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Ni(II) (dioxo[16]aneN5)-Induced Methane Formation from Methyl Coenzyme M

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to thank Prof. T. A. Albright and Dr. F. Studer for invaluable discussions.

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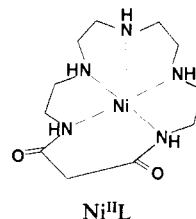
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H₂O (20 mL) was placed into a two-neck round-bottom flask equipped with a magnetic stirbar. Methyl-CoM¹⁵ (0.800 mM) was added under a heavy flow of argon and the flask connected to a gas-uptake manometer.¹⁶ Methane was identified as the sole carbon-containing gas phase product by GC, IR, and MS analysis,¹⁷ and the extent of product formation was assayed either by the gas-uptake manometer or by the integration of the methyl and ethylene ¹H NMR signals of the methyl-CoM and CoM containing final reaction mixture.¹⁸ One equivalent of methyl-CoM per equivalent of Ni^{II}L forms 0.60 ± 0.04 equiv of CoM and 0.20 ± 0.02 equiv of 2,2'-dithiobis(ethanesulfonic acid), CoM disulfide.¹⁵ As the reaction proceeds, the green solution containing Ni^{II}L and methyl-CoM becomes brown with an UV-visible spectrum identical with that of Ni^{II}L titrated with CoM (Figure 1).¹⁹ Since the reaction continues until 1.2 ± 0.1 equiv of methyl-CoM is consumed, it is evident the formation of Ni-CoM prevents additional conversion of methyl-CoM. The fact that no methane is produced when methyl-CoM is added to a solution containing an equimolar amount of Ni^{II}L and CoM supports this conclusion.

The magnetic susceptibility of the reaction mixture was measured by the Evans method.²⁰ Ni^{II}L ($\mu = 2.60 \mu_B$) and methyl-CoM were placed in a concentric NMR tube and sealed under argon. As 1 equiv of methyl-CoM was consumed during the reaction, the magnetic susceptibility slowly increased to a final value of 2.74 μ_B . This small increase in the magnetic moment is attributed to the formation of Ni^{II}(L)(CoM).¹⁹ When the reaction is run under O₂, the magnetic moment per nickel increased from 2.99 to 3.17 μ_B .²⁰

We do not believe that Ni^IL is required for methane evolution for the following reasons. In the presence of an 8:1 excess of substrate to Ni^{II}L at 21.5 ± 1 °C the initial rate is (1.94 ± 0.14) × 10⁻² (mol of CH₄) (mol of Ni)⁻¹ h⁻¹ under 1 atm of argon and (2.24 ± 0.16) × 10⁻² (mol of CH₄) (mol of Ni)⁻¹ h⁻¹ under 1 atm of O₂.²¹ It is expected that O₂ would inhibit the formation of

Ni^{II}(dioxo[16]aneN₅)-Induced Methane Formation from Methyl Coenzyme M

Sir:

The nickel tetrapyrrole containing factor, F₄₃₀, is implicated in the final methane evolution step in methanogenic bacteria¹⁻⁴ and has attracted considerable attention.⁵⁻⁸ The essential role of F₄₃₀ in methane formation was demonstrated by Ankel-Fuchs and Thauer, who reported the in vitro catalysis of H₃CSCH₂C-H₂SO₃⁻, methyl coenzyme M (methyl-CoM), to methane and CoM by purified methyl-CoM reductase under reducing conditions.⁹ Since F₄₃₀ exists in both the Ni(I) (or Ni(III)) and the Ni(II) states in *Methanobacterium thermoautotrophicum*,^{10,11} it is of interest to examine the role of the nickel ion oxidation state^{12,13} in methyl-CoM catalysis. We have found both the mono- and the divalent oxidation states of the water-soluble Ni(dioxo[16]aneN₅), NiL, complex¹⁴ catalyze methyl-CoM to methane and CoM.

In a typical reaction Ni^{II}L (0.267 mM) in deoxygenated distilled

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- (14) Kimura, E.; Machida, R.; Kodama, M. *J. Am. Chem. Soc.* **1984**, *106*, 5497. Dioxo[16]aneN₅(L) ¹H NMR (CDCl₃): δ(TMS) 7.90 (s, 2 H, amide), 3.30 (m, 4 H, amide ethylene), 3.20 (s, 2 H, malonyl methylene), 2.85 (m, 12 H, ethylene), 2.00 (b s, 3 H, amine). ¹³C NMR (CDCl₃): δ(TMS) 169.0, 49.0, 48.5, 48.0, 43.0, 38.5. The UV-vis spectrum of Ni^{II}L is pH-dependent. UV-vis [pH 9.5 borate buffer] (ε): 260, 290 (1664), 340 nm (120).

