Transition Metal Complexes with Sulfur Ligands. 117.[1] A Reaction Cycle for Nickel Mediated Thioester Formation from Alkyl, CO, and Thiolate Groups Modeling the Acetyl-Coenzyme A Synthase Function of CO Dehydrogenase

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Abstract: In quest of nickel complexes with sulfur ligation that model the acetyl-CoA synthase function of CO dehydrogenase (CODH), [Ni('$S_4C_3Me_2$')] (**1**, '$S_4C_3Me_2$'$^{2-}$ = 1,3-bis(2-mercaptophenylthio)-2,2-dimethyl-propane-(2−)) was synthesized by template alkylation of Na_2[Ni('S_2')$_2$] ('S_2'$^{2-}$ = benzene-1,2-dithiolate(2−)) with $CMe_2(CH_2Br)_2$. Acidic hydrolysis of **1** yielded the thiol "$S_4C_3Me_2$"-H_2 (**2**). Reduction of **1** with Na/Hg resulted in cleavage of the '$S_4C_3Me_2$'$^{2-}$ ligand and formation of the thermally stable trinuclear nickel(II) alkyl thiolato complex [Ni('μ-$S_2C_3Me_2$')]$_3$ (**3**, '$S_2C_3Me_2$' $^{2-}$ = 1-(2-mercaptophenylthio)-2,2-dimethylpropyl(2-)). Treatment of **3** with L = Py, THF, or PMe_3 afforded the mononuclear compounds [Ni('$S_2C_3Me_2$')(L)] (**4**, L = Py; **5**, L = PMe_3). The stoichiometric reaction of [Ni('$S_2C_3Me_2$')(L)] with CO led to the cyclic thioester '$S_2C_3Me_2CO$' (**6**, '$S_2C_3Me_2CO$' = 2,3-benzo-6,6-dimethyl-8-oxo-1,4-dithia-cyclooctane) and $Ni(CO)_4$. In the analogous reaction of **5** with CO the intermediate nickel(II) acyl thiolato complex [Ni('$S_2C_3Me_2CO$')(PMe_3)] (**7**, '$S_2C_3Me_2CO$'(2-) = 1-(2-mercaptophenylthio)-2,2-dimethyl-3-oxobutyl(2-)) could be intercepted and fully characterized. The reaction of $Ni(CO)_4$ with the thiol **2** yielded the starting Ni(II) complex **1** and allowed to close the reaction cycle that comprises the CODH sequence: [Ni] → [Ni-alkyl] → [Ni-acyl] → [Ni] + thioester. The net reaction can be formulated as '$S_4C_3Me_2$'-H_2 (**2**) + CO → '$S_2C_3Me_2CO$' (**6**) + 'S_2'-H_2 and represents the first example of nickel mediated thioester formation in a complete reaction cycle. X-ray structure determinations of complexes **1**, **3**, **4**, and **7** revealed approximately square planar coordination geometry for all Ni centers.

Introduction

In our quest of complexes that model the reactivity of oxidoreductases containing metal sulfur centers as active sites, we have been investigating also nickel complexes with thioether thiolate ligands.[2] The ultimate goal of these investigations are complexes that show enzyme-like catalytic activity but are capable of existing in the absence of proteins. It is evident that such complexes cannot be exact structural reduplications of the active sites of [MS] oxidoreductases, in particular in those cases in which the protein of the respective enzyme recognizably warrants the structural integrity and/or the reactivity of the active sites. A striking example in this respect in the FeMo cofactor of nitrogenases. The isolated FeMo cofactor does not catalyze the reduction of N_2, and it is relatively short-lived in aqueous media ($\tau_{1/2} \sim 2$ h).[3]

However, the most basic structural feature of any metal complex is the type of ligating donor atoms which can differ in size, polarizability, number of available lone pairs, etc.[4] The donor set causes specific properties of the resultant metal complexes which can be expressed in terms of structure-function relationships. Accordingly, the combination of transition metals and sulfur donors will result in structure-function relationships that are characteristic for metal sulfur centers. The elucidation of intrinsic structural and reactivity features of metal sulfur-ligand complexes is expected to reveal these basic structure-function relationships. They may also hold for the active centers of [MS] oxidoredutases, even if these centers differ in metal nuclearity and specific aspects from the synthetic complexes under investigation.

Nickel sulfur centers have been recognized as constituents of hydrogenases and CO dehydrogenases (CODH).[5,6] The exact number of sulfur donors and the coordination geometries of the nickel atoms in these enzymes remain open to discussion,[7] and they possibly vary depending on the enzyme source. Recent X-ray crystallographic studies on the hydrogenase isolated from *Desulfovibrio gigas* proved that the active site contains a nickel atom that is coordinated by four cystein sulfur donors and linked to a second metal of uncertain nature, possibly iron.[8] The exact structure of the active site(s) of CODH is still unknown, but it

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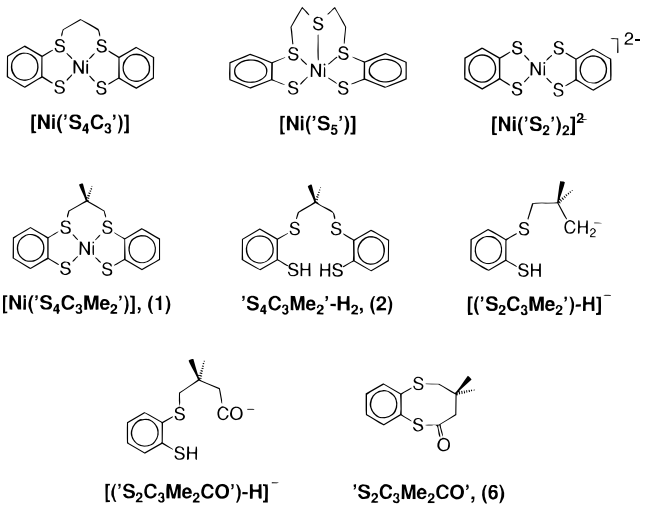
Chart 1



is taken for granted that the catalysis of acetyl-CoA synthesis being one of the key functions of CODH takes place at a nickel iron site.[9] The nickel atom has been shown to have a sulfur rich coordination sphere[7] and to be spin-coupled to an $[Fe_xS_y]$ cluster.[10] EXAFS investigations on CODH from *Clostridium thermoaceticum* suggest that a distorted square planar $[NiS_4]$ unit is bound to the $[Fe_xS_y]$ cluster.[7a,11]

CODH catalyses the syntheses of acetyl-CoA from CO, a CH_3 group, and CoA.[6,12] Recent mechanistic studies indicate that CO initially coordinates to the $[Fe_xS_y]$ cluster,[13] while the CH_3 group binds to the nickel atom.[14] Two alternative pathways are discussed for the subsequent acetyl formation either at the iron center or at the nickel center.[15,16] In both cases, acetyl-CoA is assumed to form from metal bound acetyl groups and CoA.

