

Structural and Reaction Chemistry of Nickel Complexes in Relation to Carbon Monoxide Dehydrogenase: A Reaction System Simulating Acetyl-Coenzyme A Synthase Activity

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Abstract: A series of nickel complexes $[\text{Ni}(\text{NS}_3^{\text{R}})\text{L}]^+$ derived from the tripodal ligand $\text{NS}_3^{\text{R}} = \text{N}(\text{CH}_2\text{CH}_2\text{SR})_3$ ($\text{R} = i\text{-Pr}$, $t\text{-Bu}$) has been prepared in order to investigate the stabilities and reactions of certain species potentially relevant to the nickel sites in carbon monoxide dehydrogenase (CODH). Reaction of $[\text{Ni}(\text{NS}_3^{\text{R}})\text{Cl}]^+$ with MeMgCl affords $[\text{Ni}(\text{NS}_3^{\text{R}})\text{Me}]^+$, which with CO yields $[\text{Ni}(\text{NS}_3^{\text{R}})\text{COMe}]^+$. Reaction of $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{Cl}]^+$ with NaBH_4 gives $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{H}]^+$ and the Ni(I) species $[\text{Ni}(\text{NS}_3^{\text{tBu}})]^+$. The hydride complex was obtained with minimal Ni(I) contamination by removal of ethylene from the equilibrium system $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{Et}]^+ / [\text{Ni}(\text{NS}_3^{\text{tBu}})\text{H}]^+ / \text{C}_2\text{H}_4$. Reaction of $[\text{Ni}(\text{NS}_3^{\text{tBu}})]^+$ with CO affords $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{CO}]^+$, whereas $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{H}]^+$ under the same conditions gives $\text{Ni}(\text{CO})_4$ and protonated ligand. All reactions were performed in THF, and all complexes were isolated as BPh_4^- salts. This series includes rare examples of the stabilization of Ni-methyl-, acyl-, hydride-, and carbonyl ligands in the absence of nonphysiological (C/P/As) coligands. Trigonal-bipyramidal stereochemistry has been demonstrated for five complexes with $\text{L} = \text{Cl}$, Me, COMe, H, and CO by X-ray crystallography. The methyl/acetyl transformations with carbon monoxide and the formation in high yield of the thioesters $\text{R}'\text{SCOMe}$ ($\text{R}' = \text{Et}$, CH_2Ph , Ph) upon reaction of $[\text{Ni}(\text{NS}_3^{\text{R}})\text{COMe}]^+$ with thiols in THF are two previously undocumented processes mediated at Ni(II) sites lacking nonphysiological (C/P/As) ligation. These are relevant to current views of the catalytic reaction cycle of *Clostridium thermoaceticum* CODH, which is presented. The $\text{Ni}^{\text{II}}\text{-H}$ and $\text{Ni}^{\text{I}}\text{-CO}$ species may be pertinent to the CO/CO₂ activity of CODH. Full details of all preparations, other reactions, and structures are presented. This work is an initial attempt to place the reaction chemistry of CODH on a rational basis, and provides some viability for the present reaction cycle of the enzyme.

Introduction

One of the major developments in bioinorganic chemistry in the last decade is the demonstration of a stoichiometric requirement for nickel in four enzymes: urease, carbon monoxide dehydrogenase (CODH), hydrogenase, and methyl-S-coenzyme-M reductase.¹⁻³ Our interest here is with the chemistry of CODH enzymes, which have been isolated from acetogenic, methanogenic, photosynthetic, and sulfate-reducing bacteria. These enzymes catalyze reaction 1, the interconversion of CO and CO₂ via an



intermediate C_1 species in the presence of an electron carrier. In addition to this reaction, the enzymes of *Clostridium thermoaceticum* (*Ct*) and other acetogenic and methanogenic organisms catalyze the synthesis of acetyl-coenzyme A, reaction 2 (THF = tetrahydrofolate), and related exchange processes including reaction 3. Thus, these enzymes are also acetyl-CoA synthases.⁴⁻⁷

Reaction 2 is a sum of the final steps in autotrophic CO₂ or CO fixation via acetyl-CoA synthesis, also known as the Wood pathway, which has been reviewed.⁴⁻⁶ The key elements in this anaerobic carbon cycle are summarized in the proposed scheme of Figure 1, which is based largely on the extensive and incisive investigations of *Ct* CODH by Ragsdale, Wood, and co-workers.^{4,6-15} By means of reaction 1, both CO and $[\text{CO}_2 + \text{H}_2]$ can

act as substrates. Methyl tetrahydrofolate is synthesized by a two-electron reduction of CO₂ to formate catalyzed by formate dehydrogenase, followed by a four-electron reduction of formate to CH₃-THF catalyzed by a series of THF-dependent enzymes. In reaction 4 (Figure 1), the methyl group of CH₃-THF is then enzymatically transferred to a corrinoid protein,^{8,9} generating a protein-bound methylcobamide. The subsequent steps 5 and 6 involve nonenzymatic methyl transfer⁹ to form a methyl-CODH intermediate and binding of CO at a metal site and methyl migration at that site to afford acetyl-CODH.^{9,10} The order of methyl and CO binding in Figure 1 is arbitrary inasmuch as the occurrence of these processes may well be random,^{9,11} but the net outcome is the formation of the presumed acetyl intermediate. Finally, acetyl-CODH binds CoASH, apparently in the vicinity of the metal-containing site,¹² followed by reaction 7 of the acyl and thiol groups to yield acetyl-CoA.

When the complexity of *Ct* CODH (M_r 148 000, $\alpha\beta$ subunits, 1 Zn, 2 Ni, ~12 Fe/S) and its reactions are considered, the extent of characterization since its purification to homogeneity in 1983¹³ is remarkable. There remain for clarification, however, a number of fundamental chemical aspects. Two of these, the nature of the active site and the occurrence of reactions 5-7, are of principal concern here.

While the active site of CODH is represented in Figure 1 as a single nickel center, this may be an oversimplification. In fact,

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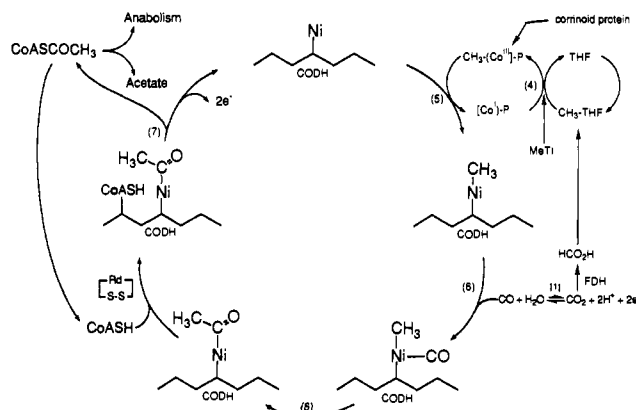


Figure 1. Proposed reaction pathway of Ni-CODH as an acetyl-coenzyme A synthase: CoASH = coenzyme A, FDH = formate dehydrogenase, MeTr = methyltransferase, P = corrinoid protein, Rd = disulfide reductase, THF = tetrahydrofolate.

EPR, Mössbauer, and ENDOR data¹⁴ on the CO-reduced form of the enzyme indicate a covalent Ni-Fe-C assembly of probable minimal stoichiometry $\text{Ni}_1\text{Fe}_{3-4}\text{S}_{2-4}\text{C}_1$, allowing for the presence of iron at the active site. The nature of this novel cluster is, at present, highly speculative. The stoichiometry may point, inter alia, to a $[\text{NiFe}_3\text{S}_4]$ cubane structure such as has been reconstituted in a protein¹⁶ and synthesized in this laboratory,¹⁷ or to a single nickel atom bridged to a Fe_4S_4 cluster. The same or similar Ni-Fe assemblies are present in at least two other CODH enzymes.^{18,19} EXAFS results on the CO-free, EPR-silent form of the *Ct* enzyme reveal a sulfur-rich nickel coordination environment,^{15,20} possibly planar NiS_4 with Ni-S 2.16 (3) Å.²⁰ Inasmuch as these experiments sample average environments, it is not yet clear that both nickel atoms are equivalent.

