

Figure 1. Structure of complex **1**⁸ and proposed structures of complexes **2** and **3**.

2 and **3**. In the reactions of **1** with methyl- or ethylmagnesium bromide, substitution of one bromide ion by the alkyl group occurs rapidly and without the loss of bipyridyl from the coordination sphere of molybdenum. A substitution of the second bromide ion appears to occur on prolonged reaction with excess Grignard reagent or at elevated temperatures but thus far afforded only ill-characterized, amorphous products. Complexes **2** and **3**, in contrast, are deep purple, crystalline solids which can be stored for extended periods of time provided that they are kept dry and anaerobic. Although the complexes can be transferred in air without appreciable decomposition, storage in bottles without precaution against exposure to oxygen and moisture causes gradual decomposition as evidenced by the appearance of brown degradation products and formation of alcohols and aldehydes due to oxidative cleavage of the Mo–C bond. The complexes **2** and **3** are also sensitive to light (see below). For both compounds, *cis*-dioxo structures are proposed in analogy to the structure of **1** on the basis of the infrared spectra which exhibit two Mo=O stretching frequencies characteristic of the *cis*-MoO₂ moiety (see Table IV). The IR spectra otherwise resemble the spectrum of **1** and show bands characteristic of the coordinated bipyridyl and the bound alkyl group. The ¹H NMR spectra of **2** and **3** are consistent with the proposed structures. Apart from the signals of the protons of bipyridyl only the signals of the molybdenum-bound CH₃ or C₂H₅ protons are observed. The signal of the CH₃ protons of **2** occurs as a singlet at 0.62 ppm relative to Me₄Si (in CDCl₃) and is sufficiently sharp to indicate the absence of paramagnetic impurities. The CH₃ triplet of the ethyl group in **3** appears at 1.10 ppm and the quartet of the –CH₂– protons at 3.3 ppm, respectively, both relative to Me₄Si in CDCl₃ as the solvent, *J*_{AB} = 8.0 Hz.

Optical absorption spectra of complexes **1–3** are shown in Figure 2. The new complexes are sparingly soluble in most common inert organic solvents; we found *N*-methylpyrrolidone (NMP) to be a suitable solvent for many purposes even though the solutions decolorize within approximately 1 h. Decomposition of the complexes in that solvent also occurs on heating. Solutions in dry tetrahydrofuran (THF) are more stable, although the solubility is low. It is lower still in CH₂Cl₂ but this solvent can be used for recrystallization of the complexes (see Experimental Section). Rapid decolorization of the purple solutions of **2** and **3** in NMP occurs if water is added. This decomposition is accompanied by a removal of bipyridyl and bromide from the coordination sphere of molybdenum but occurs without extensive hydrocarbon evolution. The Mo–C bond in the hydrolysis products of **2** and **3** remains intact at room temperature for several hours but is cleaved more rapidly on heating. From **2**, for example, only about 2–3% of the theoretical amount of CH₄ is generated in acidic aqueous solutions over a period of 1 h at room temperature. On heating to 80–85 °C the evolution of CH₄ becomes quantitative. It should be noted in passing that the solutions of the complexes in concentrated HCl or glacial acetic acid remain purple much longer than those in H₂O or alkali. Details of the hydrolytic reactions of **2** and **3** will be described below.

2. Thermolysis. Complexes **2** and **3** are remarkably stable

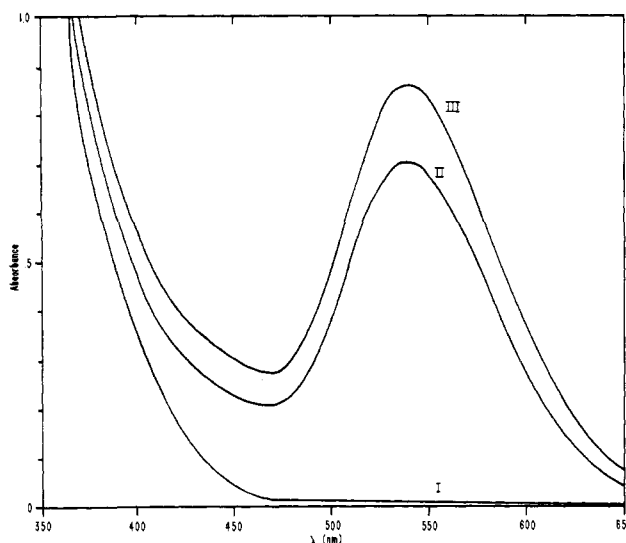


Figure 2. Optical absorption spectra of complexes **1–3** in *N*-methylpyrrolidone. I, complex **1** (1.0 mM); II, complex **2** (1.5 mM); III, complex **3** (2.0 mM), all measured at path length of 1.00 cm.