In our search for well defined nickel sulfur complexes that allow a stepwise combination of CO, alkyl, and thiol groups to give thioesters, we have previously observed that the C_nH_{2n} bridges of complexes such as [Ni('S_4C_3')], ([1,3-bis(2-mercaptophenylthio)propanenickel(II)]), and [Ni('S_5')], ([2,2′-bis(2-mercaptophenylthio)diethylsulfidenickel(II)]) are easily removed by reduction to yield the anion $[Ni('S_2')_2]^{2-}$, ([bis(benzene-1,2-dithiolato)nickelate(II)])^{2f} (cf. Chart 1).

In order to prevent these reductive C_nH_{2n} eliminations, we have now synthesized complex **1** and investigated its reactivity. Complex **1** contains a dimethylpropylene bridge between the $C_6H_4S_2$ units. This bridge has no β-hydrogen atoms at the central C atom and is also found in the tetradentate crown thioether Me_8[16]aneS_4 (Me_8[16]aneS_4 = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathia-cyclohexadecane) which is remarkably stable toward cleavage even under strongly reducing conditions.[17]

Chart 1 summarizes ligands and abbreviations. Preliminary results have been published elsewhere.[18]

Experimental Section

General Methods. Unless noted otherwise, all reactions and operations were carried out under nitrogen by using standard Schlenk techniques. Solvents were dried and distilled before use. 'S_2'$-H_2$[19] and $BrCH_2CMe_2CH_2Br$[20] were prepared as described in the literature. Instruments used for physical measurements were as follows: IR, Zeiss IMR 25 and Perkin-Elmer 983; NMR, JNM-GX 270 and JNM-EX 270; and mass spectra, Varian MAT 212. Cyclic voltammetry (CV) was carried out on an EG&G Potentiostat PAR Model 264A with a Rotel A glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. MeCN was used as solvent, NBu_4PF_6 (0.1 M) as supporting electrolyte and ferrocene/ferrocenium as internal standard (E_{Fc/Fc^+}(MeCN) = +680 mV vs NHE).[21] All potentials are referred to NHE.

X-ray Structure Determinations of [Ni('$S_4C_3Me_2$')] (1), [Ni('μ-$S_2C_3Me_2$')]$_3$ (3), [Ni('$S_2C_3Me_2$')(py)] (4), and [Ni('$S_2C_3Me_2CO$')(PMe_3)] (7). Black plates of **1** were obtained by slowly cooling a hot (100 °C) saturated solution of **1** in DMF to room temperature. Deep-red cubes of **3** formed by layering a THF solution of **3** with MeOH, and red plates of **4** were formed by layering a pyridine solution of **4** with hexane. Yellow plates of **7** separated from a THF/MeOH solution of **7** which was cooled to −78 °C. Suitable single crystals were sealed under N_2 in glass capillaries. The structures were solved by direct methods (SHELXTL-PLUS). Non-hydrogen atoms were refined anisotropically, the positions of the hydrogen atoms of **1** and **3** were calculated for ideal geometry, and the positions of the hydrogen atoms of **4** and **7** were taken from difference Fourier maps. All hydrogen atom positions were restricted during refinement with common isotropic thermal parameters. Crystal and data collection parameters for **1**, **3**, **4**, and **7** are summarized in Table 1.

Syntheses. [Ni('$S_4C_3Me_2$')] (1). (a) Template Alkylation of Na_2[Ni('S_2')$_2$] with $BrCH_2CMe_2CH_2Br$. 'S_2'-H_2 (6.29 g, 44.2 mmol) and subsequently $Ni(ac)_2 \cdot 4H_2O$ (5.50 g, 22.1 mmol) in 60 mL of MeOH were added to a solution which had been obtained by reaction of metallic sodium (2.03 g, 88.3 mmol) with 100 mL of MeOH. The resultant dark-brown solution was stirred for 20 min and evaporated to dryness, and the remaining residue was dissolved in 150 mL of DMF and combined with $BrCH_2CMe_2CH_2Br$ (9.15 g, 39.8 mmol) yielding a green-brown suspension. It was stirred for 18 h at 135 °C in the course of which a finely divided brown precipitate formed. The solvent was removed at 100 °C, and the black residue was digested with 150 mL of MeOH, separated, rinsed with MeOH (125 mL), THF (10 mL), and Et_2O (10 mL), and recrystallized from DMF (100 °C/20 °C). Yield: 7.33 g (81%). Anal. Calcd for $C_{17}H_{18}NiS_4$ (409.30): C, 49.89; H, 4.43; S, 31.34. Found: C, 50.01; H, 4.48; S, 31.14. MS(FD): m/z = 408 (M^+). ^{1}H NMR (270 MHz, DMF-d_7) δ 7.68 (d, 2, C_6H_4), 7.40 (d, 2, C_6H_4), 7.20 (t, 2, C_6H_4), 7.05 (t, 2, C_6H_4), 3.57 (s, 4, CH_2), 1.40 (s, 6,

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Table 1. Crystal and Data Collection[a] Parameters of [Ni('$S_4C_3Me_2$')] (**1**), [Ni('μ-$S_2C_3Me_2$')]$_3$ (**3**), [Ni('$S_2C_3Me_2$')(py)] (**4**), and [Ni('$S_2C_3Me_2CO$')(PMe_3)] (**7**)

compd	[Ni('$S_4C_3Me_2$')]	[Ni('μ-$S_2C_3Me_2$')]$_3$	[Ni('$S_2C_3Me_2$')(py)]	[Ni('$S_2C_3Me_2CO$')(PMe_3)]
formula	$C_{17}H_{18}NiS_4$	$C_{33}H_{42}Ni_3S_6$	$C_{16}H_{19}NNiS_2$	$C_{15}H_{23}NiOPS_2$
formula weight	409.30	807.22	348.17	373.16
crystal system	orthorhombic	cubic	monoclinic	monoclinic
space group	*Pbca*	$Pa\bar{3}$	$P2_1/c$	$P2_1/c$
a [pm]	1354.8(5)	1926.6(3)	1073.4(3)	1101.1(2)
b [pm]	1182.4(5)		972.1(2)	1545.8(2)
c [pm]	2161.8(8)		1614.8(2)	1109.2(2)
β [deg]			93.33(1)	110.67(1)
V [nm^3]	3.462(2)	7.153(3)	1.682(1)	1.766(1)
Z	8	8	4	4
ρ_{cald} [gcm^{-1}]	1.57	1.50	1.37	1.40
μ [cm^{-1}]	15.78	19.31	13.91	14.14
T[K]	293	293	293	293
R;[b] R_w[c][%]	6.1; 5.6	5.4; 4.3	4.3; 4.3	3.6; 3.3

[a] All data collected with graphite-monochromatized Mo K$_\alpha$ radiation (λ = 71.073 pm). [b] $R = \sum||F_0| - |F_c||/\sum|F_0|$. [c] $R_w = \sum[w(|F_0| - |F_c|)]/\sum[w|F_0|]$.