Methyl-transfer reactions from $[\text{CH}_3\text{-Co}^{\text{III}}]$ complexes to a variety of acceptor metals have been reported,²¹ but no such transfer to a nickel acceptor, as in reaction 5, has yet been described. Further, the numbers of characterized monomethyl- and acylnickel species are limited,²² and nearly all are stabilized by such physiologically unacceptable ligands as tertiary phosphines or arsines or other carbon-ligated species. Consequently, steps 5 and 6 of the proposed pathway, in the absence of such ligands, are unsupported by independent observations and reaction 7 is unprecedented. It is our aim to place the chemistry of reactions 1 and 2 of CODH enzymes on a rational basis using analogue reaction systems.²³ As a first step, we provide here a partial simulation of the multistep reactivity of CODH as an acetyl-CoA synthase (reaction 2) by examining the viability of several postulated intermediates and their reactivities. Also reported are hydride and CO complexes that may be related to species active in the CO/CO₂ interconversion (reaction 1). Certain leading results have been summarized.²³

Experimental Section

Preparation of Compounds. The tripod ligands tris[(isopropylthio)ethyl]amine (NS_3^{IPr}), tris[(*tert*-butylthio)ethyl]amine (NS_3^{tBu}), and

tris[(2-diphenylphosphino)ethyl]amine²⁴ (np_3) and the compounds $[\text{Ni}(\text{NS}_3^{\text{IPr}})\text{Cl}]_2(\text{BPh}_4)_2$,²⁵ $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{Cl}](\text{BPh}_4)$,²⁵ and $[\text{Ni}(\text{np}_3)\text{COMe}](\text{BPh}_4)$ ²⁶ were prepared by published methods. All other reagents were commercial samples that were used without further purification. Operations were carried out under a pure dinitrogen atmosphere with use of conventional Schlenk techniques. Solvents were dried and degassed prior to use.

$[\text{Ni}(\text{NS}_3^{\text{IPr}})\text{Me}](\text{BPh}_4)$. To a stirred slurry of 0.737 g (0.50 mmol) of $[\text{Ni}(\text{NS}_3^{\text{IPr}})\text{Cl}]_2(\text{BPh}_4)_2$ in 50 mL of THF at -78°C was added dropwise 1.0 mL (1.0 mmol) of a 1 M solution of MeMgCl in THF. The purple mixture was allowed to warm slowly to room temperature upon stirring (6 h). The solution was filtered, reduced in volume to ca. 15 mL, and stored at -40°C overnight. A white solid was separated by filtration, and to the purple filtrate was added ca. 10 mL of ethanol until signs of crystal formation were apparent. Storage of the solution at -20°C overnight followed by filtration afforded 0.39 g (55%) of purple crystalline material, which was used for subsequent reactions. Recrystallization of this material from THF/ether gave 0.25 g (35%) of an analytical sample as purple crystals. Anal. Calcd for $\text{C}_{40}\text{H}_{56}\text{BNNiS}_3$: C, 67.04; H, 7.87; S, 13.42. Found: C, 66.80; H, 7.82; S, 13.56. ¹H NMR (cation, CD_2Cl_2): δ -0.74 (3, Ni-Me), 1.45 (d, 18, Me), 2.07 (t, 6, CH_2), 2.69 (t, 6, CH_2), 3.10 (sept, 3, CH).

$[\text{Ni}(\text{NS}_3^{\text{IPr}})\text{COMe}](\text{BPh}_4)$. Carbon monoxide was bubbled through a solution of 0.358 g (0.50 mmol) of $[\text{Ni}(\text{NS}_3^{\text{IPr}})\text{Me}](\text{BPh}_4)$ in 20 mL of THF at -20°C . The initial purple color turned rapidly to red-purple; admittance of gas was continued until the volume of the solution was reduced to ca. 15 mL. Addition of ethanol until incipient crystallization and storage of the solution at -20°C overnight afforded 0.30 g (80%) of red-purple microcrystalline solid. An analytical sample was obtained by recrystallization from THF/ether under a carbon monoxide atmosphere. Anal. Calcd for $\text{C}_{41}\text{H}_{56}\text{BNNiOS}_3$: C, 66.14; H, 7.58; S, 12.91. Found: C, 66.51; H, 7.53; S, 12.68. ¹H NMR (cation, CD_2Cl_2): δ 1.46 (d, 18, Me), 1.97 (t, 6, CH_2), 2.32 (3, COMe), 2.67 (t, 6, CH_2), 3.26 (sept, 3, CH). IR (KBr): ν_{CO} 1670 cm^{-1} .

$[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{Me}](\text{BPh}_4)$. This compound was obtained in 50% yield as a blue crystalline solid by a method analogous to the preparation of $[\text{Ni}(\text{NS}_3^{\text{IPr}})\text{Me}](\text{BPh}_4)$. Recrystallization from THF/ether afforded a purified sample (35%). The compound was identified by its ¹H NMR spectrum (cation, CD_2Cl_2): δ -0.82 (3, Me), 1.46 (27, *t*-Bu), 1.94 (t, 6, CH_2), 2.67 (t, 6, CH_2).

$[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{COMe}](\text{BPh}_4)$. This compound was prepared in situ by bubbling carbon monoxide through a solution of $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{Me}](\text{BPh}_4)$ in dichloromethane. The color changed rapidly from blue to red, and the yield was quantitative as evidenced by the ¹H NMR spectrum. ¹H NMR (cation, CD_2Cl_2): δ 1.45 (27, *t*-Bu), 2.12 (t, 6, CH_2), 2.49 (3, COMe), 2.61 (t, 6, CH_2). IR (CH_2Cl_2): ν_{CO} 1685 cm^{-1} .

$[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{H}](\text{BPh}_4)$. Method A. To a stirred suspension of 0.779 g (1.00 mmol) of $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{Cl}](\text{BPh}_4)$ in 60 mL of THF was added 0.378 g (1.00 mmol) of NaBH_4 . The mixture was stirred for 8 h, during which time the solution developed a red-purple color. Reduction in solvent volume to ca. 15 mL, filtration, and addition of 10 mL of ethanol to the filtrate caused precipitation of 0.30 g (40%) of product as a red-purple microcrystalline solid. Recrystallization of this material from THF/ether yielded an analytical sample (0.15 g, 20%). Anal. Calcd for $\text{C}_{42}\text{H}_{60}\text{BNNiS}_3$: C, 67.75; H, 8.12; S, 12.92. Found: C, 67.06; H, 7.92; S, 13.14. ¹H NMR (cation, THF-*d*₆): δ -37.75 (1, Ni-H), 1.38 (27, *t*-Bu), 2.06 (t, 6, CH_2), 2.75 (t, 6, CH_2). IR (Nujol): ν_{NiH} 1878 cm^{-1} .

Method B. To a stirred slurry of 1.00 g (1.28 mmol) of $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{Cl}](\text{BPh}_4)$ in 50 mL of THF at -78°C was added dropwise 0.43 mL (1.29 mmol) of a 3 M solution of EtMgBr in diethyl ether. The blue solution was allowed to warm slowly to room temperature, and then stored at -20°C overnight. The solution was separated from the white solid, and concentrated under a stream of nitrogen to a final volume of ca. 20 mL. To the now red-purple solution was added ethanol (ca. 20 mL) until signs of crystal formation were apparent. Storage of the solution at -20°C overnight followed by filtration afforded 0.20 g (21%) of a red-purple microcrystalline solid.

$[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{CO}](\text{BPh}_4)$. Carbon monoxide was bubbled through a solution of 0.149 g (0.200 mmol) of $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{H}](\text{BPh}_4)$ (obtained from method A) in 20 mL of THF at -20°C . The initial red-purple solution turned green rapidly; it was reduced in volume to ca. 10 mL under a stream of carbon monoxide. Addition of 20 mL of ethanol caused precipitation of a green microcrystalline solid. This material was twice recrystallized from THF/ether to yield 0.031 g (20%) of an analytical sample as green polyhedra. Anal. Calcd for $\text{C}_{43}\text{H}_{59}\text{BNNiOS}_3$:

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Table I. Crystallographic Data^a for [Ni₂(NS₃^{iPr})₂Cl₂](BPh₄)₂·2THF (1), [Ni(NS₃^{tBu})Cl](BPh₄) (2), [Ni(NS₃^{iPr})Me](BPh₄) (3), [Ni(NS₃^{iPr})(COMe)](BPh₄)·EtOH (4), [Ni(NS₃^{tBu})H](BPh₄) (5), and [Ni(NS₃^{tBu})CO](BPh₄) (6)

	1	2	3	4	5	6
formula	C ₈₆ H ₁₂₂ B ₂ Cl ₂ N ₂ Ni ₂ O ₂ S ₆	C ₄₂ H ₅₉ BClNiNiS ₃	C ₄₀ H ₅₆ BNNiS ₃	C ₄₃ H ₆₂ BNNiO ₂ S ₃	C ₄₂ H ₆₀ BNNiS ₃	C ₄₃ H ₅₉ BNNiOS ₃
formula wt	1618.24	779.08	716.58	790.65	744.63	771.64
a, Å	17.962 (4)	13.908 (2)	13.364 (7)	11.384 (3)	11.864 (6)	10.796 (2)
b, Å	21.927 (4)	22.395 (4)	14.590 (6)	13.911 (3)	12.853 (6)	12.978 (3)
c, Å	22.696 (4)	26.767 (4)	20.736 (8)	14.068 (4)	13.747 (5)	15.685 (3)
α, deg			92.63 (3)	77.98 (2)	89.21 (3)	80.27 (2)
β, deg			103.46 (3)	86.07 (2)	89.02 (4)	87.63 (2)
γ, deg			90.00 (4)	88.25 (2)	82.67 (4)	73.59 (2)
space group	<i>Pcab</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
V, Å ³	8939 (3)	8337 (2)	3928 (3)	2174 (1)	2079 (2)	2078 (1)
Z	4	8	4	2	2	2
ρ _{calcd} (ρ _{obsd})	1.09 (1.10)	1.24 (1.23)	1.21 (1.21)	1.14 (1.16)	1.19 (1.20)	1.23 (1.22)
μ, cm ⁻¹	7.0	6.6	6.7	6.2	6.5	6.5
R (R _w), %	6.55 (6.96)	7.31 (7.91)	6.12 (6.07)	5.61 (5.63)	7.67 (8.11)	7.58 (8.85)

^a Mo Kα radiation; T = 298 K for all compounds except 6 (208 K).

