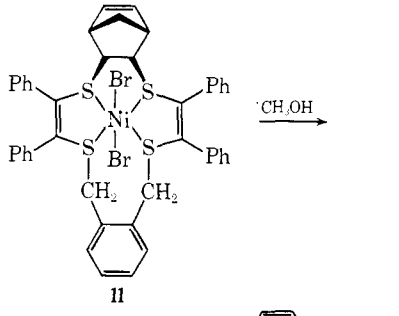
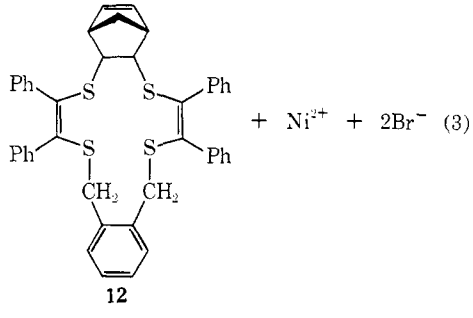
with the calculated amount of α,α'-dibromo-*o*-xylene in toluene. The green paramagnetic (μ_{eff} = 3.5 BM) crystals of **11** (mp 290° dec) decompose immediately on dissolution in methanol to yield the free macrocyclic ligand **12**, mp 258°.

Anal. Calcd for $C_{43}H_{36}S_4Br_2Ni$: C, 56.78; H, 3.99. Found: C, 56.64; H, 4.12. Calcd for $C_{43}H_{36}S_4$: C, 75.84; H, 5.33. Found: C, 75.92; H, 5.44.

The structure of **12** was confirmed through nmr measurements.



11



12

We conclude that **4** is not formed *via* **6** but rather by an independent pathway involving the labile intermediate **3**. Complex **6** is formed preferentially in the presence of a large excess of norbornadiene, *e.g.*, on refluxing **1** in norbornadiene. Only traces of **6** are produced if **1** is treated with norbornadiene at room temperature in CH_2Cl_2 solution. The reaction of $PdS_4C_4Ph_4$ with **2** at 85° yields 35% of **4** in addition to the red adduct $PdS_4C_4Ph_4 \cdot C_7H_8$ (**13**), mp 250° dec. The platinum dithiene reacts very slowly under comparable conditions and only produces the yellow $PtS_4C_4Ph_4 \cdot C_7H_8$ (**14**, mp 350° dec). Structures analogous to **6** are proposed for **13** and **14**.

The olefin adduct formation appears to be limited to the dithienes of Ni, Pd, and Pt. The formation of **4** occurs on refluxing $MoS_6C_6Ph_6$, $CrS_6C_6Ph_6$, and $VS_6C_6Ph_6$ in norbornadiene, but not with $WS_6C_6Ph_6$, $ReS_6C_6Ph_6$, $OsS_6C_6Ph_6$, or with various neutral and anionic iron and cobalt dithienes under comparable conditions. The CF_3^- substituted derivative of **4**, finally, is also produced as a by-product in the reaction of $NiS_4C_4(CF_3)_4$ with **2**. The Diels–Alder adduct formation (an orbitally allowed process) thus is observed rather generally, whereas adducts of type **6** are produced less commonly because they could originate *via* an "orbitally forbidden" reaction.

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Acetate Synthesis from Carbon Dioxide and Methylcorrinoids. Simulation of the Microbial Carbon Dioxide Fixation Reaction in a Model System

Sir:

Cell extracts of *Clostridium thermoaceticum* catalyze the formation of acetic acid from methylcorrinoids (methylcobinamide or methylcobalamin) and carbon dioxide.[1-3] For this microbial CO_2 fixation process two mechanisms are presently being discussed.[4] In the first, the acetate is assumed to be formed by a carboxylation reaction analogous to the known reaction of Grignard reagents. In the second, the methylcorrinoid is considered to react with CO_2 to produce an enzyme-bound carboxymethylcobalt derivative. The corrin would therefore have to undergo a proton abstraction at the cobalt-bound methyl group, followed by the carboxylation of the resulting methylene–corrinoid carbanion. This hypothetical reaction would give rise to a carboxymethylcobalt derivative, whose reductive Co–C bond cleavage is known to yield acetic acid.[5,6] However, both mechanisms are in serious conflict with known properties of Co-methylcorrinoids and of related model compounds. Thus, methylcobalamin or methylcobaloximes[7] have few, if any, reactions directly in common with Grignard reagents and are inert to carbon dioxide under a variety of conditions. The hydrogen atoms in Co-methyl compounds furthermore are essentially covalent and do not undergo H–D exchange in alkaline, neutral, or acidic solution.[8] Hence, both mechanisms of acetate formation are unacceptable on chemical grounds.