CH_3). ^{13}C{^{1}H} NMR (67.8 MHz, DMSO-d_6) δ 153.0, 131.0, 130.0, 129.5, 128.0, 123.0 (*C*$_6$H$_4$), 50.3 (*C*H$_2$), 34.5 (*C*H$_3$), 29 (*C*$_q$).

(b) From Ni(CO)$_4$ and 'S$_4$C$_3$Me$_2$'-H$_2$ (2). Ni(CO)$_4$ (120 μL, 153 mg, 0.91 mmol) was added to 'S$_4$C$_3$Me$_2$'-H$_2$ (320 mg, 0.91 mmol) in 20 mL of THF. The colorless solution slowly turned brown. In the course of 20 days dark-brown microcrystals of **1** separated, which were isolated and characterized by IR and NMR spectroscopy. Yield: 260 mg (70%).

'S$_4$C$_3$Me$_2$'-H$_2$ (2). [Ni('$S_4C_3Me_2$')] (**1**) (2.20 g, 5.38 mmol) was suspended in 50 mL of CH_2Cl_2 and treated with 25 mL of concentrated hydrochloric acid for 5 h. The CH_2Cl_2 phase was separated, and the remaining green-brown aqueous phase was extracted with CH_2Cl_2 (50 mL). The CH_2Cl_2 extracts were combined, washed with water, dried over Na_2SO_4, and evaporated yielding a brownish oil, which was redissolved in CCl_4 and filtered over SiO_2. Removal of the solvent yielded 'S$_4$C$_3$Me$_2$'-H$_2$ as a colorless viscous oil, which was dried for 2 days in vacuo. Yield: 1.45 g (76%). Anal. Calcd for $C_{17}H_{20}S_4$ (352.60): C, 57.91; H, 5.72; S, 36.37. Found: C, 58.38; H, 5.69; S, 34.76. MS(FD): *m*/*z* = 352 (M$^+$). IR(film): $\bar{\nu}$ = 2520 cm^{-1} (ν_{SH}). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.49−7.40 (m, 2, C$_6$H$_4$), 7.36−7.27 (m, 2, C$_6$H$_4$), 7.17−7.02 (m, 4, C$_6$H$_4$), 4.31 (s, 2, S*H*), 3.05 (s, 4, CH_2), 1.20 (s, 6, CH_3). ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$) δ 136.4, 134.9, 133.1, 129.7, 128.1, 126.5 (*C*$_6$H$_4$), 47.5 (*C*H$_3$), 37.7 (*C*Me$_2$), 27.4 (*C*H$_2$).

[Ni('μ-S$_2$C$_3$Me$_2$')]$_3$ (3). [Ni('$S_4C_3Me_2$')] (1.215 g, 2.97 mmol) in 15 mL of THF was added under vigorous stirring to sodium amalgam, which had been freshly prepared from mercury (200 g) and sodium metal (1.5 g, 65 mmol). In the course of 1 h the color of the organic phase changed from brown to deep red. The organic layer was separated, centrifugated under an atmosphere of argon in order to remove any undissolved particles, reduced in volume to 3 mL, and mixed with 25 mL of MeOH. Red crystals of [Ni('μ-$S_2C_3Me_2$')]$_3$ formed that were separated after 4 h, rinsed with MeOH, and dried. Yield: 330 mg (41%). Anal. Calcd for $C_{33}H_{42}Ni_3S_6$ (807.22): C, 49.10; H, 5.24; Ni, 21.82; S 23.83. Found: C, 49.05; H, 5.35; Ni, 21.72; S, 23.23. ^{1}H NMR (270 MHz, THF-d_8) δ 7.4−7.0 (m, 12, C$_6$H$_4$), 3.30 (dd, $^4J_{HH}$ = 2.4 Hz, $^2J_{HH}$ = 9.5 Hz, 3, SCH_2), 3.05 (d, $^2J_{HH}$ = 9.5 Hz, 3, SCH_2), 1.20 (dd, $^4J_{HH}$ = 2.4 Hz, $^2J_{HH}$ = 9.7 Hz, 3, NiCH_2), 1.08 (s, 9, CH_3), 1.06 (s, 9, CH_3) 0.80 (d, $^2J_{HH}$ = 9.7 Hz, 3, NiCH_2). ^{13}C-{^{1}H} NMR (67.8 MHz, THF-d_8) δ 144.4, 142.9, 136.5, 129.3, 128.0, 125.8 (*C*$_6$H$_4$), 56.4 (S*C*H$_2$), 46.4, 45.0 (*C*H$_3$), 30.9, 28.8 (Ni*C*H$_2$, *C*Me$_2$).

A second set of signals was observed that was assigned to the solvent complex [Ni('$S_2C_3Me_2$')(THF)]: ^{1}H NMR (270 MHz, THF-d_8) δ 7.4−7.0 (m, 4, C$_6$H$_4$), 3.22 (d, br, $^2J_{HH}$ = 8.7 Hz, 1, SCH_2), 2.88 (d, br, $^2J_{HH}$ = 8.7 Hz, 1, SCH_2), 1.15 (br, 1, NiCH_2), 1.05 (s, br, 3, CH_3), 0.93 (s, 3, CH_3) 0.19 (d, $^2J_{HH}$ = 9.1 Hz, 1, NiCH_2). ^{13}C{^{1}H} NMR (67.8 MHz, THF-d_8) δ 134.5, 131.3, 129.8, 127.8, 127.5, 126.2 (*C*$_6$H$_4$), 55.0 (S*C*H$_2$), 45.6, 43.0 (*C*H$_3$), 30.1, 29.1 (Ni*C*H$_2$, *C*Me$_2$).

[Ni('S$_2$C$_3$Me$_2$')(py)] (4). [Ni('$S_2C_3Me_2$')]$_3$ (245 mg, 0.304 mmol) was dissolved in 10 mL of pyridine yielding an orange solution. When 30 mL of *n*-hexane was added under stirring, a dark-orange powder precipitated. It was separated after 12 h, rinsed with *n*-hexane, and dried in vacuo for 5 h. Yield: 270 mg (85%). Anal. Calcd for $C_{16}H_{19}NNiS_2$ (348.17): C, 55.20; H, 5.50; N, 4.02; S, 18.42. Found: C, 55.30; H, 5.97; N, 4.06; S, 18.47. ^{1}H NMR (270 MHz, pyridine-d_5) δ 7.74 (d, 1, C$_6$H$_4$), 7.17 (d, 1, C$_6$H$_4$), 7.08 (t, 1, C$_6$H$_4$), 6.91 (t, 1, C$_6$H$_4$), 8.76 (s, C$_5$H$_5$N), 7.54 (s, C$_5$H$_5$N), 7.19 (s, C$_5$H$_5$N), 3.03 (s, br, 1, SCH_2), 2.73 (s, br, 1, SCH_2), 1.70 (s, br, 1, NiCH_2), 1.11 (s, br, 7, NiCH_2, CH_3).