C, 66.93; H, 7.71; S, 12.46. Found: C, 66.85; H, 7.98; S, 11.69. IR (KBr): ν_{CO} 2026 cm⁻¹. EPR (THF): g_⊥ = 2.119, g_∥ = 2.008, a_∥^N = 9.9 G.

Reactions of Ni-Acyl Complexes with Thiols. These reactions were monitored by ¹H NMR spectroscopy. Solutions containing 10–12 mg (ca. 30 mM) of [Ni(NS₃^{iPr})COMe](BPh₄) in 0.5 mL of THF-d₆ or CD₂Cl₂ were transferred to NMR tubes. Under a CO atmosphere, 1.2 equiv of R'SH = EtSH, PhCH₂SH, or PhSH was added using a gas-tight syringe, and the mixtures were immediately frozen in liquid nitrogen. While frozen, the tubes were flame-sealed under a dynamic vacuum. The mixtures were warmed to room temperature just prior to recording the first spectrum. Thereafter, the tubes were stored in an inverted position at room temperature between NMR samplings. The precipitated elemental nickel coated primarily the upper section of the NMR tubes; the tubes were centrifuged just prior to recording spectra. The percent conversion of [Ni(NS₃^{iPr})COMe]⁺ (δ(THF, CD₂Cl₂) 2.29, 2.31) to the thioester R'SCOCH₃ with R' = Et (δ 2.25, 2.30) and Ph (δ 2.35, 2.41) were obtained from the integrated intensities of the indicated methyl signals. In the case of R' = CH₂Ph, signal overlap required the use of the thiol (δ 3.71, 3.75) and thioester (δ 4.10, 4.11) methylene signals. The reactions of [Ni(NS₃^{tBu})COMe]⁺ with R'SH were followed similarly except that the acyl complex was prepared in situ by bubbling CO through a solution of [Ni(NS₃^{tBu})Me]⁺ for ca. 25 s. Reactions were examined in THF only because the much slower reactions in dichloromethane allowed significant equilibration of the acyl complex (δ_{COMe} 2.47) with [Ni(NS₃^{tBu})Me]⁺ and CO, making yield determinations inaccurate.

X-ray Structural Determinations. The crystal structures of the compounds 1–6 specified in Table I were determined. Suitable crystals were obtained by recrystallization from THF-ether for all compounds except 4, which was recrystallized from THF-ethanol. Diffraction data were collected on a Nicolet P3F automated diffractometer using graphite-monochromatized Mo Kα radiation. Crystals were sealed in glass capillaries under a dinitrogen atmosphere. Lattice parameters and orientation matrices were determined by the least-squares fits of the angular coordinates of *n* unique machine-centered reflections over the indicated 2θ range: *n* = 25, 20–24° (1, 4); *n* = 25, 20–28° (3); *n* = 40, 15–28° (5, 6); *n* = 50, 15–29° (2). The data were processed with the program XTape of the SHELXTL Plus structure determination program package (Nicolet XRD Corp., Madison, WI 53711). Data were corrected for Lorentz and polarization effects, and maximum decay corrections of 3–6% were applied to all data, based on three check reflections monitored throughout the data collections. Semiempirical absorption corrections were applied to the data sets using the programs PSCOR (1, 3–5) or XEMP (2, 6). Details of the intensity collections are given elsewhere.²⁷ Atom scattering factors were taken from a standard source.²⁸ The orthorhombic space groups of 1 and 2 were unambiguously identified by systematic absences, while E statistics suggested the centric triclinic space group *P* $\bar{1}$ for 3–6. Space groups were confirmed by satisfactory refinement of all structures to low error indices. Crystallographic data are summarized in Table I.

Structures were solved by standard methods. Patterson synthesis yielded the position of the Ni atom or Ni and S atoms. The remaining non-hydrogen atoms were located from successive difference Fourier

Table II. Interatomic Distances (Å) and Angles (deg) in [Ni₂(NS₃^{iPr})₂Cl₂]²⁺ (1)

Ni–S(1)	2.440 (6)	S(1)–Ni–S(2)	162.9 (2)
Ni–S(2)	2.462 (6)	S(1)–Ni–S(3)	90.6 (2)
Ni–S(3)	2.400 (6)	S(1)–Ni–N	84.8 (5)
Ni–N	2.12 (2)	S(1)–Ni–Cl	95.7 (2)
Ni–Cl	2.370 (5)	S(1)–Ni–Cl'	83.5 (2)
Ni–Cl'	2.466 (5)	S(2)–Ni–S(3)	102.2 (2)
Ni–Ni'	3.573 (5)	S(2)–Ni–N	85.0 (5)
S(3)–Ni–N	85.3 (5)	S(2)–Ni–Cl	93.6 (2)
S(3)–Ni–Cl	98.5 (2)	S(2)–Ni–Cl'	83.1 (2)
N–Ni–Cl'	91.5 (2)	Ni–Cl–Ni'	95.2 (2)
Cl–Ni–Cl'	84.8 (2)	Cl–Ni–N	176.1 (5)

Table III. Interatomic Distances (Å) and Angles (deg) in [Ni(NS₃^{tBu})Cl]²⁺ (2), [Ni(NS₃^{iPr})Me]⁺ (3), [Ni(NS₃^{iPr})(COMe)]⁺ (4), [Ni(NS₃^{tBu})H]⁺ (5), and [Ni(NS₃^{tBu})CO]⁺ (6)

	2	3 ^b	4 ^c	5	6 ^d
Ni–S(1)	2.345 (3)	2.231 (4)	2.286 (4)	2.234 (6)	2.353 (2)
Ni–S(2)	2.381 (4)	2.335 (4)	2.317 (4)	2.227 (7)	2.351 (3)
Ni–S(3)	2.379 (4)	2.228 (4)	2.274 (4)	2.218 (6)	2.384 (3)
Ni–N	2.180 (9)	2.06 (1)	2.10 (1)	2.02 (1)	2.208 (6)
Ni–L _{ax} ^a	2.295 (3)	1.94 (2)	1.90 (2)		1.85 (1)
S(1)–Ni–S(2)	117.0 (1)	110.8 (1)	109.8 (1)	119.3 (2)	119.4 (1)
S(1)–Ni–S(3)	118.8 (1)	130.3 (1)	134.0 (1)	119.7 (3)	124.1 (1)
S(2)–Ni–S(3)	120.9 (1)	118.8 (1)	115.3 (2)	120.6 (3)	113.8 (1)
N–Ni–L _{ax}	178.2 (3)	177.0 (5)	179.6 (7)		178.5 (3)
N–Ni–S(1)	84.1 (2)	89.3 (3)	86.8 (3)	92.4 (4)	84.2 (2)
N–Ni–S(2)	83.8 (3)	88.6 (3)	86.9 (3)	92.2 (5)	84.5 (2)
N–Ni–S(3)	84.1 (3)	90.1 (3)	87.4 (3)	92.5 (4)	85.1 (2)
L _{ax} –Ni–S(1)	95.8 (1)	88.5 (4)	93.2 (5)		94.4 (3)
L _{ax} –Ni–S(2)	94.6 (1)	94.0 (4)	92.7 (4)		96.4 (3)
L _{ax} –Ni–S(3)	97.5 (1)	89.9 (4)	92.8 (5)		95.6 (4)

^a L_{ax} = axial ligand. ^b Cation 1. ^c C–O, 1.18 (2); C(O)–CH₃, 1.50 (2); Ni–C–O, 123 (1); Ni–C–CH₃, 118 (1). ^d C–O, 1.15 (1); Ni–C–O, 177.5 (9).