- (15) For the preparation of methyl-CoM see: Taylor, C. D.; Wolfe, R. S. *Biochemistry* **1978**, *17*, 2374. Sodium salt of 2-mercaptoethanesulfonic acid (CoM) ¹H NMR (D₂O): δ(TMS) 2.97 (m, 2 H), 2.67 (m, 2 H). Ammonium 2-(methylthio)ethanesulfonate (NH₄(methyl-CoM)) ¹H NMR (D₂O): δ(TMS) 2.99 (m, 2 H), 2.69 (m, 2 H), 1.95 (s, 3 H). The disodium salt of 2,2'-dithiobis(ethanesulfonic acid) (CoM disulfide) was prepared by titrating an aqueous solution of CoM with I₂ until its color persisted. ¹H NMR (D₂O): δ(TMS) 3.13 (m, 4 H), 2.88 (m, 4 H). Methyl-CoM does not decompose to methane and CoM between pH 4 and pH 9.5.
- (16) Drago, R. S.; Gaul, J. H.; Zombeck, A.; Straub, D. *J. Am. Chem. Soc.* **1980**, *102*, 1033.
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- (18) After a reaction was complete, the solution was freeze-dried and reconstituted with D₂O. ¹H NMR integration of CoM and methyl-CoM was within ±4% of the yield of methane gas evolution calculated according to step 6. No carbon-containing side products were observed in the GC, GC-MS, ¹H NMR, or FT-IR measurements in either the gas or the solution phase. The background O₂ concentration observed in the GC-MS spectrum of the gas-phase products introduced significant uncertainty in the determination of [O₂].
- (19) When LNi^{II} was titrated with CoM, new UV-visible absorptions in a pH 9.5 borate buffer were observed (ε): 333 (2217), 405 (754), 510 nm (297).
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- (21) The rate of LNi^{II} decomposition under O₂ is slow compared to the initial rate.

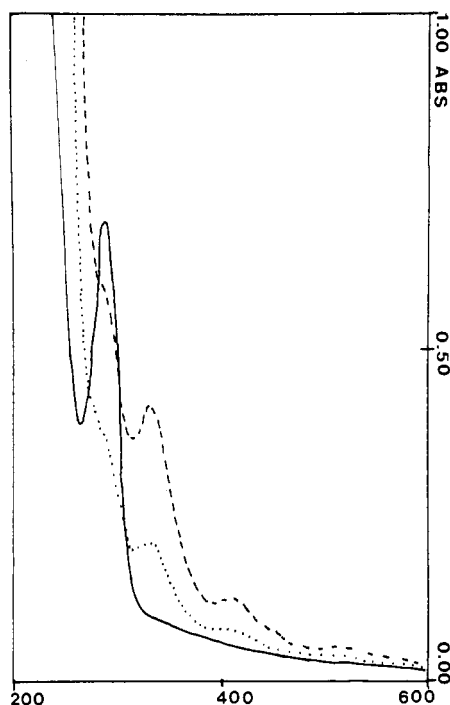


Figure 1. UV-visible spectra (nm): (—) LNi^{II} ; (- - -) LNi^{II} with 1.5 equiv of CoM; (· · ·) final reaction mixture.

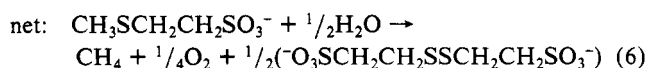
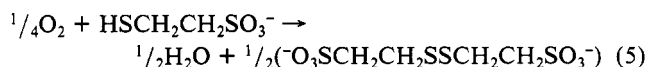
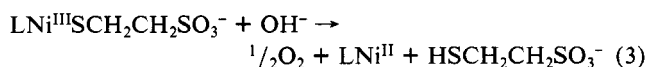
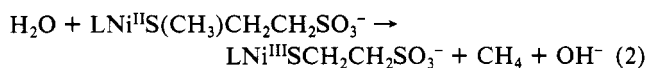
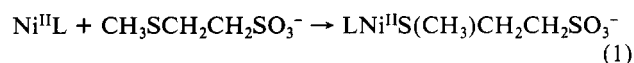
a highly air-sensitive Ni^{II} species. In addition, the initial rate of CH_4 evolution by a prepared sample^{22,23} of Ni^{II} is only $(1.80 \pm 0.13) \times 10^{-2}$ (mol of CH_4) (mol of Ni)⁻¹ h⁻¹, although 1.8 ± 0.1 equiv of methyl-CoM is converted.