To develop a plausible mechanism of acetate formation we took cognizance of the facile reductive cleavage of the Co–C bond in methylcobalamin by thiols. In this reaction methyl carbanions or related species with the reactivity of methyl carbanions are generated which react with water solvent to form methane.[8] A logical extension of this mechanism of methane formation would be to generate the CH_3^- ions in a locally anhydrous environment in the presence of CO_2. Under these conditions the formation of acetate from a methylcobalt derivative should proceed according to eq 1 [(Co) denotes the cobaloxime, B denotes a Lewis base,

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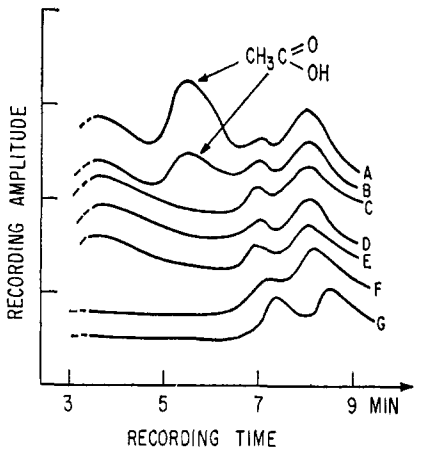
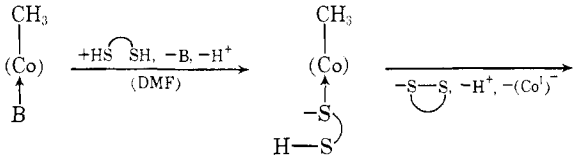
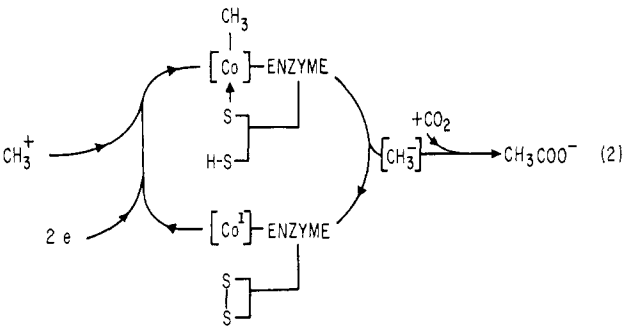


Figure 1. Gas–liquid partition chromatography tracings demonstrating acetic acid formation from methyl(pyridine)cobaloxime in DMF under the experimental conditions outlined in the text: (A) complete system, with added acetic acid as internal standard (0.01 mmol/ml); (B) complete system without added acetic acid; (C) system as in (A), but after treatment with solid NaOH; (D) system as in (B) after treatment with solid NaOH; (E) system as in (B) but run under argon instead of CO_2; (F) system as in (E) but with ethyl(pyridine)cobaloxime; (G) complete system with ethyl(pyridine)cobaloxime. Measurements were performed with a 5-ft Poropak Q column at 22 cc/min He flow rate, with H_2 flame detector. All measurement tracings were obtained at attenuation 2.

e.g., pyridine]. To verify eq 1 in a nonenzymatic model system methylcobaloximes were reductively cleaved with dithioerythritol in aqueous solution under 1 atm of CO_2. Although the main product was methane as



expected, acetic acid was nevertheless detected in yields up to 0.01% of the total cobaloxime. To increase the acetate formation the reaction was conducted in anhydrous dimethylformamide (DMF) with 1,4-butanedithiol as the reducing agent. Under these more favorable conditions, a 50-fold yield increase was observed, affording acetic acid in amounts of up to 1% of the methylcobaloxime present initially. In a specific experiment 1 mmol of methyl(pyridine)cobaloxime was dissolved in 4 ml of anhydrous DMF. After displacing the air in the reaction vessel by 1 atm of CO_2, 2 mmol of 1,4-butanedithiol was added and the reaction mixture was maintained at 65° for 12 hr. Analysis of the liquid phase was performed by glpc using a 5-ft Poropak Q column, as well as a 5-ft 5% FFAP column for separation and comparison with an authentic sample. The acetic acid peak disappears on treating the reaction solution with dilute NaOH and is absent if the reactions are run under argon. It is also not observed if ethyl- and *n*-propylcobaloximes are treated with CO_2 in the presence of thiols under similar conditions (Figure 1). We therefore conclude that a reaction analogous to eq 1 could occur enzymatically, provided that the active site is maintained in a locally aprotic environment. The available evidence indeed suggests that a thioprotein is involved in the acetate formation at least of *C. thermoaceticum*. Thus, the conversion of methylcobalamin to acetate is inhibited[2] by iodoacetamide, 4-iodoacetylsalicylic acid, and other typical sulfhydryl group blocking reagents. Assuming that one of the terminal steps in the acetate synthesis consists in the transfer of labile methyl groups to the reduced corrin cofactor, the essential steps in the enzymatic reactions can be summarized by eq 2, where [Co] denotes the corrin.



The mechanism in eq 2 has the advantage of having been directly verified by plausible model experiments and that no specific CO_2 activation is required. It furthermore relates the corrin-dependent acetate biosynthesis to methane biosynthesis and ribonucleotide reduction.[9] All three enzymatic processes are corrin dependent and utilize thioredoxin systems in the terminal electron transfer reactions.

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Syntheses of [2.2]Metacyclophane-1,9-diene and *trans*-15,16-Dihydropyrene

Sir:

The question of whether *trans*-15,16-dihydropyrene is capable of a finite existence is a long standing one. Neunhoeffer and Woggon suggested the possibility of 15,16-dihydropyrene being present in solutions from metal reductions of pyrene,[1] but this could not be confirmed,[2] and later work by Gerson, Heilbronner, Reddoch, Paskovich, and Das showed that the Birch reduction of pyrene gives two isomeric tetrahydropyrenes from which the corresponding radical is exceptionally stable.[3] Although various *trans*-15,16-dialkyldihydropyrenes have now been known for some time,[4–6] the ease of thermal rearrangement of *trans*-15,16-dialkyldihydropyrenes,[7] particularly with larger alkyl groups,[6] also raised the possibility that *trans*-

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