maps. In all structure determinations, only the atoms of the cations were refined anisotropically. Phenyl rings of the anion were fitted and refined as rigid groups with individual temperature factors for the carbon atoms. The final least-squares cycles included hydrogen atoms for all carbon atoms except those of solvate molecules. Hydrogen atoms were placed at 0.96 Å from bonded carbon atoms and were assigned an isotropic temperature factor of 0.08 Å². In the final cycles of refinement, each parameter shifted by <3% of its esd and the highest residual peak in the final Fourier difference map did not exceed 0.8 e/Å³. In compound 5, the hydridic hydrogen atom was not located with room temperature data. Using a second data set consisting of low-angle reflections measured at 180 K, a difference Fourier map calculated after refinement of the room temperature model showed the presence of a single peak (1.1 e) at 2.0 (3) Å from the Ni atom. Selected bond distances and angles are set out in Tables II and III; atom positional parameters and other crystallographic data have been deposited.²⁷

Other Physical Measurements. ¹H NMR spectra were recorded on a Bruker AM-500 spectrometer and infrared spectra on a Nicolet IR/42 spectrophotometer. FAB mass spectrometry was performed on a JOEL JMS-AX505H instrument. EPR spectra were obtained at X-band fre-

(27) See the paragraph at the end of this paper concerning supplementary material available.

(28) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

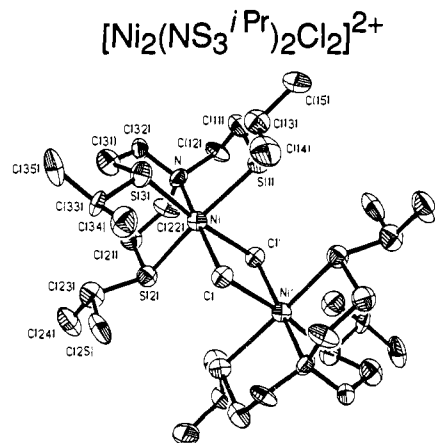


Figure 2. Structure of binuclear $[\text{Ni}_2(\text{NS}_3^{\text{iPr}})_2\text{Cl}_2]^{2+}$ showing 50% probability ellipsoids and the atom labeling scheme. Primed and unprimed atoms are related by an inversion center.

quencies on a Varian E Line spectrometer.

Results and Discussion

Reaction Systems. Given the lack of precise definition of the nickel binding site in CODH enzymes, we elected to utilize in our initial set of experiments a relatively simple, noncluster complex type. The choice of the tetradentate tripod ligands $\text{N}(\text{CH}_2\text{CH}_2\text{SR})_3$ (NS_3^{R}) was based on several considerations. Depending on the steric bulk of R, the ligand permits the formation of five- and/or six-coordinate structures.^{25,29,30} When five-coordinate, M(II) complexes assume trigonal-bipyramidal (TBP) stereochemistry. Flexibility in coordination number is a potentially useful property in associative substitution reactions, such as would be expected in the formation of the acyl from the methyl complex in Figure 1. Another relevant factor is the earlier synthesis and investigation of the set of complexes $[\text{Ni}(\text{np}_3)\text{L}]^+$, which includes several (9–12)^{26,31} of interest in the CODH problem. This suggests

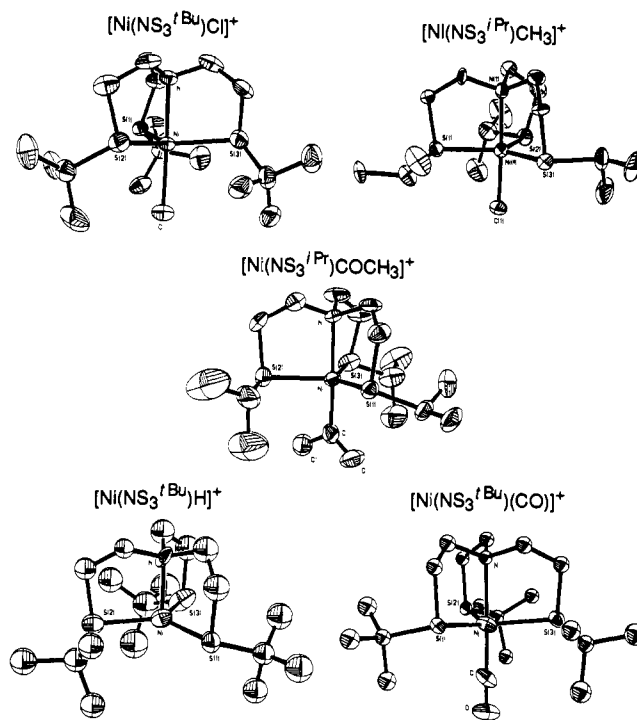
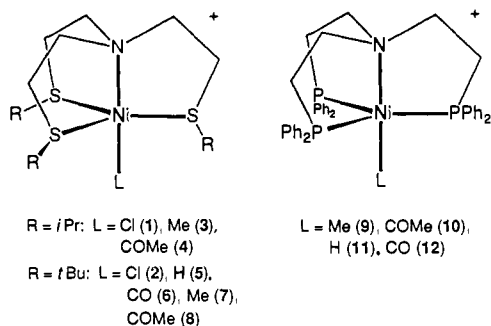


Figure 3. Structures of the complexes $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{L}]^+$ (L = Cl, H, CO) and $[\text{Ni}(\text{NS}_3^{\text{iPr}})\text{L}]^+$ (L = Me, COMe), showing 50% probability ellipsoids and distorted trigonal-bipyramidal structures. In $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{H}]^+$, the hydrogen atom is omitted.

the existence of analogous, although presumably less stable, $[\text{Ni}(\text{NS}_3^{\text{R}})\text{L}]^+$ species which lack physiologically objectionable ligands such as tertiary phosphines and arsines, carbon monoxide and other carbon ligands (hereafter, C/P/As ligands). As will be seen, complexes 1–8 possess stereochemical and reactivity properties consistent with these expectations.

$[\text{Ni}^{\text{II}}\text{—Cl}]$ Complexes. The reaction series described below has been initiated with the $[\text{Ni}^{\text{II}}(\text{NS}_3^{\text{R}})\text{Cl}]^+$ complexes 1 and 2, both of which have been previously reported²⁵ but not structurally characterized by X-ray analysis. Complex 1 as its green paramagnetic BPh_4^- salt ($3.25 \mu_{\text{B}}^{25}$) crystallizes as the centrosymmetric chloride-bridged cation $[\text{Ni}_2(\text{NS}_3^{\text{iPr}})_2\text{Cl}_2]^{2+}$, whose structure is

(29) Ciampolini, M.; Gelsomini, J.; Nardi, N. *Inorg. Chim. Acta* **1968**, *2*, 343.

(30) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* **1973**, *11*, 343.

(31) (a) Sacconi, L.; Orlandini, A.; Midollini, S. *Inorg. Chem.* **1974**, *13*, 2850. (b) Sacconi, L.; Dapporto, P.; Stopploni, P.; Innocenti, P.; Benelli, C. *Inorg. Chem.* **1977**, *16*, 1669. (c) Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1984**, *23*, 922.

shown in Figure 2; bond distances and angles are collected in Table II. The NiCl_2NS_3 coordination unit has a distorted octahedral configuration with the three sulfur atoms in meridional stereochemistry and pairs of *i*-Pr groups of trans sulfur atoms in positions facing each other across the bridge. The structure of mustard-colored paramagnetic 2 ($3.51 \mu_{\text{B}}^{25}$) with the same anion is different. Complex 2 exhibits the relatively undistorted TBP structure shown in Figure 3 with the dimensions in Table III, among which are $\text{N—Ni—Cl} = 178.2(3)^\circ$ and $\text{Ni—Cl} = 2.295(3) \text{ \AA}$. The overall stereochemistry, with three sulfur atoms in the equatorial plane and nitrogen and chlorine atoms in axial positions, is analogous to that of structurally characterized low-spin $[\text{Ni}(\text{np}_3)\text{I}]^+$.³² Because of its coordination number, 2 exhibits a shorter mean Ni—S distance ($2.37(2) \text{ \AA}$) than 1 ($2.43(3) \text{ \AA}$). These values are considerably larger than the apparent Ni—S distance ($2.16(3) \text{ \AA}^{20}$) in C₁ CODH.