Under H_2 (4 atm),²⁴ Ni^{II} converts methyl-CoM to methane at a rate similar to that for Ar (1 atm). Under D_2 (4 atm) the sole carbon-containing product observed in the gas phase by IR and MS is CH_4 , which indicates that H_2O is the source of the hydrogen incorporated into methyl-CoM. The absence of methanol or ethane in the gas phase¹⁸ indicates that the $\text{H}_3\text{C-S}$ bond is cleaved heterolytically. Solvent protonation of the methyl group is confirmed by the formation of $92 \pm 3\%$ CH_3D from a reaction mixture containing $\text{H}_2/\text{D}_2\text{O}$ (98%).²⁵ In D_2O (98%) the rate is $(2.00 \pm 0.11) \times 10^{-2}$ (mol of CDH_3) (mol of Ni)⁻¹ h⁻¹, indicating no kinetic ^2H isotope effect. Analogous experiments with methanogenic bacteria demonstrate methyl-CoM incorporates solvent hydrogen to form methane.²⁶

The evolution of dioxygen is indicated by the following qualitative test. Two flasks, one containing the O_2 indicator $[\text{Cp}_2\text{TiCl}]_2\text{ZnCl}$ (Cp = cyclopentadienyl) in toluene, the other containing the standard reaction mixture, are connected in order to allow the diffusion of gaseous products. As the reaction proceeds, the blue-green reduced titanium solution becomes orange. The indicator remains unchanged in a blank, where the second

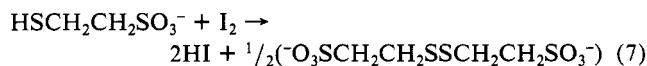
flask contains only methyl-CoM and H_2O . This result suggests the formation of O_2 occurs during the catalysis of methyl-coenzyme M by Ni^{II} .

A reaction sequence for the Ni^{II} -induced cleavage of methyl-CoM is



Steps 1–5 are a set of balanced equations that represent the catalysis of methyl-CoM to CH_4 and CoM disulfide.²⁷ There are two reasons we believe only about 1.2 mol of methyl-CoM is consumed per mole of Ni^{II} : (a) the oxidant, O_2 , escapes from solution, resulting in incomplete formation of the disulfide in step 5, and (b) the binding constant $K(\text{b}) = 145 (\pm 11\%) \text{ L M}^{-1}$ in step 4, resulting in unreactive $\text{LNi}^{\text{II}}\text{SCH}_2\text{CH}_2\text{SO}_3^-$.

The addition of I_2 oxidizes free CoM to CoM disulfide according to step 7, and the reduced concentration of CoM drives the equilibrium in step 4 to the left, generating free Ni^{II} . When



an aqueous solution of the brown Ni-CoM complex is shaken with hexane containing I_2 ,²⁸ the solution turns green and has the same UV-visible spectrum as Ni^{II} (Figure 1). After the organic layer is removed, the remaining green solution evolves methane from freshly added methyl-CoM at the same rate as for fresh Ni^{II} .

A mechanism has been proposed¹² for methyl-coenzyme M reductase where $\text{Ni}^{\text{II}}\text{F}_{430}$ is first reduced to $\text{Ni}^{\text{I}}\text{F}_{430}$, which homolytically cleaves methyl-CoM to produce methyl- $\text{Ni}^{\text{I}}\text{F}_{430}$ followed by the protonation of methyl- $\text{Ni}^{\text{I}}\text{F}_{430}$ to yield CH_4 and $\text{Ni}^{\text{II}}\text{F}_{430}$. The final protonation step is consistent with the hydrolysis of highly air-sensitive alkyl- Ni^{I} tetraaza macrocycles.¹³ The recent discovery of a heterodisulfide derived from CoM and (7-mercaptoheptanoyl)threonine phosphate (HS-HTP) formed during methanogenesis²⁹ was predicted by this mechanism. CoM disulfide is also observed in the model system. In addition, we have found that the reactivity of Ni^{II} does not typify nickel(II) chemistry. Aqueous solutions of nickel(II) acetate, nickel(II) tetraethylenepentamine, or nickel(II) 1,4,8,11-tetraazacyclotetradecane-5,7-dione³⁰ do not convert methyl-CoM to methane under either argon or H_2 . It is clear the ligand (L) activates $\text{Ni}(\text{II})$ toward methyl-CoM. The ligand in F_{430} might also play an important part in activating nickel toward methyl-CoM.