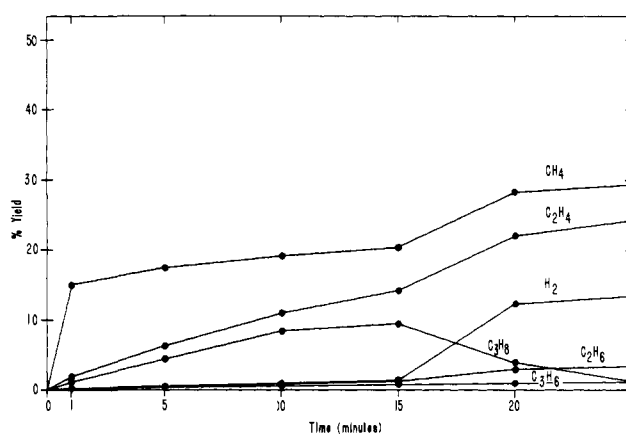


Figure 3. Formation of hydrocarbons and of hydrogen during the thermolysis of complex **2** at 400–500 °C under argon in the dark.

thermally. If heated under exclusion of oxygen they begin to decompose only above 200 °C. We noticed that bipyridyl dissociates off first without significant hydrocarbon evolution. Even on rapid heating, only a fraction of the theoretical amounts of hydrocarbons appear in the gas phase. From **2**, approximately 15% of the theoretical amounts of CH₄ and less than 5% of C₂H₄, C₂H₆, C₃H₈, and C₃H₆ are formed after 1 min of heating to 400 °C. On continued heating C₂H₄ and C₃H₈ yields increase more significantly than CH₄, C₂H₆, and C₃H₆. As the gas-phase concentration of C₃H₈ reaches 10%, its decomposition is initiated, giving rise mainly to CH₄, C₂H₄, C₂H₆, and H₂ (see Figure 3). After about 25 min of reaction at 400–500 °C, the total carbon and hydrogen balance reaches the theoretical values. The thermolysis of **3** occurs similarly except that C₂H₄ and C₂H₆ are the major products after 1 min reaction time (see Figure 4). As heating is continued, CH₄ and C₃H₈ are formed more rapidly while C₂H₆ and C₃H₆ remain nearly constant and only traces of H₂ are produced. Eventually, i.e., after 15 min of reaction under the conditions of the experiment of Figure 4, C₃H₈ yields begin to decline with attendant increases in the concentrations of CH₄, C₂H₄, H₂, and C₃H₆. Interestingly, the amounts of C₂H₆ change only slightly during this terminal phase. The C and H balance from the analysis of the gas phase becomes quantitative after 20–25 min of reaction at 400–500 °C.

3. Photolysis. Complexes **2** and **3** decompose on irradiation

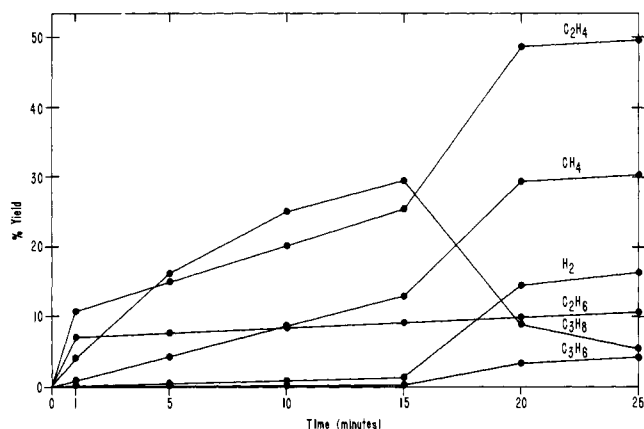


Figure 4. Formation of hydrocarbons and of hydrogen during the thermal decomposition of complex 3 at 400–500 °C under argon in the dark.

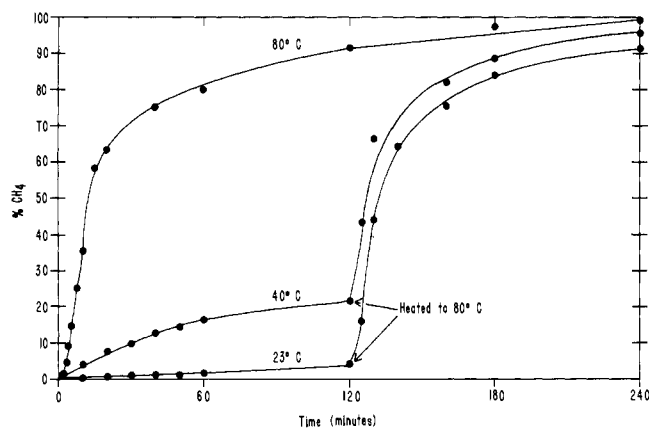


Figure 5. Methane evolution on hydrolysis of complex 2 in 1 M aqueous HCl at various temperatures, under argon in the dark.