The structural properties of complexes 1 and 2 confirm the coordination sphere geometries assigned from d–d spectra by Fallani et al.²⁵ The differences in structure are associated with the larger steric requirements of the *t*-Bu groups, which destabilize the ($\mu\text{-Cl}$)₂ bridge arrangement in 1. This complex is reported to be partly associated in solution;²⁵ it is depicted as a monomer, which presumably is its more reactive form. We will also show that the NS_3^{iPr} and NS_3^{tBu} ligands differ appreciably in their ability to stabilize certain $[\text{Ni}(\text{NS}_3^{\text{R}})\text{L}]^+$ species.

(32) Dapporto, P.; Sacconi, L. *J. Chem. Soc. A* **1970**, 1804.

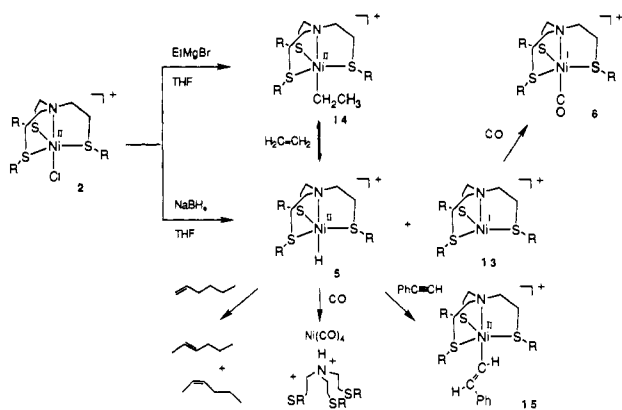


Figure 5. Preparation of the Ni(II) hydride **5** and its reactions, including formation of the ethyl (**14**) and phenylvinyl (**15**) species and isomers of 2-hexene. Also shown is the Ni(I) species **13** formed with **5** and its reaction with CO to give the Ni(I) carbonyl **6**.

Reaction Series. Transformations of $[\text{Ni}-\text{L}]$ groups in the series of TBP complexes $[\text{Ni}(\text{NS}_3^{\text{R}})\text{L}]^+$ are set out in Figures 4 and 5. All compounds were isolated as BPh_4^- salts. Relevant structures and molecular dimensions are presented in Figure 3 and Table III, respectively.

(a) $[\text{Ni}^{\text{II}}-\text{Cl}] \rightarrow [\text{Ni}^{\text{II}}-\text{CH}_3]$. Methyl-transfer reaction 5 of the proposed CODH pathway (Figure 1) is executed by the $[\text{CH}_3-\text{Co}^{\text{III}}]$ group of a corrin moiety. Whether the initial transfer is to a nickel atom or to a protein group followed by transfer to nickel, the process most probably involves a nucleophilic nickel center (Ni(I)). Compounds that stabilize Ni(I) in a sulfur-rich environment have not been isolated. Entry to the desired methyl compounds was achieved by chloride substitution using a Grignard reagent (Figure 4). Thus, reaction of **1** and **2** with 1 equiv of MeMgCl in THF affords purple $[\text{Ni}(\text{NS}_3^{\text{iPr}})\text{Me}]^+$ (**3**) and blue $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{Me}]^+$ (**7**), both diamagnetic, in 50–55% yield. Some black intractable material was also obtained, the amount of which could be kept to a minimum by initiating the reaction at -78°C and allowing the reaction mixture to warm slowly to room temperature. The products were identified by their Ni–Me resonances: $\delta -0.74$ (**3**) and -0.82 (**7**) in dichloromethane. Under strictly anaerobic, anhydrous conditions in THF solution, these complexes are stable for at least 3 days.

In addition, $[\text{3}](\text{BPh}_4)$ was structurally characterized by X-ray diffraction, and found to contain two inequivalent distorted TBP (d-TBP) cations, in which methyl has replaced chloride. The overall stereochemistry is similar to that of **2** and low-spin $[\text{Ni}(\text{np}_3)\text{Me}]^+$ (**9**),^{31b} with $\text{N}-\text{Ni}-\text{C} = 177.0$ (5°). The principal features causing deviation from idealized trigonal symmetry are the longer Ni–S(2) distance of 2.335 (4) Å and two of the Ni–S angles in the equatorial plane which have values close to 110° and 130° . Corresponding bond distances are shorter in **3** than in high-spin **2**. In particular, the axial Ni–N distance has decreased by 0.12 Å owing to the absence of a $\sigma^*(d_{z^2})$ electron. The Ni–C distance of 1.94 (2) Å is somewhat shorter than that in $[\text{Ni}(\text{np}_3)\text{Me}]^+$ (**9**; 2.02 (2) Å^{31b}), possibly because of larger steric requirements of the six phenyl groups in the former. Complex **3** is one of the very few isolated Ni(II)–methyl complexes without C/P/As ligands.²² Of these, the best previously characterized example is paramagnetic square-pyramidal $[\text{Ni}((\text{NMe})_4\text{-cycclam})\text{Me}]^+$.³³

(b) $[\text{Ni}^{\text{II}}-\text{CH}_3] \rightarrow [\text{Ni}^{\text{II}}-\text{COCH}_3]$. The insertion reaction of **3** with carbon monoxide in THF solution at -20°C was instantaneous and resulted in a slight but distinctive change of color from deep purple to red-purple. Workup under a carbon monoxide atmosphere afforded the acylated product $[\text{Ni}(\text{NS}_3^{\text{iPr}})\text{COMe}]^+$ (**4**) as its BPh_4^- salt in good yield (80%). The acyl group was identified by $\delta_{\text{COMe}} = 2.32$ and $\nu_{\text{CO}} = 1670\text{ cm}^{-1}$. Similarly, reaction of **7** with carbon monoxide in dichloromethane or THF im-

mediately generated a red species. It was formed quantitatively in situ and was identified as $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{COMe}]^+$ (**8**; $\delta_{\text{COMe}} = 2.47$, THF; $\nu_{\text{CO}} = 1685\text{ cm}^{-1}$, CH_2Cl_2). Attempts to isolate pure **8** (BPh_4^-) failed owing to partial reversal of the equilibrium in favor of **7**.

The crystal structure determination of $[\text{4}](\text{BPh}_4)$ revealed a d-TBP stereochemistry of the cation with distortions from trigonal symmetry very similar to those of **3**. The acyl group occupies the methyl site with $\text{N}-\text{Ni}-\text{C} = 179.6$ (7°), $\text{Ni}-\text{C}-\text{CH}_3 = 118$ (1°), $\text{Ni}-\text{C}-\text{O} = 123$ (1°), and $\text{Ni}-\text{C} = 1.90$ (2) Å. The spectroscopic and structural parameters of the $[\text{Ni}-\text{COMe}]$ group are very similar to those for TBP $[\text{Ni}(\text{np}_3)\text{COMe}]^+$ (**10**).²⁶ This compound was prepared as a mixture with $[\text{Ni}(\text{np}_3)\text{CO}]^+$ (**12**) by the reaction of **9** with carbon monoxide and was subsequently separated.²⁶ This complication does not arise in the isolation of **4**; the corresponding carbonyl complex can be prepared separately (vide infra).

All other Ni(II) acyls include P/As/C ligation. Of these, the complexes $[\text{Ni}(\text{acac})(\text{PMe}_3)(\text{COMe})\text{X}]$ (acac = acetylacetonate(1 $-$)) and $[\text{Ni}(\text{PMe}_3)_2(\text{COMe})\text{X}]$ (X = halide) have been prepared by the reaction of the corresponding methyl species with carbon monoxide.^{34,35} Similarly, $[\text{Ni}(\text{bpy})(\text{COEt})(\text{OAr})]$ was obtained from $[\text{Ni}(\text{bpy})\text{Et}(\text{OAr})]$ ³⁶ (bpy = 2,2'-bipyridyl).

(c) $[\text{Ni}^{\text{II}}-\text{Cl}] \rightarrow [\text{Ni}^{\text{II}}-\text{H}]$. The hydride complex was sought because of the possibility of a hydride species in the CO/CO_2 interconversion reaction 1 and in the proposed last step (reaction 7, Figure 1) of overall acetyl-coenzyme A synthase reaction 2. Attempts to prepare $[\text{Ni}(\text{NS}_3^{\text{iPr}})\text{H}]^+$ from **1** and NaBH_4 failed owing to extensive decomposition to black intractable products. However, the analogous reaction (method A) utilizing the more hindered complex **2** gave a moderate yield (40%) of red-purple $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{H}]^+$ (**5**). The presence of hydride was confirmed by $\nu_{\text{NiH}} = 1878\text{ cm}^{-1}$ and the very high field chemical shift $\delta_{\text{H}} = -37.75$ (THF). These parameters fall within the range of similar data for other Ni(II) hydrides.³⁷ An X-ray structural analysis of $[\text{5}](\text{BPh}_4)$ detected minimal electron density at a position trans to the nitrogen atom, amounting to no more than 1.1 e^- at 2.0 (3) Å from the nickel atom. Otherwise, the X-ray results confirmed the stereochemical resemblance of **5** to other members of the series and to $[\text{Ni}(\text{np}_3)\text{H}]^+$ (**11**), which was obtained in non-stoichiometric form as a mixture with the Ni(I) complex $[\text{Ni}(\text{np}_3)]^+$.^{31a} Distortions from trigonal symmetry, as seen from Ni–S distances and S–Ni–S angles, are slight.