[Ni('S$_2$C$_3$Me$_2$CO')(PMe$_3$)] (7). PMe_3 (150 mg, 1.99 mmol) was added to [Ni('μ-$S_2C_3Me_2$')]$_3$ (535 mg, 0.663 mmol) in 25 mL of THF yielding a red-brown solution of [Ni('$S_2C_3Me_2$')(PMe_3)]. CO (50 mL, 2.2 mmol) was injected via a syringe in several portions in the course of 4 h. The color of the solution changed to yellow-brown, MeOH (30 mL) was added, and the resultant solution was cooled to −78 °C. Yellow microcrystals precipitated which were separated after 16 h were rinsed with Et_2O and dried for 1 day in vacuo. Yield: 700 mg (94%). Anal. Calcd for $C_{15}H_{23}NiOPS_2$ (373.16): C, 48.28; H, 6.21. Found: C, 48.09; H, 6.15. IR(KBr) $\bar{\nu}$ = 1630 cm^{-1} (ν_{CO}). ^{1}H NMR (270 MHz, THF-d_8) δ 7.47 (d, 1, C$_6$H$_4$), 7.41 (d, 1, C$_6$H$_4$), 6.98 (t, 1, C$_6$H$_4$), 6.83 (t, 1, C$_6$H$_4$), 3.31 (s, 2, SCH_2), 2.45 (s, br, 2, COCH_2), 1.33 (d, $^2J_{PH}$ = 9.7 Hz, 9, P(CH_3)$_3$), 1.10 (s, 6, CH_3). ^{13}C{^{1}H} NMR (67.8 MHz, THF-d_8) δ 262.3 (d, $^3J_{PC}$ = 23.5 Hz, *C*O) 155.8 (d, $^3J_{PC}$ = 13.4 Hz) 136.3, 131.0, 130.6, 128.6, 121.5 (*C*$_6$H$_4$), 61.1 (d, $^3J_{PC}$ = 4.3 Hz), 53.1 (S*C*H$_2$, *C*H$_2$CO), 33.7 (*C*Me$_2$), 28 (br, C(*C*H$_3$)$_2$), 14.2 (d, $^1J_{PC}$ = 29.5 Hz, P(*C*H$_3$)$_3$).

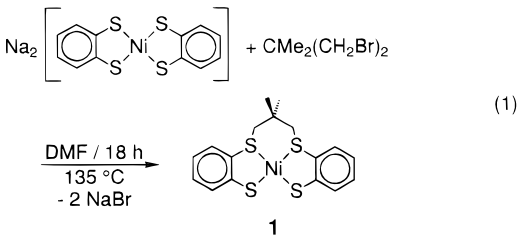
'S$_2$C$_3$Me$_2$CO' (6). (a) From [Ni('μ-S$_2$C$_3$Me$_2$')]$_3$ and CO. In several portions, CO (200 mL, 8.93 mmol) was injected via a syringe into a red suspension of [Ni('$S_2C_3Me_2$')]$_3$ (250 mg, 0.31 mmol) in 40 mL of THF. A colorless solution resulted which was stirred for 1 h and evaporated to dryness, volatile materials being condensed in a trap at −196 °C. 'S$_2$C$_3$Me$_2$CO' remained as colorless oil, and in the trap Ni(CO)$_4$ was identified by its ν_{CO} IR band at 2042 cm^{-1}. Yield of **6**: 210 mg (95%). MS(FD): *m*/*z* = 238 (M$^+$). IR($CHCl_3$) $\bar{\nu}$ = 1671 cm^{-1} (ν_{CO}). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.90 (dd, 1, C$_6$H$_4$), 7.62 (dd, 1, C$_6$H$_4$), 7.48−7.33 (m, 2, C$_6$H$_4$), 2.81 (s, 2, CH_2), 2.41 (s, 2, CH_2), 1.10 (s, 6, C*H*3). ^{13}C{^{1}H} NMR (67, 8 MHz, $CDCl_3$) δ 200.5 (*C*O), 141.3, 138.2, 137.5, 133.2, 130.7, 129.3 (*C*$_6$H$_4$) 51.9, 50.3 (*C*H$_2$), 28 (br, *C*H$_3$).

(b) From [Ni('S$_2$C$_3$Me$_2$')(PMe$_3$)] and CO. [Ni('$S_2C_3Me_2$')(PMe_3)] was synthesized in situ from [Ni('μ-$S_2C_3Me_2$')]$_3$ (620 mg, 0.77 mmol) and PMe_3 (175 mg, 2.3 mmol) in 50 mL of THF. CO (52 mL, 2.3 mmol) was injected via a syringe, and the formation of [Ni('$S_2C_3Me_2$-CO')(PMe_3)] was monitored by IR spectroscopy. A gentle stream of CO was bubbled through the resultant yellow solution, and the temperature was raised to 60 °C in the course of which the solution became colorless. IR spectroscopic monitoring proved the formation of Ni(CO)$_4$ and 'S$_2$C$_3$Me$_2$CO'.

Results

Syntheses and Reactions. [Ni('$S_4C_3Me_2$')] (**1**) was obtained by template alkylation of Na_2[Ni('S_2')$_2$] according to eq 1.

In contrast to the template syntheses of related complexes such as the parent compund [Ni('S_4C_3')] or [Ni('N_HS_4')] which occur at room temperature,[2g] the synthesis of **1** required drastic reaction conditions. Brown **1** is stable toward air, diamagnetic, and well soluble in DMF and DMSO. Number and splitting of

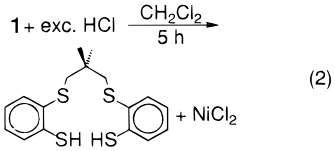


(1)

1

the signals in the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra indicated that **1** contains a twofold element of symmetry in solution.

Decoordination of the ligand and synthesis of the neutral thiol '$S_4C_3Me_2$'-H_2 (**2**) was achieved by hydrolysis of **1** with hydrochloric acid according to eq 2.



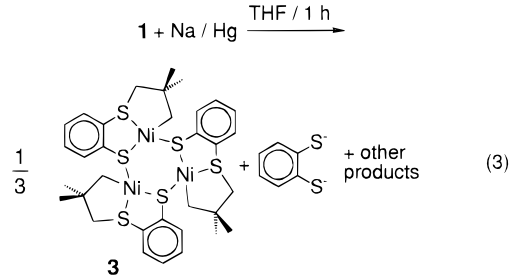
(2)

2

2 is a colorless oil, exhibits a characteristic, sharp ν_{SH} band at 2520 cm^{-1} in its IR spectrum, and, according to its NMR spectra, also contains a twofold element of symmetry.

Cyclic voltammetry indicated reversible reducibility of **1** (Figure 1).

