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Ni^{II}(dioxo[16]aneN$_5$)-Induced Methane Formation from Methyl Coenzyme M

Sir:

The nickel tetrapyrrole containing factor, F_{430}, is implicated in the final methane evolution step in methanogenic bacteria[1–4] and has attracted considerable attention.[5–8] The essential role of F_{430} in methane formation was demonstrated by Ankel-Fuchs and Thauer, who reported the in vitro catalysis of $H_3CSCH_2CH_2SO_3^-$, methyl coenzyme M (methyl-CoM), to methane and CoM by purified methyl-CoM reductase under reducing conditions.[9] Since F_{430} 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]aneN$_5$), NiL, complex[14] catalyze methyl-CoM to methane and CoM.

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

Ni^{II}L

H_2O (20 mL) was placed into a two-neck round-bottom flask equipped with a magnetic stirbar. Methyl-CoM[15] (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 ^{1}H 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 (μ = 2.60 μ_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 O_2, the magnetic moment per nickel increased from 2.99 to 3.17 μ_B.[20]

We do not believe that Ni^{I}L 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 CH_4) (mol of Ni)$^{-1}$ h^{-1} under 1 atm of argon and (2.24 ± 0.16) × 10^{-2} (mol of CH_4) (mol of Ni)$^{-1}$ h^{-1} under 1 atm of O_2.[21] It is expected that O_2 would inhibit the formation of

(1) Wolfe, R. S. *Trends Biochem. Sci.* (*Pers. Ed.*) **1985**, *10*, 396.
(2) Ankel-Fuchs, D.; Huester, R.; Moerschel, E.; Albracht, S. P. J.; Thauer, R. K. *Syst. Appl. Microbiol.* **1986**, *7*, 383.
(3) Diekert, G.; Klee, B.; Thauer, R. K. *Arch. Microbiol.* **1980**, *124*, 103.
(4) Whitman, W. B.; Wolfe, R. S. *Biochem. Biophys. Res. Commun.* **1980**, *92*, 1196.
(5) Pfaltz, A.; Jaun, B.; Fassler, A.; Eschenmoser, A.; Jaenchen, R.; Gilles, H. H.; Diekert, G.; Thauer, R. K. *Helv. Chim. Acta* **1982**, *65*, 828.
(6) Livingston, D. A.; Pfaltz, A.; Scheiber, J.; Eschenmoser, A.; Ankel-Fuchs, D.; Moll, J.; Jaenchen, R.; Thauer, R. K. *Helv. Chim. Acta* **1984**, *67*, 334.
(7) Fassler, A.; Pfaltz, A.; Krautler, B.; Eschenmoser, A. *J. Chem. Soc., Chem. Commun.* **1984**, 1365.
(8) Hausinger, R. P.; Orme-Johnson, W. H.; Walsh, C. *Biochemistry* **1984**, *23*, 801.
(9) Ankel-Fuchs, D.; Thauer, R. K. *Eur. J. Biochem.* **1986**, *155*, 171. The rate in the purified methyl coenzyme M reductase system is 6 × 10^{-3} (mol of CH_4)(g of protein)$^{-1}$ h^{-1}.
(10) Jaun, B.; Pfaltz, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1327.
(11) Albracht, S. P. J.; Ankel-Fuchs, D.; Van der Zwaan, J. W.; Fontijn, R. D.; Thauer, R. K. *Biochim. Biophys. Acta* **1986**, *870*, 50.
(12) Walsh, C. T.; Orme-Johnson, W. H. *Biochemistry* **1987**, *26*, 4901.
(13) (a) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 5353. (b) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 3267. (c) Stoltzenberg, A.; Stershic, M. T. *Inorg. Chem.* **1987**, *26*, 3082.
(14) Kimura, E.; Machida, R.; Kodama, M. *J. Am. Chem. Soc.* **1984**, *106*, 5497. Dioxo[16]aneN$_5$ (L) ^{1}H NMR (CDCl$_3$): 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). ^{13}C NMR (CDCl$_3$): 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) ^{1}H NMR (D$_2$O): δ(TMS) 2.97 (m, 2 H), 2.67 (m, 2 H). Ammonium 2-(methylthio)ethanesulfonate (NH$_4$(methyl-CoM)) ^{1}H NMR (D$_2$O): 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 I$_2$ until its color persisted. ^{1}H NMR (D$_2$O): 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.
(17) (a) Bode, J. H. G.; Smit, W. M. A. *J. Phys. Chem.* **1980**, *84*, 198. IR: CH_4, 3000 cm^{-1}; CDH_3, 2950 cm^{-1}.
(18) After a reaction was complete, the solution was freeze-dried and reconstituted with D$_2$O. ^{1}H 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, ^{1}H NMR, or FT-IR measurements in either the gas or the solution phase. The background O_2 concentration observed in the GC-MS spectrum of the gas-phase products introduced significant uncertainty in the determination of [O_2].
(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).
(20) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Becker, E. D. *High Resolution NMR: Theory and Chemical Applications*, 2nd ed.; Academic: New York, 1980; pp 42–61. (c) Shifts are based on *tert*-butyl alcohol. The reproducibility between samples is about ±0.15 μ_B, but the magnitude of the magnetic susceptibility increase during each run is reproducible within ±0.02 μ_B. Magnetic susceptibility measurements were taken every $^1/_2$ h for the initial 4 h and every 4 h thereafter.
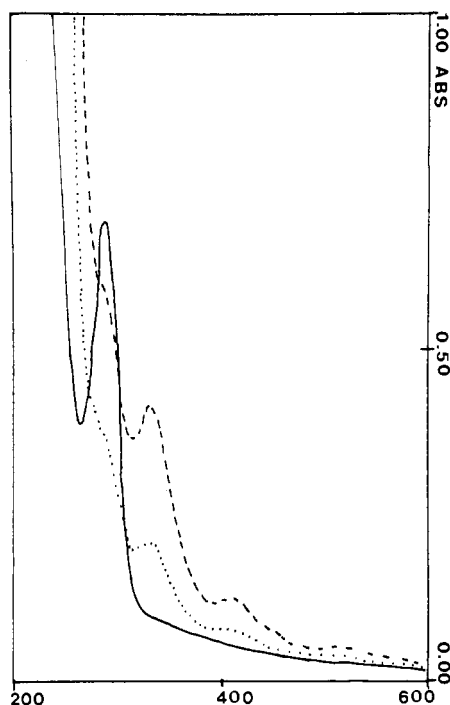(21) The rate of LNi^{II} decomposition under O_2 is slow compared to the initial rate.