Acknowledgment. We are particularly grateful to Professor S. G. Baxter for many helpful discussions and M. A. Edelman

(22) $\text{Ni}^{\text{II}}\text{L}$ ($\mu = 1.77 \mu\text{B}$) is produced by treating $\text{Ni}^{\text{II}}\text{L}$ with a one-electron equivalent of $\text{Na}_2\text{S}_2\text{O}_4$. Sodium dithionite does not react with methyl-CoM in the absence of $\text{Ni}^{\text{II}}\text{L}$. $\text{Na}_2\text{S}_2\text{O}_4$ reactions were run in a pH 8.5 buffer.

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(24) Hydrogen reactions were run on a Parr apparatus.

(25) This is based on the ratio of the intensities of the $m/e = 17$ (CDH_3^+) and the $m/e = 16$ (CH_4^+) lines in the low-resolution mass spectrum of the gas evolved from the reaction. Other ions, including CDH_2^+ , could contribute to $m/e = 16$, resulting in an underestimate of the CDH_3/CH_4 ratio (MIT Chemistry Spectroscopy Facility).

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(28) A 4:1 excess of I_2 over $\text{Ni}^{\text{II}}\text{L}$ was used. I_2 slowly oxidizes methyl-CoM. $\text{Ni}^{\text{II}}\text{L}$ incubated with a 2-fold excess of CoM disulfide prior to the addition of methyl-CoM does not inhibit methane formation.

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for modifying the synthetic procedure for Ni^{II}L.

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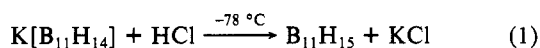
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Synthesis of the New Boron Hydride *nido*-Undecaborane(15), B₁₁H₁₅, and the X-ray Structure of Its Conjugate Base Tetradecahydroundecaborate(1-), [B₁₁H₁₄]⁻

Sir:

We recently reported¹ syntheses of alkali-metal (Li, Na, K) salts of the tetradecahydroundecaborate(1-) ion, [B₁₁H₁₄]⁻, via a convenient, "one-pot", essentially quantitative procedure from the reaction of pentaborane(9), B₅H₉, with MH (M = Na, K) or (*t*-Bu)Li. In light of this new synthesis an investigation into the chemistry of [B₁₁H₁₄]⁻ was begun. Reported, herein, is the preparation of *nido*-undecaborane(15), B₁₁H₁₅, from the protonation of K[B₁₁H₁₄] and the subsequent deprotonation of B₁₁H₁₅ by P(CH₃)₃ to give [P(CH₃)₃H][B₁₁H₁₄], the structure of which has been determined from single-crystal X-ray data.

Protonation of NaB₁₁H₁₄·2.5C₄H₈O₂ in C₄H₈O₂ has been reported² to produce B₁₁H₁₅·2C₄H₈O₂ and in S(CH₃)₂ to produce B₁₁H₁₃·S(CH₃)₂ with the evolution of H₂ gas. We find that the reaction of K[B₁₁H₁₄] with anhydrous HCl at -78 °C gives undecaborane(15), B₁₁H₁₅, in quantitative yield according to eq 1.



In a typical preparation, K[B₁₁H₁₄] (125 mg, 0.725 mmol) was treated with excess HCl (25 mmol) at -78 °C for 12 h. No noncondensable gas was produced. The excess HCl was pumped away from the reactor at -78 °C over a period of 12 h. On the basis of the amount of recovered HCl (24.3 mmol), 0.7 mmol of HCl was consumed, indicating a 1:1 reactant ratio of HCl to K[B₁₁H₁₄]. Toluene-*d*₈ (0.7 mL) was condensed onto the product, and the resulting solution was filtered at low temperature into an NMR tube. The solid remaining on the frit was washed with tetrahydrofuran and identified as KCl by powder X-ray diffraction. Undecaborane(15) is not stable above 0 °C. In the solid state or in solution it decomposes with the evolution of about 0.5 mol of H₂/mol of [B₁₁H₁₄]⁻ and the formation of a white solid,³ insoluble in ethers, CH₃CN, toluene, and CH₂Cl₂.