On account of this, we tried to reduce **1** also chemically by lithium butyl or sodium naphthalene. In both cases, however, desalkylation of **1** took place leading to removal of the C_3Me_2 bridge between the 'S_2' units and formation of [Ni('S_2')$_2$]$^{2-}$. In a further experiment we used sodium amalgam in THF in order to reduce **1**. Again, no Ni(I) or Ni(0) species could be isolated, but cleavage of S−C bonds took place. In this case, however, not the C_3Me_2 bridge but one of the 'S_2' units of **1** was eliminated, and trinuclear [Ni('μ-$S_2C_3Me_2$')]$_3$ (**3**) formed according to eq 3.



(3)

3

Formation of 1,2-benzenedithiolate, 'S_2'$^{2-}$, was detected by ^{1}H NMR spectroscopy, and **3** was isolated as red microcrystals. Complex **3** contains one nickel alkyl bond per [Ni('μ-$S_2C_3Me_2$')] unit and possesses C_3 symmetry in solid state. It is thermally stable up to +60 °C and thus exhibits a remarkably high stability for nickel(II) alkyl complexes.[22] Complex **3** dissolves sparingly only in polar solvents such as DMF or THF. NMR spectra of such solutions indicate that **3** partially dissociates forming mononuclear solvent complexes such as [Ni('$S_2C_3Me_2$')(L)], L = DMF or THF. For instance, the ^{1}H NMR spectrum of **3** in THF exhibits one set of four sharp CH_2 and two sharp CH_3 signals, which can be assigned to [Ni('μ-$S_2C_3Me_2$')]$_3$, and, in addition, a second and less intensive set of slightly broadened CH_2 and CH_3 signals that indicate another species [Ni('$S_2C_3Me_2$')(L)]. In accordance, the ^{13}C{^{1}H} NMR spectrum of **3** in THF exhibited one set of 11 intensive signals and a second set of 11 weak signals. Dissociation of **3** and formation of

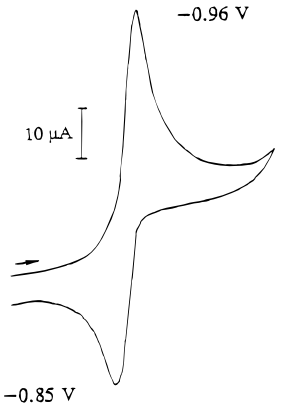
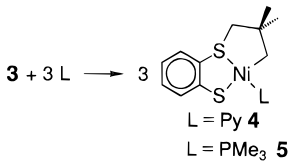


Figure 1. Cyclic voltammogram of [Ni('$S_4C_3Me_2$')] (10^{-4} M in MeCN, 10^{-1} M NBu_4PF_6, ν = 100 mVs^{-1}, 298 K, E vs NHE).

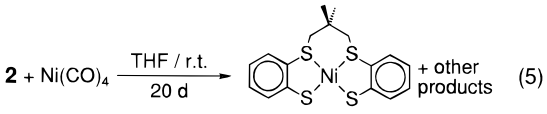
mononuclear [Ni('$S_2C_3Me_2$')(L)] complexes was proved by the reaction of **3** with pyridine or PMe_3 yielding [Ni('$S_2C_3Me_2$')(py)] (**4**) and [Ni('$S_2C_3Me_2$')(PMe_3)] (**5**) according to eq 4.



(4)

Yellow-red **4** dissolves only in pyridine without decomposition. In solvents such as THF, DMF, or CH_2Cl_2, the pyridine ligand dissociated and trinuclear **3** regenerated. The molecular structure of **4** was determined by X-ray structure analysis. The number of signals in the ^{1}H NMR spectrum showed that **4** is C_1 symmetric also in solution because the protons of the CH_2 groups give rise to four separate signals. Complex **5** was prepared in situ only and characterized by its reaction product with CO (see below).

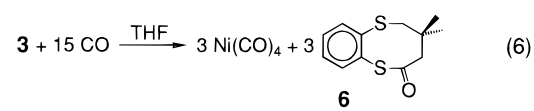
In a "side-step", which later on proved important, we tried to add oxidatively SH bonds of the neutral '$S_4C_3Me_2$'-H_2, (**2**) to $Ni(CO)_4$ in order to obtain nickel sulfur hydride complexes. Such complexes could not be obtained; however, at ambient temperatures the Ni(II) complex **1** formed according to eq 5 in good yields. The fate of electrons, protons, and CO which must be released in this reaction was not elucidated.



(5)

1

One of the key reactions catalyzed by CO dehydrogenase is the formation of C−C bonds between CH_3 and CO groups.[23] Such reactions could be observed when **3**, **4**, and **5** reacted with CO. For example, the reaction of CO with **3** led to instantaneous formation of $Ni(CO)_4$ and of the thioester '$S_2C_3Me_2CO$' (**6**) according to eq 6.



(6)

6

Monitoring this reaction by IR spectroscopy showed that the reaction was complete after addition of 15 equiv of CO. (15 CO is the stoichiometric amount of CO that is required in order to convert 1 mol of **3** into $Ni(CO)_4$ and the thioester **6**). $Ni(CO)_4$

(22) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185−206.

(23) Kumar, M.; Ragsdale, S. W. *J. Inorg. Biochem.* **1993**, *51*, 233.

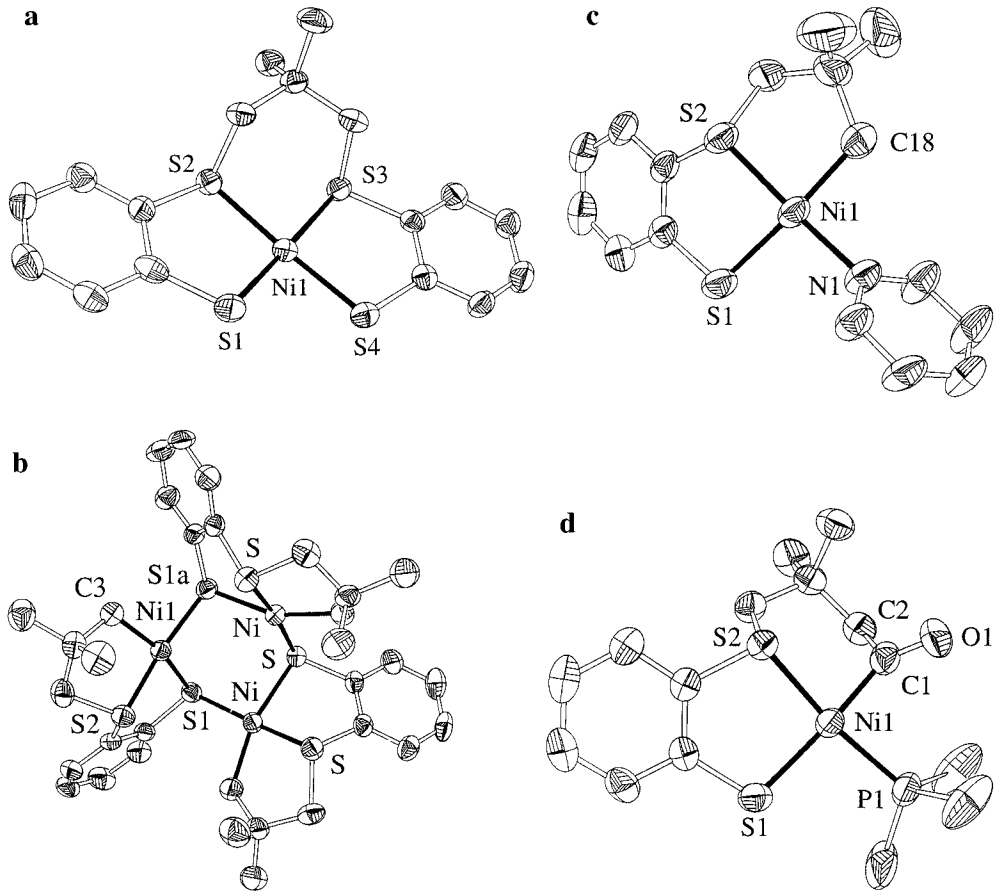
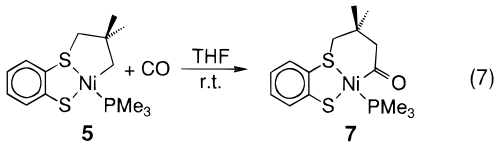


