous investigations.[1] Few of these investigations, however, have dealt with the particular case of radical attack at saturated carbon; hence, the mechanistic scope of SH2 attack at saturated carbon remains a subject of speculation.[2] With this background in mind, we have undertaken a mechanistic study of the bimolecular homolytic ring-opening reactions of cyclopropanes. The cyclopropanes represent a particularly informative compound series in that they have been extensively studied with regard to both electrophilic and nucleophilic attack.[3] It is our expectation that a comparison of our homolytic results with those obtained for the two polar modes of ring opening will prove to be of considerable theoretical interest.[4] In this communication we wish to report the results of studies which show that the ring-opening attack of chlorine atoms on 1,1-dichlorocyclopropane proceeds predominately with inversion of configuration.

When 1,1-dichlorocyclopropane is subjected to photochlorination at 0° in CCl_4, two major products are obtained: 1,1,1,3-tetrachloropropane (**1**) and 1,1,1,3,3-pentachloropropane (**2**). A most logical sequence which may be postulated to explain these products is shown in Scheme I, and is the same as that proposed independently by Applequist, Fanta, and Hendrikson,[5] and Walling and Fredricks[6] for the photochlorination of various cyclopropane derivatives.

Scheme I

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \qquad (1)$$



$$Cl\cdot + \ldots \longrightarrow ClCH_2CH_2\dot{C}Cl_2 \qquad (2)$$

$$ClCH_2CH_2\dot{C}Cl_2 + Cl_2 \longrightarrow \underset{\mathbf{1}}{ClCH_2CH_2CCl_3} + Cl\cdot \qquad (3)$$

$$ClCH_2CH_2CCl_3 \xrightarrow{Cl_2} \underset{\mathbf{2}}{Cl_2CHCH_2CCl_3} + HCl \qquad (4)$$

It was found that the chlorination of 1,1-dichlorocyclopropane is promoted by free-radical initiators and inhibited by free-radical scavengers. When 1-ml aliquots of a CCl_4 solution, 0.50 M in molecular chlorine and 3.14 M in 1,1-dichlorocyclopropane, were subjected to irradiation for 35 min at 0–5°, yields of **1** and **2** of 36 and 45%, respectively, were afforded.[7] In contrast, those aliquots[8] which were maintained in the dark at 0° for 24 hr afforded no detectable quantities of **1** or **2** (as determined by glpc analysis for **1** and **2**).[9] Similarly, those aliquots which were treated with 0.2 ml of HCl-saturated CCl_4 solution and subsequently maintained in the dark at 0° for 24 hr afforded no detectable quantities of **1** or **2** (glpc analysis). In the case of the "dark reactions," pmr analysis demonstrates that not less than 99% of the initially present 1,1-di-

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[1] W. A. Pryor, *Chem. Eng. News*, **49**, 34 (June 7, 1971).

[2] K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley, New York, N. Y., 1971, pp 5–6.

[3] S. J. Cristol, W. Y. Lim, and A. R. Dahn, *J. Amer. Chem. Soc.*, **92**, 4013 (1970), and references therein.

[4] J. A. Berson, *Angew. Chem., Int. Ed. Engl.*, 7, 779 (1968).

[5] D. E. Applequist, G. F. Fanta, and B. W. Hendrikson, *J. Amer. Chem. Soc.*, **82**, 2368 (1960).

[6] C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962).

[7] Irradiation was provided using a 150-W G.E. sunlamp.

[8] All of the aliquots referred to in this paragraph were taken from the same standard solution and were 0.50 M in molecular chlorine and 3.14 M in 1,1-dichlorocyclopropane.

[9] Using solutions prepared from authentic samples of **1** and **2** we have ascertained that yields of **1** or **2** as low as 1.5% would have been detected by glpc.