with UV light; the yields of hydrocarbons formed and experimental conditions are listed in Table I. A slow decomposition of the compounds also occurs on irradiation with visible light. However, hydrocarbon yields were not quantitative because the solutions of the complexes bleach during the experiments, giving rise to compounds which still contain the Mo–C bond but which are less light sensitive. Brief warming of the solutions of 3 in NMP also causes decolorization without Mo–C bond cleavage (see section 1 above). If such solutions are subsequently irradiated with UV light C₂H₆ and C₂H₄ are formed but at different ratios than with the original complex 3. The bleaching of the complexes is undoubtedly associated with the loss or displacement of bipyridyl from the coordination sphere of molybdenum. This process is also light accelerated and occurs simultaneously with the Mo–C bond cleavage reactions but was not investigated in detail.

4. Hydrolysis. The evolution of hydrocarbons from aqueous solutions of complexes 2 and 3 was monitored under a variety of conditions. Because of the resistance of the Mo–C bond to hydrolysis at room temperature most experiments were performed anaerobically at 85 °C. Typical results are summarized in Tables II–IV and Figure 5. Reductive hydrolysis of the complexes with V²⁺(aq) as the reductant in 1 M HCl was quantitative (based on hydrocarbon yields) within 5 min of reaction at 23 °C, affording only CH₄ from 2 and C₂H₆ from 3. In the presence of oxidizing metal ions the reactions are considerably slower, yielding mixtures of CH₄ and C₂H₆ from 2 and of C₂H₄ and C₂H₆ from 3 (Table IV). Table III indicates that the reductive Mo–C bond cleavage with NaBH₄ or Na₂S₂O₄ as the reductants is accelerated in the presence of L(+)-cysteine and other thiols. Under most conditions of hy-

Table I. Anaerobic Photolysis of Complexes 2 and 3 under Various Experimental Conditions

| no. | solvent/irradn time/light source | products (gas phase) from complex | |
|-----|---|---|---|
| | | 2 CH ₄ /C ₂ H ₆ (% yields) | 3 C ₂ H ₆ /C ₂ H ₄ (% yields) |
| 1 | NMP/1 h/UV ^a | 100/0 (25) | 66/33 (16) |
| 2 | NMP/4 h/UV | 100/0 (98) | 50/50 (62) |
| 3 | NMP/4 h/vis ^b | 100/0 (1.5) | 39/61 (1.6) |
| 4 | THF/1 h/UV | 100/trace (13) | 66/33 (15) |
| 5 | CH ₂ Cl ₂ /1 h/UV | 100/trace (2.5) | 52/48 (2.5) |
| 6 | none/4 h/UV | 100/trace (1.1) | 25/75 (1.2) |
| 7 | NMP/1 h/dark | trace/0 | trace/0 |

^a Hanovia mercury arc lamp, 360 W. ^b G.E. 150-W flood light.

Table II. Relative Yields and Product Ratios from the Hydrolysis of Complexes 2 and 3 under Various Conditions

| no. | solvent | rel rates of Mo–C bond hydrolysis (total hydrocarbons) ^a | | terminal yields ^b and product ratios from | |
|-----|------------------|--|-----|---|---|
| | | 2 | 3 | 2 CH ₄ /C ₂ H ₆ | 3 C ₂ H ₆ /C ₂ H ₄ |
| 1 | 6 N NaOH | 100 | 92 | 100/0 | 95/5 |
| 2 | 3 N NaOH | 94 | 71 | 100/0 | 91/9 |
| 3 | 1 N NaOH | 90 | 35 | 100/0 | 63/37 |
| 4 | H ₂ O | 16 | 50 | 100/0 | 50/50 |
| 5 | 1 N HCl | 43 | 59 | 93/7 | 47/53 |
| 6 | 3 N HCl | 55 | 67 | 63/37 | 46/54 |
| 7 | 6 N HCl | 58 | 100 | 59/41 | 46/54 |

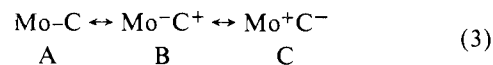
^a Rates determined after 30 min of reaction at 85 °C. ^b After 4 h of reaction at 85 °C.

drolysis, coordinated bipyridyl and bromide are displaced first prior to the hydrolytic cleavage of the Mo–C bond.

5. Miscellaneous Reactions. Complexes 2 and 3 react with gaseous Br₂ to yield CH₃Br or C₂H₅Br and 1, demonstrating the close relationship between the alkylated compounds and the dibromide starting material. To demonstrate the carbanionic reactivity of the molybdenum-bound alkyl groups, 2 and 3 were reacted with hydroxocobalamin and chloro(pyridine)cobaloxime in neutral aqueous solution. The formation of methyl- and ethylcobalamin and of the corresponding cobaloximes was demonstrated by a combination of chromatographic and spectrophotometric techniques (see Experimental Section). The methylation of Hg²⁺ by 2 in 1 M HCl was also observed. A methylation of As³⁺ was demonstrated qualitatively by gently heating a mixture of 2 with solid NaAsO₂, giving rise to the characteristic stench of cacodyl.