Figure 2. Molecular structures (H atoms omitted) of (a) [Ni('$S_4C_3Me_2$')] (**1**), (b) [Ni('μ-$S_2C_3Me_2$')$_3$ (**3**), (c) [Ni('$S_2C_3Me_2$')(py)] (**4**), and (d) [Ni('$S_2C_3Me_2CO$')(PMe_3)] (**7**).

was identified by its ν_{CO} IR band at 2042 cm^{-1}; **6** was isolated as a colorless oil in nearly quantitative yield (95%) and characterized by NMR and mass spectroscopy and its IR band at 1678 cm^{-1} in THF solution.

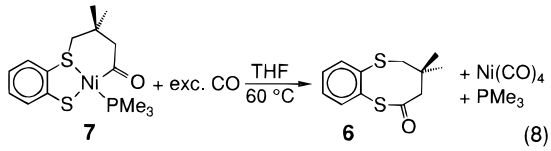
In order to trap potential intermediates the reaction according to eq 6 was also carried out with a highly concentrated suspension of **3** in THF. In this case, in addition of **6** and $Ni(CO)_4$ an orange powder formed. The IR spectrum (KBr) of the orange powder exhibited strong ν_{CO} bands at 1658 and 1641 cm^{-1} indicating the formation of acyl complexes. However, ^{1}H-NMR spectra of solutions of the orange powder showed it to be a mixture of products which so far could neither be separated nor characterized unambiguously.

In contrast, a fully characterizable acyl complex could be isolated in pure form when the PMe_3 complex **5** was treated with 1 equiv of CO according to eq 7.



(7)

[Ni('$S_2C_3Me_2CO$')(PMe_3)] (**7**) was obtained as yellow crystals which proved thermally stable in solid state and in THF solutions up to 60 °C. Complex **7** exhibits a ν_{CO} IR band at 1630 cm^{-1} which compares to the ν_{CO} bands of other Ni(II) acyl complexes such as [Ni($COCH_3$)(PMe_3)$_2$(acac)] (1634 cm^{-1})[24] and [Ni($COCH_3$)(N($SiMe_2CH_2PPh_2$)$_2$)] (1615 cm^{-1}).[25] Complex **7** was further characterized by NMR spectroscopy and X-ray structure analysis proving its mononuclearity. Although **7** is unaffected by CO at room temperature it reacts at 60 °C with an excess of CO yielding again the thioester **6**, $Ni(CO)_4$, and PMe_3 according to eq 8.



(8)

X-ray Structure Analyses of [Ni('$S_4C_3Me_2$')] (1), [Ni('μ-$S_2C_3Me_2$')$_3$ (3), [Ni('$S_2C_3Me_2$')(py)] (4), and [Ni('$S_2C_3Me_2$-CO')(PMe_3)] (7). Figure 2 shows the molecular structures of **1**, **3**, **4**, and **7**; Table 2 lists selected distances and angles.

In all four complexes, the nickel centers exhibit approximately planar coordination geometries. The donor sets comprise four sulfur (**1**), three sulfur and one carbon (**2**), two sulfur, one carbon, and one nitrogen (**4**), or two sulfur, one carbon, and one phosphorus atom (**7**). The structural parameters show that NiS distances can cover a wide range from 209−229 pm. This may be traced back to particular steric constraints as well as bonding situations. **1** containing only thiolate and thioether S donors revealed no anomalies. The Ni−S(thiolate) and Ni−S(thioether) distances lie in the expected range of 217−220 pm,[2g,26,27] and their nearly identical values can be traced back to the σ-donor−π-donor and σ-donor−π-acceptor character of the respective bonds.[28] Less common is the molecular structure

(24) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524−2532.
(25) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Organomet. Chem.* **1987**, *332*, 345−360.
(26) Sellmann, D.; Schillinger, H.; Knoch, F. *Inorg. Chim. Acta* **1992**, *198*, 351−357.
(27) (a) Desper, J. M.; Gellman, S. H.; Wolf, R. E., Jr.; Cooper, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8663−8671. (b) Baidya, N.; Mascharak, P. K.; Stephan, D. W.; Campagna, C. F. *Inorg. Chim. Acta* **1990**, *177*, 233−238.
(28) Sellmann, D.; Neuner, H.-P.; Knoch, F. *Inorg. Chim. Acta* **1991**, *190*, 61−69.

Table 2. Selected Distances (pm) and Angles (deg) of **1**, **3**, **4**, and **7**