Complex **5** is air-sensitive and decomposes slowly in ether solvents and acetone; it reacts rapidly with chlorinated hydrocarbons to yield the initial complex **2**. ^1H NMR spectra of different preparations of $[\text{5}](\text{BPh}_4)$ consistently integrated correctly for hydride content. Additionally, the Ni–S and Ni–N distances are in the range of the Ni(II) complexes **2–4** and are much shorter than those for the authentic Ni(I) species **6** (Table III). Nonetheless, there is clear indication that the hydride was not obtained in strictly stoichiometric form. An analytical sample of $[\text{5}](\text{BPh}_4)$ exhibited an axial powder EPR spectrum at 100 K with $g_{\perp} = 2.375$ and $g_{\parallel} = 1.989$. This spectrum is retained, with much reduced intensity, in frozen THF or acetone solution where two new axial species appear ($g_{\perp} = 2.275, 2.224$; $g_{\parallel} \approx 2$). The ratio of these species varies with concentration, the second being favored in dilute solution. Spin quantitation of different preparations gave 0.14–0.20 spin/Ni.³⁸ The identities of the paramagnetic species have not been established; the likely possibilities are unsolvated and/or solvated $[\text{Ni}^{\text{I}}(\text{NS}_3^{\text{tBu}})]^+$ (**13**), which are not detectable by

(34) (a) Klein, H.-F.; Karsch, H. H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 402; *Chem. Ber.* **1976**, *109*, 2524. (b) Saruyama, T.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 546.

(35) Hüttner, G.; Orama, O.; Bejenke, V. *Chem. Ber.* **1976**, *109*, 2533.

(36) Kohara, T.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1979**, 1519.

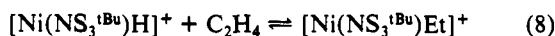
(37) Darenbourg, M. Y.; Ludwig, M.; Riordan, C. G. *Inorg. Chem.* **1989**, *28*, 1630.

(38) X-band spectra at 77 K were doubly integrated against a standard aqueous $\text{Cu}(\text{ClO}_4)_2$ solution spectrum. It was assumed that there is not a significant difference in the molecular weights of the hydride **5** and the paramagnetic species. The nature of these species is currently under investigation.

(33) D'Anello, M. J., Jr.; Barefield, E. K. *J. Am. Chem. Soc.* **1976**, *98*, 1610.

^1H NMR at room temperature. The unsolvated species would presumably resemble $[\text{Ni}(\text{np}_3)]^+$, in which one axial position is vacant.^{31a}

In other respects, complex **5** in THF solution shows a reactivity pattern, set out in Figure 5, consistent with its hydride formulation. It reacts quantitatively with ethylene in THF solution to afford blue diamagnetic $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{Et}]^+$ (**14**), identified by its ^1H NMR spectrum: δ 0.56 (q, 2, CH_2CH_3), 0.09 (t, 3, CH_2CH_3). In the presence of excess ethylene, **14**(BPh_4^-) can be precipitated as blue polyhedra by addition of ethanol to or diffusion of ether into a THF solution. Evaporation of a THF solution of this compound results in a reversal of equilibrium **8** by loss of ethylene to form

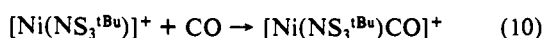


the red-purple solution of **5**(BPh_4^-) as monitored by ^1H NMR. This interconversion provides an alternative route (method B) to the hydride complex. After reaction of **2** with EtMgBr to form **14**, **5** is generated by passage of nitrogen through the solution or is isolated as the BPh_4^- salt by solvent reduction and addition of ethanol. A sample obtained in this way exhibits a ^1H NMR spectrum identical to that of the product of Method A, but with a much lower content of paramagnetic impurity. The EPR active species are identical in both cases, but the latter preparation gave a spin quantitation of only 0.03 spin/Ni.

Treatment of **5** with 1 equiv of phenylacetylene affords the vinyl species **15**. It was detected by its two doublets at δ 6.19 (1, $^3J_{\text{HH}} = 15.2$ Hz) and 5.39 (1, $^3J_{\text{HH}} = 15.2$ Hz) and the $^3J_{\text{HH}}$ coupling constant, characteristic of *trans* $\text{PhCH}=\text{CH}-$ stereochemistry. Conversion to **15** was 30%, owing to some decomposition of nickel species evidenced by the appearance of free ligand resonances. Lastly, addition of 10 equiv of 1-hexene to a solution of **5** generates an intense blue solution similar to the colors encountered in the preparations of **7** and **14**. This color reverts to the original red-purple of **5** upon completion of the reaction. Examination of the reaction mixture by ^1H NMR reveals >90% conversion to a mixture of *cis*- and *trans*-2-hexene, while the major Ni-containing species is **5**. To our knowledge, **5** is the only stable nickel hydride without C/P/As ligation.

(d) Reaction of $[\text{Ni}^{\text{II}}-\text{H}]$ with CO and $[\text{Ni}^{\text{I}}] + \text{CO} \rightarrow [\text{Ni}^{\text{I}}-\text{CO}]$. The product(s) from method A for the preparation of **5** and carbon monoxide at -20°C react rapidly to afford green, paramagnetic $[\text{Ni}(\text{NS}_3^{\text{tBu}})\text{CO}]^+$ (**6**), which was isolated in 20% yield as its BPh_4^- salt. In THF solution, the complex shows an axial EPR spectrum with $g_{\perp} = 2.119$, $g_{\parallel} = 2.008$, and $a_{\parallel}^{\text{N}} = 9.9$ G and the intense IR band $\nu_{\text{CO}} = 2026$ cm^{-1} .

In the preparation of **6**, the remaining nickel is lost as $\text{Ni}(\text{CO})_4$, whose formation was confirmed by a solution IR spectrum of the volatile components of the reaction mixture ($\nu_{\text{CO}} = 2041$ cm^{-1} , THF). ^1H NMR analysis of the remaining reaction products showed only the presence of free protonated ligand and BPh_4^- . A similar reaction of **5**, prepared by method B, produced **6** in 3% yield as determined by EPR spin quantitation. These observations strongly indicate that *carbonyl complex 6 is formed by the reaction of Ni(I) species 13 and carbon monoxide*. EPR spectra of samples of **6** generated in situ showed complete conversion of the Ni(I) species present in preparations of **5** to the EPR spectrum of authentic **6**. Spin quantitation of this spectrum (0.20 spin/Ni from method A; 0.03 spin/Ni from method B) is closely consistent with the amount of paramagnetic species present in the different preparations of **5** by these methods. These results indicate the two independent reactions 9 and 10. Only trace amounts of



molecular hydrogen were detected by GC, which is an indication that equilibrium 11 is inoperative. The occurrence of reaction 12^{31c} is noted. In this case, intramolecular hydrogen transfer occurs, resulting in ligand protonation and reduction to Ni(0).

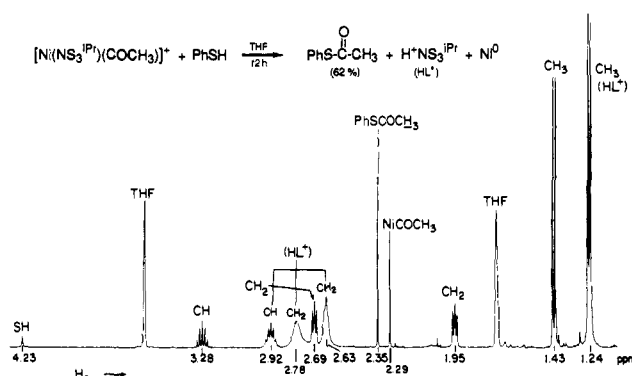
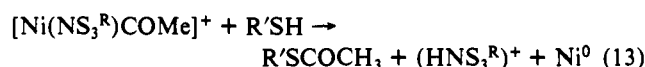


Figure 6. ^1H NMR spectrum of the reaction of ca. 30 mM $[\text{Ni}(\text{NS}_3^{\text{IPr}})\text{COMe}]^+$ with 1.2 equiv of PhSH in THF- d_8 after 12 h at 297 K, illustrating the formation of thioester and protonated ligand. Signal assignments are indicated; CH resonances not labeled as HL* derive from the Ni-acyl complex. At this stage of the reaction, 62% of the complex had been converted to thioester.