The boron-11 NMR spectrum of B₁₁H₁₅ (96.3 MHz), obtained at -40 °C in toluene-*d*₈, consists of two resonances (-14.8 ppm (*J* = ~200 Hz, d) and -17.4 ppm (*J* = 145 Hz, d), BF₃·OEt₂ at 0.00 ppm), which upon proton decoupling become singlets with relative areas of 6:5, respectively. This is consistent with a boron framework based upon an icosahedron with one vertex removed if it is assumed that the resonance due to the unique boron atom overlaps with the low-field signal that arises from one of the sets of five equivalent boron atoms. The proton NMR spectrum (300 MHz), with ¹¹B decoupling, in toluene-*d*₈ at -80 °C consists of two resonances in the terminal region at 2.43 and 1.29 ppm and only one resonance in the bridge hydrogen region at -3.53 ppm. The resonance due to the hydrogen atom on the unique boron atom was not observed and is believed to overlap the higher field terminal signal arising from one of the sets of five equivalent terminal hydrogen atoms. This is supported by the relative areas of the

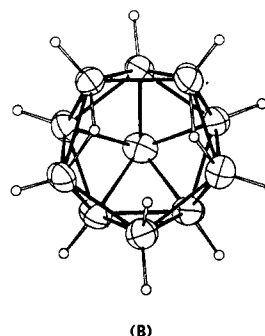
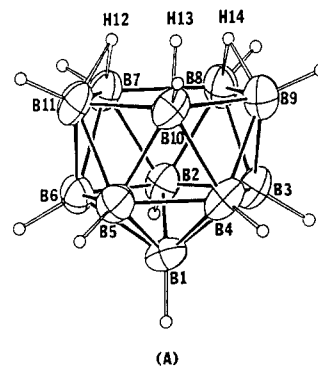
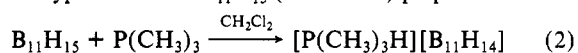


Figure 1. Views of the molecular structure of [B₁₁H₁₄]⁻ (ORTEP plots with 50% probability ellipsoids).

resonances, 1.2:1.4:1, which are consistent with the theoretical values of 1.25:1.5:1.

Undecaborane(15) is readily deprotonated. It yields [B₁₁H₁₄]⁻ in (CH₃)₂O, and the reaction (2) with P(CH₃)₃ yields an isolable salt. In a typical reaction B₁₁H₁₅ (0.60 mmol) prepared as above



was reacted with P(CH₃)₃ (0.70 mmol) at -35 °C, in CH₂Cl₂, with slow warming to room temperature over a period of 20 h. No noncondensable gas was formed, and the solid remaining after removal of the volatiles was washed twice with CH₂Cl₂ (~3 mL) and then extracted with acetonitrile. [P(CH₃)₃H][B₁₁H₁₄] (64.8 mg, 0.36 mmol, 60%) was obtained and characterized, by spectroscopy and from a single-crystal X-ray study.⁴

Crystals of [P(CH₃)₃H][B₁₁H₁₄] were obtained by slow diffusion of diethyl ether into a concentrated methylene chloride solution of [P(CH₃)₃H][B₁₁H₁₄]. The molecular structure of [P(CH₃)₃H][B₁₁H₁₄] was determined from single-crystal X-ray diffraction data.⁶ The boron framework of the [B₁₁H₁₄]⁻ anion (Figure 1) is based upon a regular icosahedral structure with one vertex removed. The structure has pseudo-C₃ symmetry. An interesting feature of this structure is the arrangement of the three hydrogen atoms associated with the open face of the cage that are not exo terminal hydrogens. Early in the development of polyhedral borane chemistry it was suggested⁷ that the [B₁₁H₁₄]⁻ ion could be described as a H₃⁺ triangle interacting with a

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- IR spectrum of the insoluble decomposition product (cm⁻¹): 2528 (br, s); 2211 (br, m); 2101 (br, m); 900-1500, broad absorption with maxima at 1384 (m), 1205 (m), 1100 (m), 1033 (m).

- NMR spectra are in accord with those reported previously for the [P(CH₃)₃H]⁺ cation⁵ and the [B₁₁H₁₄]⁻ anion.¹
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- Crystal data for [P(CH₃)₃H][B₁₁H₁₄]: space group *P* $\bar{1}$, *a* = 7.296 (2) Å, *b* = 8.956 (5) Å, *c* = 10.673 (4) Å, α = 81.2 (5)°, β = 88.3 (3)°, γ = 85.0 (3)°, *V* = 686.3 Å³, ρ (calcd) = 1.017 g cm⁻³, *M_r* = 210.15, *Z* = 2, μ (Mo K α) = 1.5 cm⁻¹. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. Crystallographic computations were carried out on a PDP 11/44 computer using SDP (Structure Determination Package). The structure was solved by a combination of the direct method MULTAN 11/82 and difference Fourier syntheses. Full-matrix least-squares refinements were employed. *R_F* = 0.054 and *R_{wF}* = 0.069 (232 variables refined) for 1570 reflections [*I* > 3.0 σ (*I*)] of 2414 independent reflections collected over the range 4 < 2 θ < 50°.
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