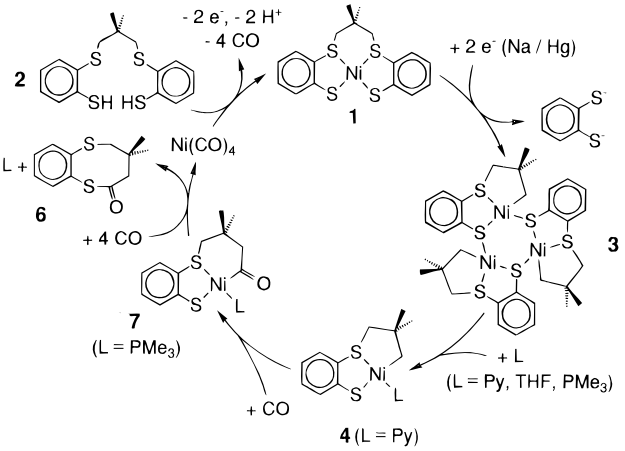
	[Ni('$S_4C_3Me_2$')] (**1**)		
Ni(1)−S(1)	217.3(2)	S(1)−Ni(1)−S(2)	91.8(1)
Ni(1)−S(2)	219.1(2)	S(1)−Ni(1)−S(3)	176.6(1)
Ni(1)−S(3)	217.9(2)	S(2)−Ni(1)−S(3)	87.7(1)
Ni(1)−S(4)	217.7(3)	S(1)−Ni(1)−S(4)	88.6(1)
		S(2)−Ni(1)−S(4)	171.3(1)
		S(3)−Ni(1)−S(4)	91.4(1)
	[Ni('μ-$S_2C_3Me_2$')]$_3$ (**3**)		
Ni(1)−S(1)	228.9(2)	S(1)−Ni(1)−S(2)	87.8(1)
Ni(1)−S(2)	213.4(2)	S(1)−Ni(1)−C(3)	159.9(2)
Ni(1)−C(3)	195.0(6)	S(2)−Ni(1)−C(3)	86.7(2)
Ni(1)−S(1A)	219.1(2)	S(1)−Ni(1)−S(1A)	91.6(1)
		S(2)−Ni(1)−S(1A)	172.1(1)
		C(3)−Ni(1)−S(1A)	96.3(2)
	[Ni('$S_2C_3Me_2$')(py)] (**4**)		
Ni(1)−S(1)	224.2(3)	S(1)−Ni(1)−S(2)	89.9(1)
Ni(1)−S(2)	209.7(3)	S(1)−Ni(1)−N(1)	96.6(2)
Ni(1)−N(1)	191.9(7)	S(2)−Ni(1)−N(1)	166.6(2)
Ni(1)−C(18)	194.8(10)	S(1)−Ni(1)−C(18)	160.4(3)
		S(2)−Ni(1)−C(18)	85.7(3)
		N(1)−Ni(1)−C(18)	91.8(4)
	[Ni('$S_2C_3Me_2CO$')(PMe_3)] (**7**)		
Ni(1)-S(1)	221.2(3)	S(1)−Ni(1)−S(2)	91.5(1)
Ni(1)−S(2)	217.4(2)	S(1)−Ni(1)−P(1)	94.7(1)
Ni(1)−P(1)	216.6(3)	S(2)−Ni(1)−P(1)	170.7(1)
Ni(1)−C(1)	187.3(6)	S(1)−Ni(1)−C(1)	173.3(2)
C(1)−O(1)	121.2(5)	S(2)−Ni(1)−C(1)	86.5(2)
		P(1)−Ni(1)−C(1)	88.0(2)

of **3**. Chiral **3** contains a C_3 axis and consists of three identical subunits which are linked to each other via bridging thiolate donors. The Ni−S distances distinctly differ and cover the wide range of 213−229 pm. Only the Ni−S(1A) distance (219.1(2) pm) in the Ni−S(thiolate) bridge lies in the expected range. The Ni−S(2)(thioether) distance trans to this bond is relatively short (213.4(2) pm), and the Ni−S(1) distance (228.9(2) pm) trans to the alkyl ligand is strongly elongated, probably due to the trans influence of the alkyl group.[29] The central [Ni_3S_3] ring exhibits a chair conformation like cyclohexane such that the square planar coordination of each Ni center becomes tetrahedrally distorted. The Ni−C(1) distance of **3** compares with those in other Ni alkyl complexes.[26,30] **4**, too, exhibits a significant elongation of the Ni−S(1) bond (224.2(3) pm) that is trans to the alkyl ligand. In contrast, the Ni−S(2)thioether distance (209.7(3) pm) is extraordinarily short, while Ni−C and Ni−N distances are in the expected range. The Ni−C(1) distance (187.3(6) pm) of the acyl complex **7** is rather similar to that of other square planar nickel acyl complexes,[30,31] the Ni−S distances (221.2(3) and 217.4(2) pm) are in the expected range.

Discussion

In the search for nickel complexes that possess sulfur rich coordination spheres and are able to model reactions catalyzed by CO dehydrogenase, the new sulfur ligand '$S_4C_3Me_2$'-H_2 (**2**) and its nickel complex [Ni('$S_4C_3Me_2$')] (**1**) have been synthesized. Complex **1** contains nickel in a square planar coordination of sulfur donors and does not exhibit biologically irrelevant ligands such as phosphines or cyclopentadienyl.

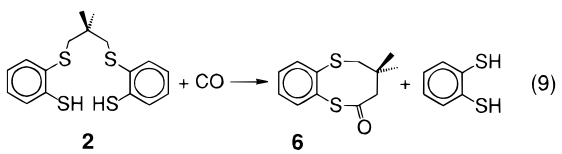
Scheme 1



Complex **1** also results from the reaction of the neutral thioether-thiol '$S_4C_3Me_2$'-H_2 (**2**) and $Ni(CO)_4$. This reaction possibly involves oxidative addition of S−H bonds to the nickel(0) center leading to an intermediary nickel sulfur hydride species. This species, however, could not be intercepted.

In contrast to the parent complex [Ni('S_4C_3')],[2f] the dimethyl derivative **1** is redoxactive and exhibits a quasi-reversible cathodic wave in the cyclic voltammogram. This wave can tentatively be assigned to the formation of an Ni(I) species. Efforts to synthesize this Ni(I) species by chemical reduction of **1** remained unsuccessful. However, reduction of **1** by sodium amalgam yielded the trinuclear Ni(II) alkyl complex **3**. Investigation of the reactivity of this trinuclear complex **3** toward two electron donors including CO has led to a reaction cycle that relates to the acetyl-CoA formation catalyzed by CODH. The cycle models the stepwise formation of nickel bound alkyl and acyl groups, the nickel mediated formation of thioesters, and the final regeneration of the starting complex. The cycle is outlined in Scheme 1, and it shows only those key intermediates that have been completely characterized.

A two electron reduction of **1** yields **3**. In the presence of donor ligands L (L = Py, THF, DMF, PMe_3), complex **3** reversibly dissociates into mononuclear four coordinate nickel alkyl complexes [Ni('$S_2C_3Me_2$')(L)] of which **4** (L = py) has been isolated. The mononuclear complexes react with CO in order to give the acyl complexes [Ni('$S_2C_3Me_2CO$')(L)] of which **7** (L = PMe_3) could be trapped. In the presence of an excess of CO the acyl complexes give the cyclic thioester '$S_2C_3Me_2CO$' (**6**) and $Ni(CO)_4$. Finally, the reaction of $Ni(CO)_4$ with the thioether-thiol **2** regenerates **1** and closes the reaction cycle. Thus, the net reaction is the nickel mediated formation of a thioester from alkyl, CO, and thiol groups and can be expressed by eq 9.