Complex **12**, analogous to **6**, is prepared in a different way.^{31a}

Complex **6** has a d-TBP structure with $\text{Ni}-\text{Ni}-\text{C} = 178.5$ (3°), $\text{Ni}-\text{C}-\text{O} = 177.5$ (9°), and $\text{Ni}-\text{C} = 1.85$ (1) \AA . Reduction to Ni(I) increases the Ni-S distances (mean 2.36 (2) \AA), and the Ni-N distance expands by at least 0.1 \AA over the low-spin Ni(II) species owing to the occupancy of the $\sigma^*(d_{z^2})$ orbital. Although stable as a solid, complex **6** slowly loses carbon monoxide in solution and forms an oily, presumably polymeric product. Very few Ni(I) carbonyls have been characterized, among which are $[\text{Ni}(\text{np}_3)\text{CO}]^+$ (**12**)^{26,31a} and a tetraazamacrocyclic complex,³⁹ the only previous example lacking C/P/As ligands.

(e) $[\text{Ni}-\text{COCH}_3] \rightarrow \text{R}'\text{SCOCH}_3$. (i) Thioester Formation. Our approach to the acetyl-CoA formation reaction 7 in the Ni-CODH reaction pathway of Figure 1 is based on reaction systems consisting of acyl complexes **4** or **8** (ca. 30 mM) and the thiols $\text{R}'\text{SH}$ with $\text{R}' = \text{Et}$, CH_2Ph , and Ph in small excess in THF or dichloromethane solution. Reactions proved to be relatively slow and were readily monitored by ^1H NMR. In THF solution after 24 h, the conversion of **4** to thioester with EtSH is about 50% complete, while reactions of the more acidic thiols PhCH_2SH and PhSH resulted in 75% and 80% conversions, respectively. Demonstration of the overall reaction 13 is provided by the typical



NMR spectrum in Figure 6. After 12 h in THF, the extent of thioester formation from **4** and PhSH is 62%. The acyl complex and thioester are readily distinguished by their methyl chemical shifts of 2.29 and 2.35 ppm, respectively. Also evident are resonances due to unreacted thiol and the uncomplexed protonated ligand, whose shifts were verified in a separately prepared sample. As the reaction proceeds, there is a gradual accumulation of a black film on the NMR tube and a slight amount of black solid, which we attribute to elemental nickel. The nucleophilic attack of the thiol on the acyl carbon atom results in a two-electron reduction of Ni(II). The NS_3^{R} ligand system is unable to stabilize Ni(0), resulting in its precipitation.

The time course of the reaction of **4** with PhSH in THF solution is illustrated by the NMR spectra in Figure 7. As the reaction proceeds, there is a smooth decrease in the intensities of thiol and Ni-acyl resonances and an increase in the intensity of the thioester signal. Yields are readily calculated from integrated intensities and increase from 7% after 1 h to 93% after 72 h. Yield data are collected in Table IV, from which it is seen that reactions of acyl complex **8** with the three thiols in THF are faster than those of **4** and are essentially complete at 12 h. Indeed, significant amounts of thioesters (30–40%) are formed after only 15–20 min.

(39) Gagné, R. R.; Ingle, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 1444; *Inorg. Chem.* **1981**, *20*, 420.

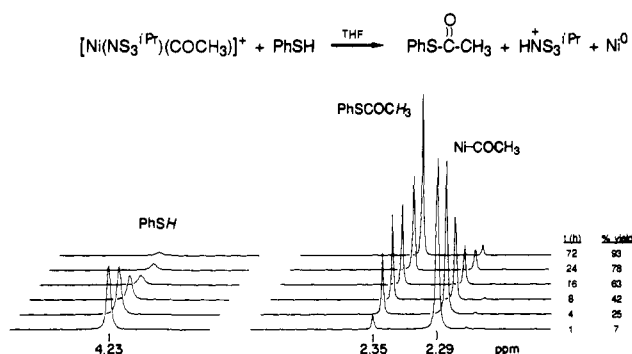


Figure 7. Time course (1–72 h) of the reaction of ca. 30 mM $[\text{Ni}(\text{NS}_3^{\text{iPr}})\text{COMe}]^+$ with equimolar PhSH in THF- d_6 at 297 K, showing thiol, thioester, and Ni–acyl signals. Signal assignments and percent conversions of the acyl complex to thioester are indicated.

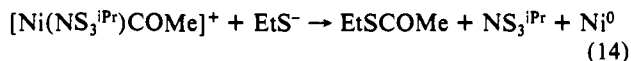
Table IV. Thioester Formation in the Systems $[\text{Ni}(\text{NS}_3^{\text{R}})\text{COMe}]^+ / 1.2\text{R}'\text{SH} / \text{THF}^a$

R	R'	yield, %		
		12 h	24 h	48 h
<i>i</i> -Pr	Et	34	47	58
	Ph	62	75	83
	CH ₂ Ph	65	80	85
<i>t</i> -Bu	Et	>95		
	Ph	>95		
	CH ₂ Ph	>95		

^a For conditions and procedures, cf. Experimental Section.

In dichloromethane, reaction of either **4** or **8** with any of the three thiols is much slower than in THF. Thus, with **4** and these thiols, thioester formation has proceeded to the extent of only 20–30% after 48 h.

In contrast to the rather slow reactions of the acyls **4** and **8** with thiols, treatment of **4** in dichloromethane with 1 equiv of NaSEt resulted in quantitative formation of the thioester in less than 15 min and production of free ligand. Reaction 14 was established by ¹H NMR.



(ii) Related Reactions. The possibility that Ni(II) thiolates might intervene in the reaction of acyl complexes with thiols or thiolates in the probable form $[\text{Ni}(\text{NS}_3^{\text{R}})\text{SR}]^+$ led to attempts to prepare species of this type. Reaction of chloride complex **2** with 1 equiv of NaSEt in THF afforded a red-brown solution, from which was isolated by solvent removal a solid of the same color, soluble in toluene and hexane. From mass spectrometry and ¹H NMR,⁴⁰ the nickel-containing products were found to be the cyclic oligomers Ni₃(SEt)₁₀⁴¹ and Ni₆(SEt)₁₂⁴² together with the free ligand. Evidently, NS₃^R ligands do not compete effectively with thiolate, even in substoichiometric amounts. We conclude that no soluble nickel species is formed in detectable amounts in reactions 13 and 14.

The inability of NS₃^R ligands to capture Ni(0) led to several additional experiments with the intention of producing a soluble nickel product in the reaction of acyl complexes with thiol or thiolate. The cluster $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ proved unsuitable as a potential electron acceptor inasmuch as it reacted immediately with **4** to give thioester.⁴³ Because the np₃ ligand is capable of stabilizing Ni(0) in the trigonal complex $[\text{Ni}(\text{np}_3)]$ with a vacant

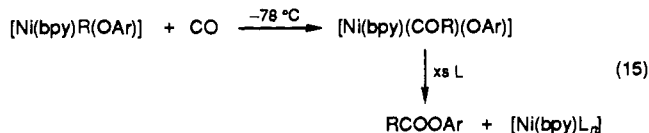
(40) $[\text{Ni}_3(\text{SEt})_{10}]$: *m/e* 904; $\delta(\text{CD}_2\text{Cl}_2)$ 1.96, 1.85 (q, CH₂), 1.27, 1.09 (t, CH₃). $[\text{Ni}_6(\text{SEt})_{12}]$: *m/e* 1084; $\delta(\text{CD}_2\text{Cl}_2)$ 2.15, 1.76 (q, CH₂), 1.47, 1.05 (t, CH₃).

(41) Kriege, M.; Henkel, G. *Z. Naturforsch.* **1987**, *42b*, 1121.

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(43) This reaction is similar to that of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ with acyl halides: Wong, G. B.; Bobrik, M. A.; Holm, R. H. *Inorg. Chem.* **1978**, *17*, 578. Stack, T. D. P.; Holm, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2484.

axial site⁴⁴ that can be protonated to the Ni(II) hydride **11**,^{31c} it was thought that reaction of the acyl complex **10** with thiol might proceed with formation of thioester and **11**. However, reactions of **10** with thiols in THF or dichloromethane under conditions analogous to those of reaction 13 were so slow that little or no NMR evidence of thioester formation was observed after 36 h. Nonetheless, these experiments have the benefit of demonstrating that the NS₃^R ligand system is far more effective in conditioning the Ni(II) site for at least one of the transformations thought to occur in the CODH reaction cycle. Lastly, reaction 15 (R = Me, Et) in THF³⁶ is most closely analogous to reactions 13 and 14.