Discussion

Complexes 2 and 3 are the members of a new class of organomolybdenum compounds in which an alkyl group is attached to a dioxomolybdenum(VI) moiety carrying an additional bidentate ligand. It may be expected that analogous complexes of W(VI) and perhaps even of Cr(VI) can be prepared, although the latter, if they exist, would be undoubtedly less stable in view of the higher oxidation power of Cr(VI) relative to Mo(VI). The Mo–C bonds in 2 and 3 are essentially covalent. Even though the (bpy)Mo(O)₂Br group is estimated^{9,10} to have the electronegativity of 3.2, which is similar to that of chlorine, the Mo-bound alkyl groups display carbanionic reactivity. The Mo–C bond is evidently stabilized through contributions of ionic resonance forms such as A, B, and C:



In the following, some of the main features of the reactions of the complexes will be discussed in greater detail.

Table III. Relative Rates of Reductive Mo-C Bond Hydrolysis of Complexes **2** and **3** under Different Conditions at 23 °C

| no. | reaction conditions ^a | additive | complex 2 | complex 3 | |
|-----|---|---|---|-------------------------------------|--|
| | | | rel rates of CH ₄ production | rel rates of hydrocarbon production | C ₂ H ₆ /C ₂ H ₄ |
| 1 | pH 9.6, 0.8 M NaBH ₄ | 0.1 M cysteine | 100 (CH ₄) ^b | 100 | 99.9/0.1 |
| 2 | pH 9.6, 0.8 M NaBH ₄ | 0.1 M HO(CH ₂) ₂ NH ₂ | 82 | 92 | 99.9/0.1 |
| 3 | pH 9.6, 0.8 M NaBH ₄ | 0.1 M HS(CH ₂) ₂ NH ₂ | 92 | 90 | 99.9/0.1 |
| 4 | pH 9.6, 0.8 M NaBH ₄ | none | 88 | 85 | 99.1/0.9 |
| 5 | pH 9.6, 0.8 M NaBH ₄ | 0.1 M HS(CH ₂) ₂ OH | 92 | 81 | 99.1/0.9 |
| 6 | pH 9.6, 1 M Na ₂ S ₂ O ₄ | 0.1 M cysteine | 20 | 25 | 56/44 |
| 7 | pH 9.6, 1 M Na ₂ S ₂ O ₄ | 0.1 M HS(CH ₂) ₂ NH ₂ | 19 | 21 | 52/48 |
| 8 | pH 9.6, 1 M Na ₂ S ₂ O ₄ | 0.1 M HS(CH ₂) ₂ OH | 7 | 7 | 64/36 |
| 9 | pH 9.6, 1 M Na ₂ S ₂ O ₄ | HO(CH ₂) ₂ NH ₂ | 6 | 3 | 75/25 |
| 10 | pH 9.6, 1 M Na ₂ S ₂ O ₄ | none | 2 | 2 | 85/15 |
| 11 | pH 9.6 | 0.1 M cysteine | 2 | 7 | 48/52 |
| 12 | pH 9.6 | 0.1 M HS(CH ₂) ₂ NH ₂ | 2 | 5 | 47/53 |
| 13 | pH 9.6 | 0.1 M HS(CH ₂) ₂ OH | 3 | 4 | 50/50 |
| 14 | pH 9.6 | 0.1 M HO(CH ₂) ₂ NH ₂ | 5 | 1 | 65/35 |
| 15 | pH 9.6 | none | 1 | 1 | 55/45 |

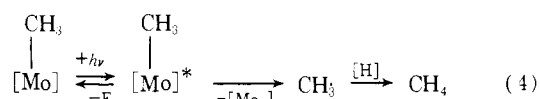
^a Reaction temperature 23 °C. Yields measured after 1 h corresponded to 25% from **2** and 30.4% from **3** under conditions of experiment no. 1. ^b CH₄ was only hydrocarbon observed in gas phase.