Figure 1. UV–visible spectra (nm): (—) LNi^{II}; (---) LNi^{II} with 1.5 equiv of CoM; (⋯) final reaction mixture.
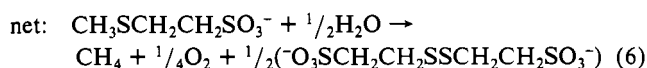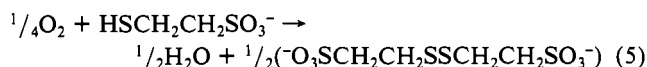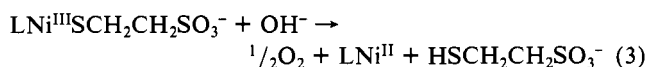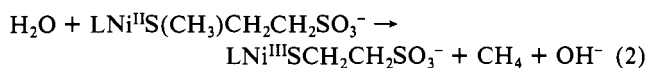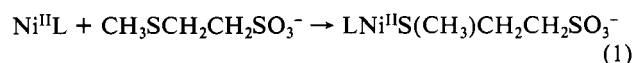
a highly air-sensitive $Ni^{I}L^{13}$ species. In addition, the initial rate of CH_4 evolution by a prepared sample[22,23] of $Ni^{I}L$ is only $(1.80 \pm 0.13) \times 10^{-2}$ (mol of CH_4) (mol of Ni)$^{-1}$ h^{-1}, although 1.8 ± 0.1 equiv of methyl-CoM is converted.

Under H_2 (4 atm),[24] $Ni^{II}L$ 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 phase[18] indicates that the $H_3C–S$ bond is cleaved heterolytically. Solvent protonation of the methyl group is confirmed by the formation of 92 ± 3% CH_3D from a reaction mixture containing H_2/D_2O (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 $[Cp_2TiCl]_2ZnCl$ (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 $Ni^{II}L$.