The acyl intermediate is formed at -78°C and treated with L = π -acid (olefin, CO) to afford the ester. In this system, Ni(0) is trapped as the π -acid complex rather than separating as the metal. Walsh and Orme-Johnson² earlier noted a possible relationship of reaction 10 to thioester formation in the CODH reaction cycle.

Summary. The following are the principal findings and conclusions of this investigation.

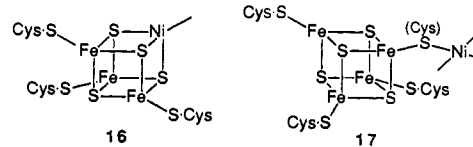
(1) The NS₃^R ligand system stabilizes a series of complexes of the type $[\text{Ni}(\text{NS}_3^{\text{R}})\text{L}]^+$ with L = Cl, CH₃, COCH₃, H, CO, and solv/vacant. Trigonal-bipyramidal structures of all but the last species have been proven by X-ray analysis. $[\text{Ni}(\text{NS}_3^{\text{R}})\text{Cl}]^+$ complexes provide a convenient preparative entry to the series.

(2) The group transformations $[\text{Ni}^{\text{II}}\text{Cl}] \rightarrow [\text{Ni}^{\text{II}}\text{CH}_3] \rightarrow [\text{Ni}^{\text{II}}\text{COCH}_3]$, $[\text{Ni}^{\text{II}}\text{Cl}] \rightarrow [\text{Ni}^{\text{II}}\text{H}]$, and $[\text{Ni}^{\text{II}}] \rightarrow [\text{Ni}^{\text{II}}\text{CO}]$ have been demonstrated with the molecules in (1), which lack nonphysiological (C/P/As) coligation. The $[\text{Ni}^{\text{II}}\text{H}]$ complex is not a direct precursor to the $[\text{Ni}^{\text{II}}\text{CO}]$ complex.

(3) The methyl/acetyl transformation in (2) and the formation in high yield of thioesters R'SCOCH₃ in the reaction of $[\text{Ni}(\text{NS}_3^{\text{iBu}})\text{COCH}_3]^+$ with thiols in THF solution are two previously undocumented processes mediated at Ni(II) sites. These are relevant to the reaction cycle representing the acetyl-CoA synthase activity of *Ct* CODH (Figure 1).

(4) The hydride and carbonyl complexes in (2) may be pertinent to the CO/CO₂ activity of CODH, and the $[\text{Ni}^{\text{II}}\text{CO}]$ species may play a part in the acetyl-CoA synthase pathway, particularly if CO binding precedes methyl transfer or if the order of the two processes is random.

This work is our initial attempt to place the reaction chemistry of Ni-CODH enzymes on a rational basis. The existence and reactivity of the foregoing $[\text{Ni}(\text{NS}_3^{\text{R}})\text{L}]^+$ species lend some viability to currently held views of certain steps in the operation of *Ct* CODH. Yet the systems developed here must be considered as a starting point for the evolution of more realistic models of site structures and reactivities. In particular, catalysis of reactions 1–3 will require a nickel site capable of sustaining reversible electron transfer. If, as current spectroscopic evidence suggests,^{14,15,19,20} the nickel atom of the acetyl-CoA synthase catalytic site is integrated into a Ni-Fe-S cluster in a sulfur-rich coordination environment, our systems will require elaboration toward individual or bridged clusters. Possibilities include the NiFe₂S₄ cubane cluster **16** (although a Ni-Fe interaction at ca. 2.7 Å is apparently absent²⁰) and the cysteinyl- or sulfido-bridged clusters **17**. As noted at the outset, we have recently synthesized examples of **16**;¹⁷ the preparation of bridged assemblies is in progress.



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Acknowledgment. This research was supported by NSF Grant CHE 89-03283. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247. We thank Russell Larsen for assistance in obtaining EPR spectra.

Supplementary Material Available: ORTEP structures of [Ni-

(NS₃^{iPr})Me](BPh₄) and tables of crystallographic data, intensity collection and structure refinement parameters, positional and thermal parameters, bond distances and angles, and calculated hydrogen atom positions for the six compounds in Table I (40 pages); calculated and observed structure factors (163 pages). Ordering information is given on any current masthead page.

Novel Visible-Light-Driven Catalytic CO₂ Fixation. Synthesis of Malonic Acid Derivatives from CO₂, α,β -Unsaturated Ester or Nitrile, and Diethylzinc Catalyzed by Aluminum Porphyrins

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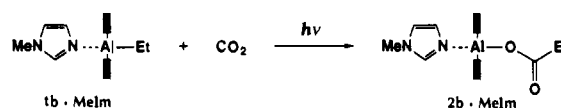
Abstract: Reaction of carbon dioxide, methacrylic esters or methacrylonitrile, and (5,10,15,20-tetraphenylporphinato)aluminum methyl or ethyl took place upon irradiation with Xenon arc light ($\lambda > 420$ nm), affording the corresponding (porphinato)aluminum malonate species under atmospheric pressure at ambient temperature. When diethylzinc was present in the above reaction systems, (porphinato)aluminum ethyl was regenerated by the exchange reaction of the malonate species with diethylzinc, and malonic acid derivatives were catalytically formed with respect to aluminum porphyrins. Detailed investigations revealed that all the elementary steps involved in the catalytic cycle were accelerated under irradiation.

Introduction

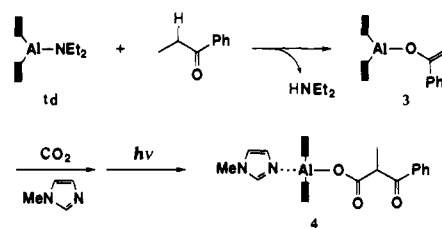
Biological photosynthesis, the fixation of carbon dioxide by green plants and some microorganisms using solar energy, is the most important chemical process running on Earth. The concentration of carbon dioxide in the atmosphere has been rapidly increasing due to the accelerating consumption of fossil fuels, and it is anticipated that the accumulation of carbon dioxide in the atmosphere should cause serious environmental problems. Artificial fixation of carbon dioxide is of much interest from these viewpoints.¹

Carbon dioxide is the ultimate oxidation product of organic compounds and is inert under ordinary conditions. Therefore, activation of carbon dioxide is a prerequisite for developing artificial fixation of carbon dioxide. Because of the chemical inertness, only a few industrial processes have been developed using carbon dioxide as a raw material. The representative examples include production of urea, salicylic acid, and terephthalic acid. However, recent progress in fundamental research has provided a number of potentially useful reactions of carbon dioxide:¹ electro- or photochemical reduction of carbon dioxide, reaction of carbon dioxide with unsaturated hydrocarbons catalyzed by transition-metal complexes, and biomimetic fixation of carbon dioxide. In particular, photochemical fixation of carbon dioxide is not only of great interest in relation to biological photosynthesis but also of potential importance for artificial recycling of carbon dioxide using solar energy without sacrificing fossil energy. Examples of photochemical fixation of carbon dioxide so far reported include photoreduction of carbon dioxide into formic acid,^{2,3} acetic acid,² formate,⁴ and methane.⁵

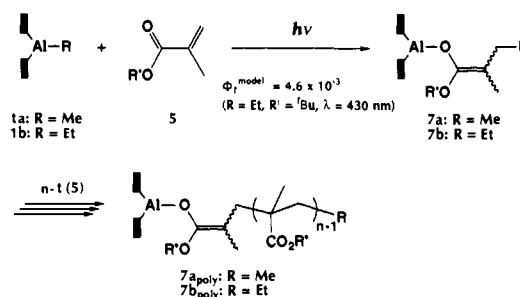
Scheme I



Scheme II



Scheme III



(1) (a) Vol'pin, M. E.; Kolomnikov, I. S. *Organomet. React.* **1975**, *5*, 313. (b) *Organic and Bio-organic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Kodansha: Tokyo, 1981. (c) *Carbon Dioxide as a Source of Carbon*; Aresta, M., Forti, G., Eds.; D. Reidel Publishing Co.: Dordrecht, 1987. (d) Braustein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747.
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 (3) Ishida, H.; Tanaka, K.; Tanaka, T. *Chem. Lett.* **1987**, 1035.
 (4) Mandler, D.; Willner, I. *J. Am. Chem. Soc.* **1987**, *109*, 7884.

Photochemistry of metalloporphyrins is of interest in connection with the role of chlorophyll in photosynthesis. We have investigated the photochemistry of aluminum porphyrins **1** and found that the nucleophilicity of the axial ligands of some aluminum porphyrins can be enhanced upon irradiation with visible light.⁶⁻¹⁰

(5) Maidan, R.; Willner, I. *J. Am. Chem. Soc.* **1986**, *108*, 8100.