Table IV. Effects of Oxidizing and Reducing Additives on the Production of Hydrocarbons in the Hydrolysis of Complexes **2** and **3** under Various Conditions

| no. | conditions and additives ^a | hydrocarbon product ratios from complex | |
|-----|--|--|--|
| | | 2 CH ₄ / C ₂ H ₆ | 3 C ₂ H ₆ / C ₂ H ₄ |
| 1 | 6 M HCl, 80 °C, 1 h reaction time | 60/40 | 45/55 |
| 2 | as in 1, + 0.1 M Na ₂ MoO ₄ | 15/85 | 45/55 |
| 3 | as in 1, + 0.1 M MoCl ₅ | 70/30 | 45/55 |
| 4 | as in 1, + 0.1 M Cu(CH ₃ COO) ₂ | 15/85 | 45/55 |
| 5 | as in 1, + 0.1 M Cu(CH ₃ COO) | 25/75 | 45/55 |
| 6 | 3 M HCl, 80 °C, 1 h reaction time | 55/45 | 45/55 |
| 7 | as in 6, + 0.1 M Na ₂ MoO ₄ | 61/39 | 45/55 |
| 8 | as in 6, + 0.1 M MoCl ₅ | 86/14 | 45/55 |
| 9 | as in 6, + 0.1 M Cu(CH ₃ COO) ₂ | 47/53 | 45/55 |
| 10 | as in 6, + 0.1 M Cu(CH ₃ COO) | 47/53 | 45/55 |
| 11 | H ₂ O (pH 4), 80 °C, 1 h reaction time | 100/0 | 45/55 |
| 12 | as in 11, + 0.1 M Na ₂ MoO ₄ | 100/0 | 45/55 |
| 13 | as in 11, + 0.1 M Cu(CH ₃ COO) ₂ | 100/0 | 45/55 |
| 14 | 6 M HCl, 0.1 M V ²⁺ (aq), 23 °C, 1 h | 100/0 | 100/0 |
| 15 | 1 M HCl, 0.1 M V ²⁺ (aq), 23 °C, 1 h | 100/0 | 100/0 |
| 16 | 6 M HCl, 0.1 M Cr ²⁺ (aq), 23 °C, 1 h | 100/0 | 100/0 |
| 17 | 1 M HCl, 0.1 M Cr ²⁺ (aq), 23 °C, 1 h | 100/0 | 100/0 |

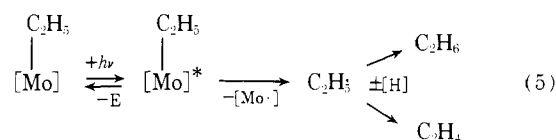
^a All reactions were run in under 1 atm of argon in the dark.

Photochemical Mo-C Bond Cleavage. The observed light sensitivity of complexes **2** and **3** is typical of the behavior of predominantly covalent organometallic complexes. The photolysis of the methyl derivative **2** may be described in terms of the schematic reaction eq 4, wherein [Mo] denotes the (bpy)-

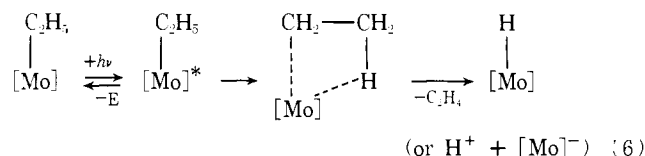


Mo(O)₂Br residue and [H] a source of abstractable hydrogen or a reducing equivalent plus a proton—a distinction between the two need not be made at this point. The photochemical Mo-C bond cleavage thus is assumed to take place by way of homolysis and formation of methyl radicals which terminate

through H abstraction. For the photolysis of **3** a similar mechanism is proposed which differs from eq 4 only by an additional termination step of the C₂H₅· radical to yield C₂H₄:



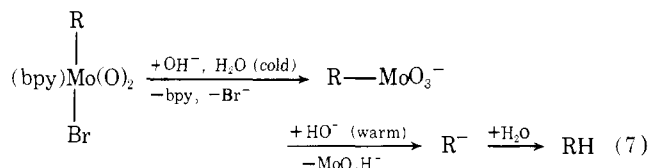
The possibility exists that C₂H₄ is formed from **3** with the intermediate formation of a hydridomolybdenum or equivalent species (eq 6). The photolysis of ethylcobalamin proceeds in this fashion:^{11,12}



Thermolysis. The comparatively high thermal stability of the new alkylmolybdenum complexes is surprising inasmuch as the cleavage of the Mo-C bond begins above 200 °C but must be continued at temperatures as high as 500 °C to become quantitative. In the thermolysis of **2**, CH₄ is the main initial product and is apparently formed by way of a hydrogen abstraction reaction from a neighboring methyl group. This gives rise to the formation of what may be described as carbene complexes of dioxomolybdate(VI). These may be regarded as the precursors of C₂H₄, the second most abundant hydrocarbon product (see Figure 3). It is noteworthy that only traces of C₂H₆ are formed, even though ethane could be readily formed by way of the coupling of two methyl radicals. Instead of ethane, significant amounts of C₃H₈ are generated. On prolonged heating this hydrocarbon decomposes mainly into CH₄ and C₂H₄. Such presumably radical-chain reactions of propane are well known to occur on thermolysis, but the present results suggest that in our system they are molybdenum catalyzed, proceeding via organomolybdenum intermediates capable of undergoing Mo-C insertion, H abstraction, and C-C cleavage reactions under the reaction conditions. The thermolysis of **3** is as complex, initially affording C₂H₄ and C₂H₆ as the main products. However, on further heating, C₃H₈ appears and declines, causing the formation of more C₂H₄, CH₄, H₂, and C₃H₆ (Figure 4). The discussion of these hydrocarbon formation and cracking reactions is outside the scope of the present paper.¹³ However, it appears that complexes such as

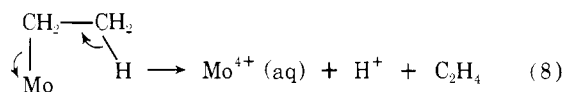
2 and **3** may serve as valuable model compounds for the study of reactions of this type.