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

$$Ni^{II}L + CH_3SCH_2CH_2SO_3^- \rightarrow LNi^{II}S(CH_3)CH_2CH_2SO_3^- \quad (1)$$

$$H_2O + LNi^{II}S(CH_3)CH_2CH_2SO_3^- \rightarrow$$
$$LNi^{III}SCH_2CH_2SO_3^- + CH_4 + OH^- \quad (2)$$

$$LNi^{III}SCH_2CH_2SO_3^- + OH^- \rightarrow$$
$$^1/_2O_2 + LNi^{II} + HSCH_2CH_2SO_3^- \quad (3)$$

$$LNi^{II} + HSCH_2CH_2SO_3^- \rightleftharpoons LNi^{II}S(H)CH_2CH_2SO_3^- \quad (4)$$

$$^1/_4O_2 + HSCH_2CH_2SO_3^- \rightarrow$$
$$^1/_2H_2O + ^1/_2(^-O_3SCH_2CH_2SSCH_2CH_2SO_3^-) \quad (5)$$

net: $$CH_3SCH_2CH_2SO_3^- + ^1/_2H_2O \rightarrow$$
$$CH_4 + ^1/_4O_2 + ^1/_2(^-O_3SCH_2CH_2SSCH_2CH_2SO_3^-) \quad (6)$$

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 $Ni^{II}L$: (a) the oxidant, O_2, escapes from solution, resulting in incomplete formation of the disulfide in step 5, and (b) the binding constant K(b) = 145 (±11%) L M^{-1} in step 4, resulting in unreactive $LNi^{II}SCH_2CH_2SO_3^-$.

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 $Ni^{II}L$. When

$$HSCH_2CH_2SO_3^- + I_2 \rightarrow$$
$$2HI + ^1/_2(^-O_3SCH_2CH_2SSCH_2CH_2SO_3^-) \quad (7)$$
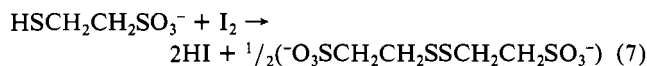
an aqueous solution of the brown Ni-CoM complex is shaken with hexane containing I_2,[28] the solution turns green and has the same UV–visible spectrum as $Ni^{II}L$ (Figure 1). After the organic layer is removed, the remaining green solution evolves methane from freshly added methyl-CoM at the same rate as for fresh $Ni^{II}L$.

A mechanism has been proposed[12] for methyl-coenzyme M reductase where $Ni^{II}F_{430}$ is first reduced to $Ni^{I}F_{430}$, which homolytically cleaves methyl-CoM to produce methyl-$Ni^{II}F_{430}$ followed by the protonation of methyl-$Ni^{I}F_{430}$ to yield CH_4 and $Ni^{II}F_{430}$. 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 methanogenesis[29] was predicted by this mechanism. CoM disulfide is also observed in the model system. In addition, we have found that the reactivity of $Ni^{II}L$ 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-dione[30] do not convert methyl-CoM to methane under either argon or H_2. It is clear the ligand (L) activates Ni(II) toward methyl-CoM. The ligand in F_{430} might also play an important part in activating nickel toward methyl-CoM.

(22) $Ni^{I}L$ (μ = 1.77 μ_B) is produced by treating $Ni^{II}L$ with a one-electron equivalent of $Na_2S_2O_4$. Sodium dithionite does not react with methyl-CoM in the absence of NiL. $Na_2S_2O_4$ reactions were run in a pH 8.5 buffer.

(23) Pettit, G. R. In *Organic Reactions*; Adams, R., Ed.; Wiley: New York, 1962; Vol. 12, p 356. Raney nickel in water desulfurizes methyl-CoM to a mixture of nickel sulfide, methane, ethane, ethanol, methanol, and an uncharacterized oil, consistent with known Raney nickel chemistry. When a two-electron equivalent of $Na_2S_2O_4$ is added to $Ni^{II}L$, a black precipitate forms, which is ascribed to Ni(0). Since demetalation of the complex does not occur in our reactions, we rule out $Ni^{0}L$ as a likely species.

(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).