(9)

Furthermore, a comparison of eq 9 and the reaction sequence in Scheme 1 demonstrates that the nickel center performs two functions. Firstly, it acts as mediator of the two electron transfer reactions during which S−C bonds are cleaved and formed (1 → 3 and 7 → 6). Secondly, it facilitates the formation of an acyl group from an alkyl group and CO (4 → 7). The formation of acyl groups from metal bound alkyl groups and gaseous CO is well established and presumably requires prior coordination

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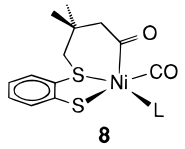
of CO in cis position to the alkyl group.[32,33] Such a coordination of CO can be expected to be favored if the metal center is coordinatively unsaturated. Trinuclear **3** and all complexes [Ni('$S_2C_3Me_2$')(L)] are four-coordinate Ni(II) alkyl species. The highest (common) coordination number of Ni(II) is six and numerous four coordinate Ni(II) complexes are known to readily add at least one additional fifth ligand. In this respect complex **3** and its mononuclear [Ni('$S_2C_3Me_2$')(L)] derivatives can be considered coordinatively unsaturated such that additional coordination of CO is favored. Due to the planar nickel coordination, addition of CO may take place cis to the alkyl group.

In contrast to the well established formation of metal bound acyl groups from metal alkyl species and CO, nickel acyl complexes with physiologically acceptable coordination spheres are extremely rare. Likewise rare are the examples for the nickel mediated formation of thioesters. Only three model systems are known that undergo the reaction sequence Ni → Ni alkyl → Ni acyl → thioester. Holm et al. showed that $[Ni^{II}(N(C_2H_4SR)_3)]^{2+}$ (R = *i*-Pr, *t*-Bu) fragments can add CH_3^- and subsequently CO yielding the acyl derivative $[Ni^{II}(COMe)(N(C_2H_4SR)_3)]^+$. This acyl complex slowly reacts with RSH to form the thioester RSC(O)Me, nickel metal, and the protonated free ligand $HN(C_2H_4SR)_3)_3^+$.[32a,b] Recently, Tucci and Holm described the reaction of [Ni(bpy)(R′)(SR)] with CO that yields thioesters RSCOR′ and [Ni(bpy)$(CO)_2$] (R′ = CH_3, C_2H_5; various aryl substituents, e.g., 2,6-$C_6H_3(CH_3)_2$ or 2,6-$C_6H_3Cl_2$).[32c] Matsunaga and Hillhouse[34] demonstrated that thietan, C_3H_6S, oxidatively adds to [Ni(bpy)(COD)] yielding the Ni(II) alkyl thiolato complex [Ni(bpy)(C_3H_6S)] that further reacts with CO to give the thiolactone $(CH_2)_3SCO$ in 28% yield. IR spectroscopic evidence suggests formation of a thioester in the reaction between $[Ni(CH_3)('Me\text{-}S_2')_2]^-$ and CO.[26]

The reaction sequence outlined in Scheme 1 contrasts these systems in several regards. First of all, Scheme 1 demonstrates that the nickel mediated thioester synthesis can be achieved in a cyclic reaction sequence at nickel centers exhibiting sulfur rich coordination spheres. Secondly, with the exception of **7**, the nickel centers in Scheme 1 exhibit sulfur-only coordination spheres. Finally, Scheme 1 is also of interest with regard to the question whether the thioester formation proceeds via intramolecular or intermolecular pathways. Isolation and reactivity of the complexes **3**, **4**, and **7** and above all the cyclic structure of the thioester **6** imply an intramolecular mechanism. However, simultaneously the important question must be raised in which way the final step of the thioester S−C bond formation takes place.

The last isolable intermediate before release of the thiolactone **6** is the acyl complex **7**. Complex **7** contains thiolate and acyl C donors in trans positions. This trans arrangement is unfavorable for the thioester S−C bond formation. It may also explain why additional CO is necessary in order to induce the final step of thioester formation. The reaction of **7** with CO could yield a four-coordinate species by substitution of L through CO, but this substitution is expected to leave the acyl group and thiolate donor in the unfavorable trans positions. More likely is the addition of CO leading to a five-coordinate species such as [Ni('$S_2C_3Me_2CO$')(CO)(L)], (**8**).



8

Five-coordinate nickel complexes of this type can be expected to be fluxional[2c] and to have elongated (labilized) nickel−ligand bonds. The elongation of nickel ligand bonds in such species is demonstrated, for example, by the comparison of the molecular structures of the square-planar [Ni('S_4C_3')][2g] and its five-coordinate square-pyramidal PMe_3 adduct [Ni(PMe_3)('S_4C_3')].[2f] The labilization of all nickel−ligand bonds and the potential cis configuration of thiolate and acyl groups in **8** can be expected to favor the reductive elimination of the thiolactone **6**.

Another question of interest is why the trinuclear complex **3** reacts with CO to give instantaneously $Ni(CO)_4$ and the thioester **6**. This very rapid reaction contrasts the reaction between the mononuclear **5** and CO which allows to intercept the acyl intermediate **7**. It could be speculated that trinuclear **3** contains one nickel center which mediates the thioester synthesis, while the other two [NiS] centers assist this reaction by transferring CO and/or electrons.[35] In this respect, the arrangement of a "reactive nickel site" linked to additional metal sulfur centers would resemble the conditions in CODH, where a $[Fe_xS_y]$ cluster is linked to the sulfur-rich nickel site. However, this assumption does not explain the rapid conversion of all three nickel centers of **3** into $Ni(CO)_4$ and **6**. Thus, the different reactivity of trinuclear **3** toward CO in comparison to mononuclear **5** may be traced back rather to the high reactivity of the mononuclear solvent complexes such as [Ni('$S_2C_3Me_2$')(THF)] which result from partial dissociation of **3** in THF.

In conclusion, the principal findings of this investigation are that the nickel sulfur centers of the complexes described here provide sites for the nickel mediated thioester formation from complex bound thiolate, alkyl, and CO groups. The absence of an $[Fe_xS_y]$ cluster, which is found in the nickel iron site of CODH, requires the nickel center(s) to act as electron relays via formation of $Ni(CO)_4$. For the first time, the overall reaction that models the acetyl-CoA synthesis catalyzed by CODH could be carried out in a cyclic reaction sequence. The results lend support to a pathway of acetyl-CoA formation that comprises CO insertion into a Ni−CH_3 bond and an intramolecular S−C bond formation between nickel bound acyl groups and thiolate ligands.

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Supporting Information Available: Listings of complete crystal and data collection parameters, atomic coordinates, isotropic thermal parameters, anisotropic displacement parameters, and interatomic distances and bond angles of **1**, **3**, **4**, and **7** (11 pages). For ordering information see any current masthead page. Further details of the X-ray crystal structure analyses have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen by citing the depository Nos. CSD 404007 [Ni('$S_4C_3Me_2$')] (**1**), CSD 404008 [Ni('μ-$S_2C_3Me_2$')$_3$ (**3**), CSD 404004 [Ni('$S_2C_3Me_2$')(py)] (**4**), CSD 404005 [Ni('$S_2C_3Me_2CO$')(PMe_3)] (**7**), the authors, and the reference.

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(35) This question has been raised by one of the referees.