Hydrolysis. Decomposition of the complexes in aqueous media occurs rapidly but at room temperature and neutral pH is not accompanied by extensive Mo–C bond cleavage. Hydrocarbons in the expected amounts are generated only upon prolonged heating (see Figure 5). Since both bipyridyl and bromide are displaced especially on alkaline hydrolysis, we conclude that alkylmolybdates RMoO_3H or equivalent anionic species with Mo–C bonds are formed. These are stable in cold aqueous solution and with appropriate precautions should even be isolable in the solid state. Our work has thus far concentrated mainly on the behavior of these hydrolysis products in solution, with emphasis on reactions causing the cleavage of the Mo–C bond. The decomposition in warm, alkaline solutions appears particularly straightforward since only CH_4 is gen-

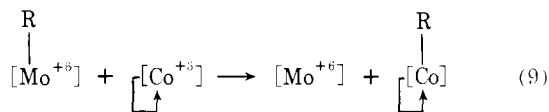


erated from **2**, and C_2H_6 is formed exclusively from **3**. The overall reactions are summarized in eq 7.

Hydrolysis of the complexes in neutral aqueous media proceeds in part by reactions similar to those in eq 7, but the observed formation of both C_2H_6 and C_2H_4 from **3** indicates that a reduction of Mo(VI) occurs as well. We believe that C_2H_4 is generated by an intramolecular elimination as formulated in eq 8. The $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ ratios remain unchanged if



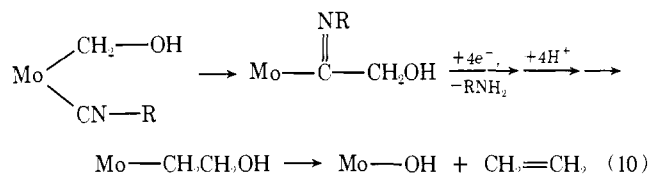
3 is hydrolyzed in the presence of added Mo(VI), Mo(V), Cu(II), or Cu(I) salts (Table IV), supporting the intramolecular mechanism (eq 8) of C_2H_4 formation even in acidic media. The Mo(IV) species formed according to eq 8 will undoubtedly undergo secondary reaction with Mo(VI) to yield Mo(V) derivatives; the latter are in fact observed. On the other hand, Table IV also reveals that the yields of CH_4 and C_2H_6 released from **2** on hydrolysis in acidic solution are strongly influenced by adding oxidizing or reducing metal ions. This suggests that CH_3^- anions are oxidized to radicals which in turn combine to yield C_2H_6 ; these processes are obviously not intramolecular. Consistent with the carbanionic mechanism of Mo–C bond hydrolysis, transalkylation reactions may be expected to occur and have been observed using the Co(III) ions in hydroxocobalamin and a cobaloxime as acceptors for the alkyl groups. These reactions do not occur via free alkyl carbanions since they take place rapidly at room temperature, i.e., under conditions where Mo–C bond hydrolysis is slow (eq 9). The alkylation of Hg^{2+} appears similarly straightforward



and is not surprising in the light of known reactions in other systems.¹⁴

Relation to Reactions of Nitrogenase and Nitrogenase Model Systems. The accelerated formation of hydrocarbons from **2** and **3** under reducing conditions in the presence of thiol ligands (see Table III) suggests that hydrolysis products of the complexes interact with the thiols to form new complexes in solution which are more susceptible to Mo–C bond cleavage. In this manner reactive systems are obtained which offer an opportunity to test our previous³⁻⁵ mechanistic postulates of hy-

drocarbon formation in the reduction of nitriles, isonitriles, and cyanide by N_2 -ase and in the model systems, at least inasmuch as the terminal reaction steps are concerned. In the enzymatic reduction of isonitriles by N_2 -ase, the $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ product ratios are dependent on the quality of the enzyme preparation.^{1,2,15} As a rule, more C_2H_4 and less C_2H_6 are generated if the efficiency of electron transfer is lowered through partial denaturation of the enzyme or other activity-impairing conditions. Assuming that the terminal reaction intermediate contains an ethyl group attached to the molybdenum active site it indeed follows from the present work that more C_2H_4 relative to C_2H_6 would be generated under these nonoptimal conditions of substrate reduction. Apart from this mechanism of C_2H_4 formation other possibilities exist.^{3,16} One invokes the decomposition of a hydroxyethylmolybdenum intermediate in terms of reaction eq 10. In this reaction, C_2H_4 is generated