(26) (a) Spencer, R. W.; Daniels, L.; Fulton, G.; Orme-Johnson, W. H. *Biochemistry* **1980**, *19*, 3678. (b) Daniels, L.; Filton, G.; Spencer, R. W.; Orme-Johnson, W. H. *J. Bacteriol.* **1980**, *141*, 694.

(27) Both inner-sphere and outer-sphere redox processes are known for Ni(III) complexes. (a) Raycheba, J. M.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 1441. (b) Kushi, Y.; Machida, R.; Kimura, E. *J. Chem. Soc., Chem. Commun.* **1985**, 217. (c) Machida, R.; Kimura, E.; Kushi, Y. *Inorg. Chem.* **1986**, *25*, 3461. (d) McAuley, A.; Xu, C. *Inorg. Chem.* **1988**, *27*, 1204.

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

(29) (a) Ellermann, J.; Hedderich, R.; Böcher, R.; Thauer, R. K. *Eur. J. Biochem.* **1988**, *192*, 669. (b) Hauska, G. *Trends Biochem. Sci.* (*Pers. Ed.*) **1988**, *13*, 2.

(30) Fabbrizzi, L.; Poggi, A.; Seghi, B. *Inorg. Synth.* **1985**, *23*, 82.

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

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Synthesis of the New Boron Hydride *nido*-Undecaborane(15), $B_{11}H_{15}$, and the X-ray Structure of Its Conjugate Base Tetradecahydroundecaborate(1-), $[B_{11}H_{14}]^-$

Sir:

We recently reported[1] syntheses of alkali-metal (Li, Na, K) salts of the tetradecahydroundecaborate(1-) ion, $[B_{11}H_{14}]^-$, via a convenient, "one-pot", essentially quantitative procedure from the reaction of pentaborane(9), B_5H_9, with MH (M = Na, K) or (*t*-Bu)Li. In light of this new synthesis an investigation into the chemistry of $[B_{11}H_{14}]^-$ was begun. Reported, herein, is the preparation of *nido*-undecaborane(15), $B_{11}H_{15}$, from the protonation of $K[B_{11}H_{14}]$ and the subsequent deprotonation of $B_{11}H_{15}$ by $P(CH_3)_3$ to give $[P(CH_3)_3H][B_{11}H_{14}]$, the structure of which has been determined from single-crystal X-ray data.

Protonation of $NaB_{11}H_{14}\cdot2.5C_4H_8O_2$ in $C_4H_8O_2$ has been reported[2] to produce $B_{11}H_{15}\cdot2C_4H_8O_2$ and in $S(CH_3)_2$ to produce $B_{11}H_{13}\cdot S(CH_3)_2$ with the evolution of H_2 gas. We find that the reaction of $K[B_{11}H_{14}]$ with anhydrous HCl at -78 °C gives undecaborane(15), $B_{11}H_{15}$, in quantitative yield according to eq 1.

$$K[B_{11}H_{14}] + HCl \xrightarrow{-78\ °C} B_{11}H_{15} + KCl \qquad (1)$$
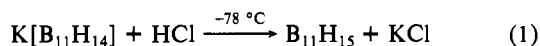
In a typical preparation, $K[B_{11}H_{14}]$ (125 mg, 0.725 mmol) was treated with excess HCl (25 mmol) at -78 °C for 12 h. No noncondensible gas was produced. The excess HCl was pumped away from the reactor at -78 °C over a period of 12 h. On the basis of the amount of recovered HCl (24.3 mmol), 0.7 mmol of HCl was consumed, indicating a 1:1 reactant ratio of HCl to $K[B_{11}H_{14}]$. 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 H_2/mol of $[B_{11}H_{14}]^-$ and the formation of a white solid,[3] insoluble in ethers, CH_3CN, toluene, and CH_2Cl_2.