from a hydroxymethylmolybdenum precursor of the ethyl group whose formation would be also favored under conditions of diminished electron transfer efficiency. That such alternative mechanisms of C_2H_4 production take place may be concluded from the fact that C_2H_6 is the apparently exclusive product of reduction of CH_3CN , both enzymatically and in the model systems. In the reduction of this substrate the terminal molybdenum intermediate cannot be a β -hydroxyethyl derivative since the CH_3 group in β position is already preformed. Hence, in this case reactions such as shown in eq 10 cannot occur and C_2H_6 would indeed be expected to be the exclusive product under optimal conditions. It remains to be demonstrated if some C_2H_4 is generated from CH_3CN using deactivated enzyme. At any rate, the formation of alkylmolybdenum complexes in protic media in molybdenum-catalyzed enzymatic and nonenzymatic reductions of nitriles, isonitriles, and cyanide is now well substantiated.

Experimental Section

Reagents and Chemicals. Molybdenum hexacarbonyl (Alfa-Ventron), 2,2'-bipyridyl (Aldrich), and methyl and ethyl bromide (Aldrich) were of highest available purity and used without additional purification. *N*-Methylpyrrolidone (NMP, from General Aniline & Film Corp.) was vacuum distilled from BaO and stored over molecular sieves 3A. Tetrahydrofuran (Mallinckrodt) was dried over LiAlH_4 and distilled immediately prior to use. Methylene chloride (Mallinckrodt) was distilled from P_2O_5 under argon and stored over molecular sieve 3A. Protective gases (argon and nitrogen) were both of 99.998% purity and were dried by passage over KOH pellets.

Preparation of (bpy)Mo(O)₂Br₂ (1). The complex was prepared by the reaction of tetracarbonylmono-2,2'-bipyridylmolybdenum(0) with Br_2 in ethanol/ CH_2Cl_2 according to ref 7.

Methyl(dioxobromo)-2,2'-bipyridylmolybdenum(VI) (2). Methylmagnesium bromide was prepared in tetrahydrofuran according to standard methods and was filtered through a fritted Schlenk tube for purification. To a stirred suspension of 4.5 g (10 mmol) of **1** in 50 mL of dry THF, 25 mL of a 1 M solution of methylmagnesium bromide in THF was added dropwise while a protective stream of dry argon was passing through the system and the reacting mixture was cooled with ice. The reaction mixture gradually attained a deep purple color and was allowed to react for 30 min during which purple crystals separated which were collected by filtration through a fritted Schlenk tube. The product (3.6 g) was washed with ice-cold THF followed by anhydrous ether and dried at 85 °C (1 mmHg) for 24 h. Recrystallization was effected by addition of dry *n*-heptane to solutions of complex in CH_2Cl_2 or THF maintaining strictly anhydrous conditions during all operations. It is not necessary to work in complete darkness as extensive photolysis occurs only on irradiation with intense light

sources. In this manner samples of analytically pure **2** have been obtained. However, this method of recrystallization is not recommended for the purification of large amounts of the complex. Anal. Calcd for $C_{11}H_{11}N_2O_2BrMo$: C, 34.85; H, 2.92; Mo, 25.31; Br, 21.08. Found: C, 34.25; H, 2.75; Mo, 25.0; Br, 22.08. Complex **2** begins to decompose above 200 °C in an argon atmosphere.

Ethyl(dioxobromo)-2,2'-bipyridylmolybdenum(VI) (3). This complex can be prepared by the method described above for the methyl derivative **2**. It was also obtained by the dropwise addition of 11.0 mL of a filtered 1 M solution of ethylmagnesium bromide in THF to a suspension of 4.5 g (10 mmol) of $(bpy)Mo(O)_2Br_2$ in 50 mL of THF at room temperature. After all the Grignard reagent was added the reaction mixture was stirred for an additional 5 min. The product (3.5 g) was purified as described above for the methyl complex. Anal. Calcd for $C_{12}H_{13}N_2O_2BrMo$: C, 36.67; H, 3.33; Mo, 24.41; Br, 20.33. Found: C, 36.21; H, 3.23; Mo, 22.94; Br, 21.04. On heating, **3** begins to decompose above 200 °C under argon. Magnetic properties $\chi_M = -1.64 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ (Faraday method);¹⁷ calcd $\chi_M = -1.74 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$.

¹H NMR, IR, and UV-Vis Spectra. Fourier-transform ¹H NMR spectra were obtained for solutions of **2** and **3** in dry, distilled $CDCl_3$ using a Varian HR-220/Nicolet TT-100 spectrometer. Important bands in the IR spectra of **2** and **3** and other physical properties are summarized in Table V.