The boron-11 NMR spectrum of $B_{11}H_{15}$ (96.3 MHz), obtained at -40 °C in toluene-d_8, consists of two resonances (-14.8 ppm ($J = \sim200$ Hz, d) and -17.4 ppm ($J = 145$ Hz, d), $BF_3\cdot OEt_2$ 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 ^{11}B 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
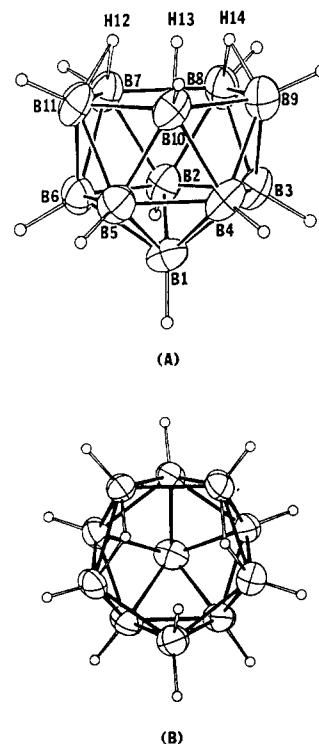
(1) Hosmane, N. S.; Wermer, J. R.; Hong, Z.; Getman, T. D.; Shore, S. G. *Inorg. Chem.* **1987**, *26*, 3638.
(2) Edwards, L. J.; Makhlouf, J. M. *J. Am. Chem. Soc.* **1966**, *88*, 4728.
(3) IR spectrum of the insoluble decomposition product (cm⁻¹): 2528 (br, s); 2211 (br, m); 2101 (br, m); 900-1500, broad absorption with maxima at 1384 (m), 1205 (m), 1100 (m), 1033 (m).

Figure 1. Views of the molecular structure of $[B_{11}H_{14}]^-$ (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 $[B_{11}H_{14}]^-$ in $(CH_3)_2O$, and the reaction (2) with $P(CH_3)_3$ yields an isolable salt. In a typical reaction $B_{11}H_{15}$ (0.60 mmol) prepared as above

$$B_{11}H_{15} + P(CH_3)_3 \xrightarrow{CH_2Cl_2} [P(CH_3)_3H][B_{11}H_{14}] \qquad (2)$$
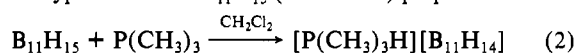
was reacted with $P(CH_3)_3$ (0.70 mmol) at -35 °C, in CH_2Cl_2, with slow warming to room temperature over a period of 20 h. No noncondensible gas was formed, and the solid remaining after removal of the volatiles was washed twice with CH_2Cl_2 (~3 mL) and then extracted with acetonitrile. $[P(CH_3)_3H][B_{11}H_{14}]$ (64.8 mg, 0.36 mmol, 60%) was obtained and characterized, by spectroscopy and from a single-crystal X-ray study.[4]

Crystals of $[P(CH_3)_3H][B_{11}H_{14}]$ were obtained by slow diffusion of diethyl ether into a concentrated methylene chloride solution of $[P(CH_3)_3H][B_{11}H_{14}]$. The molecular structure of $[P(CH_3)_3H][B_{11}H_{14}]$ was determined from single-crystal X-ray diffraction data.[6] The boron framework of the $[B_{11}H_{14}]^-$ anion (Figure 1) is based upon a regular icosahedral structure with one vertex removed. The structure has pseudo-C_s 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 suggested[7] that the $[B_{11}H_{14}]^-$ ion could be described as a H_3^+ triangle interacting with a

(4) NMR spectra are in accord with those reported previously for the $[P(CH_3)_3H]^+$ cation[5] and the $[B_{11}H_{14}]^-$ anion.[1]
(5) Moedritzer, K.; Maier, L.; Greonweghe, L. C. D. *J. Chem. Eng. Data* **1962**, *7*, 307.
(6) Crystal data for $[P(CH_3)_3H][B_{11}H_{14}]$: space group $P\bar{1}$, $a = 7.296$ (2) Å, $b = 8.956$ (5) Å, $c = 10.673$ (4) Å, $\alpha = 81.2$ (5)°, $\beta = 88.3$ (3)°, $\gamma = 85.0$ (3)°, $V = 686.3$ Å³, ρ(calcd) = 1.017 g cm⁻³, $M_r = 210.15$, $Z = 2$, μ(Mo Kα) = 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 [$I > 3.0\sigma(I)$] of 2414 independent reflections collected over the range $4 < 2\theta < 50$°.
(7) Moore, E. B., Jr.; Lohr, L. L., Jr.; Lipscomb, W. N. *J. Chem. Phys.* **1961**, *35*, 1329.