Photolysis Experiments. Solutions of the complexes in dry NMP, THF, and CH_2Cl_2 were placed into Pyrex test tubes and exposed to light emitted from a 360-W Hg-arc Hanovia UV lamp at a distance of about 20 cm. A stream of cold air was blown over the tubes to maintain the temperature near 30 °C. At regular intervals, gas samples (0.5 mL) were withdrawn for hydrocarbon determinations by GLC using a Hewlett-Packard Model 700 gas chromatograph equipped with a 8 ft \times 1/8 in. column packed with phenyl isocyanate on Poracil C operating at ambient temperature; a FID detector was used. Routine tests for alcohols were performed using a Varian 1200 Aerograph gas chromatograph fitted with a 6 ft \times 1/8 in. column packed with Porapak Q operating at 130 °C, also employing FID for detection.

Thermolysis Experiments. The thermal decomposition of complexes **2** and **3** was performed in serum-capped Pyrex test tubes filled with argon; the tubes were carefully heated in the flame of a Bunsen burner, and gas samples (0.5 mL) for hydrocarbon analysis by GLC were withdrawn at regular intervals. The results of typical experiments are shown in Figures 3 and 4. The gas phase was analyzed for H_2 by GLC using a column of 6-ft length filled with molecular sieve (5A), operating at 27 °C, employing TC detection.

Hydrolysis. Hydrolysis experiments were usually performed in serum-capped glass bottles (Pierce Chemical Co., Rockford, Ill.) of 38 mL total capacity. A known amount of complex (10–20 mg) was placed into the empty bottle which was then sealed and flushed with pure argon. The hydrolysis reaction was initiated by injecting a known volume (usually 10 mL) of water, aqueous acid, or base. For experiments at elevated temperatures, these solutions were prewarmed prior to injection. Gas-phase samples were withdrawn at regular intervals and analyzed for hydrocarbons by GLC as described above.

Transalkylation Experiments. A. Reactions of Complexes 2 and 3 with Hydroxocobalamin. Five milligrams of complexes **2** or **3** was added to freshly prepared solutions of 1 mg of hydroxocobalamin in 5 mL of H_2O . After 15 min of reaction at ambient temperature the solutions were phenol extracted. The cobalamins were isolated from the phenol extracts by the addition of acetone and diethyl ether and identified by thin layer chromatography on cellulose, using 1-butanol-ethanol-water (10:3:1 v/v) as the ascending phase and cochromatography with authentic methyl- or ethylcobalamin. The two alkylcobalamins were further identified by measurements of their UV-vis absorption spectra in aqueous solution before and after aerobic photolysis and by gas chromatographic analysis of the hydrocarbon photolysis products (CH_4 , C_2H_6 , C_2H_4).

Table V. Summary of Physical Properties of Complexes **2** and **3**

| complex no. | IR $\nu_{Mo=O}$, cm^{-1} ^a | UV-vis λ_{max} , nm (ϵ) ^b | ¹ H NMR | |
|-------------|--|---|--------------------|---------------------------------------|
| | | | δ_{bpy} | δ_{RH} , ppm [N] ^c |
| 2 | 927.4, 907.8 | 538 (450) | 7.5–9.5 [8] | 0.62 [3] |
| 3 | 931.3, 899.5 | 538 (450) | 7.5–9.5 [8] | 1.1 [3] 3.3 [2] $J_{AB} = 8$ Hz |

^a In Nujol mull. ^b Measured in *N*-methylpyrrolidone immediately after solution was prepared. ^c Chemical shifts are relative to Me_4Si , measured in $CDCl_3$.

B. Reactions of Complexes 2 and 3 with Chloro(pyridine)cobaloxime(III). These experiments were carried out exactly as described under A above except that chloro(pyridine)cobaloxime¹⁸ was substituted for hydroxocobalamin. The reaction solutions were worked up by extraction with CH_2Cl_2 and recrystallization from CH_2Cl_2 -*n*-hexane. The methyl- and ethylcobaloximes were identified by their characteristic Co–C CT band in the near-UV region¹⁹ and their behavior on photolysis, giving rise to a mixture of CH_4 and C_2H_6 (methylcobaloxime) and C_2H_4 (ethylcobaloxime).

C. Reaction of 2 with $HgCl_2$. Complex **2** (30 mg) was added to 10 mL of a saturated solution of $HgCl_2$ in 1 N HCl. After 15 min of reaction the solution was extracted with CCl_4 . The CCl_4 phase was washed with water, dried, and evaporated to dryness. The solid residue was shown to contain methylated mercury by pyrolysis under argon, giving rise to a mixture of methane and ethane. Mercury in the thermolysis residue was detected after dissolution in HNO_3 , using the dithizone method.

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