trans-bis(carbene) complex. A moderately stable *trans*-bis(carbene) complex (TTP)Os[$=C(p\text{-}C_6H_4\text{-}CH_3)_2]_2$ (4) can be prepared by treating (TTP)Os$=C(p\text{-}C_6H_4\text{-}CH_3)_2$ (1) with additional $N_2C(p\text{-}C_6H_4\text{-}CH_3)_2$.[19] A signal at 305 ppm in the ^{13}C NMR spectrum of 4 is clearly diagnostic of the carbene ligand. However, the bis(carbene) complex 4 is always contaminated with the monocarbene complex 1 and has not yet been isolated in pure form. The olefin-forming step may involve attack of a diazo reagent at the least hindered carbene ligand of the bis(carbene) complex or may involve direct coupling between two bis(carbene) complexes in a binuclear process. Evidence for the binuclear mechanism was established by monitoring a 70:1 mixture of 4:1. Over the period of days, the bis(carbene) complex 4 decomposes to produce tetratolylolefin and the mono(carbene) complex 1 (eq 2). Binuclear pathways for the formation of olefins from carbene complexes have been proposed for a number of metal complexes.[2e,f,20] Alternative processes such as oxidative pathways involving radical cations[21] cannot be ruled out at this time. Further work is in progress to address the mechanistic issues of our osmium-catalyzed processes.

$$\underset{4}{(\mathrm{TTP})\mathrm{Os}[=C(p\text{-}C_6H_4\text{-}CH_3)_2]_2} \rightarrow \underset{1}{(\mathrm{TTP})\mathrm{Os}=C(p\text{-}C_6H_4\text{-}CH_3)_2} + (p\text{-}C_6H_4\text{-}CH_3)_2C=C(p\text{-}C_6H_4\text{-}CH_3)_2 \quad (2)$$

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[19] Analytical data for (TTP)Os($=C(p\text{-}C_6H_4\text{-}CH_3)_2)_2$: ^1H NMR (C_6D_6) 8.63 (s, 8 H, β-H), 7.99 (d, 8 H, aryl), 7.33 (d, 8 H, aryl), 5.97 (d, 8 H, carbene-aryl), 3.12 (d, 8 H, carbene-aryl), 2.42 (s, 12 H, CH_3), 1.68 (s, 12 H, carbene-CH_3) ppm; ^{13}C NMR (C_6D_6) 305.5 ppm (s, Os$=$C).

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Transition-Metal Complexes with Sulfur Ligands. 89.[†] Unexpected Formation of the Highly Stable Binuclear Nickel Carbene Complex $[Ni(S_2C)]_2$ from Nickel(II) Salts, Diamine–Dithiolate Ligands, and C_1 Components (S_2C^{2-} = 1,3-Imidazolidine-1,3-diylbis(2-benzenethiolate)(2–))

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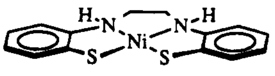
Summary: In quest of model compounds for CO dehydrogenases the interaction of nickel amine–thiolate complexes with CO and other C_1 sources was investigated, and a new type of nickel–carbene complex, $[Ni(S_2C)]_2$ (**2**), was obtained. **2** contains two $[Ni(S_2C)]$ fragments whose extreme stability is traced back to the tridenticity of the carbene ligand and the nickel–thiolate bonds. **2** is stable toward concentrated H_2SO_4 and boiling HCl but reacts rapidly with nucleophiles to give mononuclear $[NiL(S_2C)]$ complexes (L = PMe_3, PPh_3, CN^-).

Nickel complexes with thiolate and amine ligands are of interest as model compounds for the active sites of CO dehydrogenases (CODH) if they react with C_1 compounds as CO_2, CO, or CH_3 species.[1] CODH's contain nickel centers surrounded by sulfur and nitrogen donors and catalyze the CO_2/CO conversion as well as acetyl-CoA synthesis from CH_3, CO, and CoA.[2]

For these reasons we investigated the reaction of $[Ni(N_2H_2S_2)]$ (1; $N_2H_2S_2^{2-}$ = 1,2-ethanediamine-*N*,*N*′-bis(2-benzenethiolate)(2–))[3] with CO. 1 does not react with CO gas. When recrystallized from DMF, however, it unexpectedly yielded the red carbene dithiolate complex $[Ni(S_2C)]_2\cdot$DMF (**2**·DMF; S_2C^{2-} = 1,3-imidazolidine-1,3-diylbis(2-benzenethiolate)(2–)) in minimum amounts. **2** is the formal product of CO insertion from DMF into the Ni–N bonds of 1, followed by elimination of H_2O and dimerization of the resulting fragments. Systematic experiments



$[Ni(N_2H_2S_2)]$

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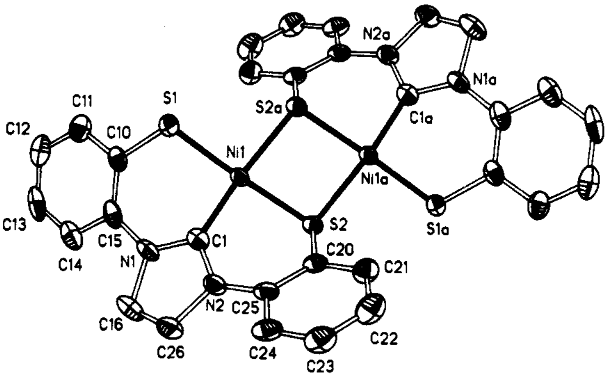

Figure 1. Molecular structure of $[Ni(S_2C)]_2$·DMF (**2**·DMF) (H atoms and DMF omitted, 50% thermal ellipsoids). Selected distances (pm) and angles (deg): Ni1–S1 = 214.6 (2), Ni1–S2 = 217.9 (2), Ni1–C1 = 186.3 (5), Ni1–S2a = 224.5 (2), S1–C10 = 174.2 (7), C15–N1 = 141.7 (10), N1–C1 = 134.9 (10), N1–C16 = 148.3 (7), C16–C26 = 150.6 (14); S1–Ni1–S2 = 177.2 (1), S1–Ni1–C1 = 91.9 (2), S2–Ni1–C1 = 90.9 (2), S1–Ni1–S2a = 92.9 (1), S2–Ni1–S2a = 84.3 (1), Ni1–C1–N1 = 127.9 (5), N1–C1–N2 = 107.6 (5), Ni1–C1–N2 = 124.6 (6).

with different C_1 sources showed that **2** forms in equally small amounts also from **1** and formic acid but in preparative yields in the one-pot synthesis according to eq 1.[4]

$$NiCl_2 + \text{'}N_2H_2S_2\text{'-}H_2 + CH(OEt)_3 \xrightarrow[153\,^{\circ}C/3h]{DMF} \underset{\mathbf{2}}{[Ni(\text{'}S_2C\text{'})]_2\cdot DMF} \quad (1)$$

$$+ \text{ other products}$$

Crystals of **2**·DMF obtained in this reaction were characterized by an X-ray structure determination (Figure 1).[5] **2** exhibits crystallographic C_i symmetry. The nickel atoms are each surrounded by one carbene C atom and three thiolate S atoms; the $[Ni(S_2C)]$ fragments are linked by two thiolate bridges. Nickel and bridging thiolate atoms form a plane from which the carbene C atoms C1 and C1a both deviate ±30 pm but the nonbridging thiolate donors S1 and S1a only ±1 pm. Ni–S distances within one $[Ni(S_2C)]$ fragment (214.6 (2) and 217.9 (2) pm) are distinctly shorter than the bridging Ni–S distances (224.5 (2) pm); all Ni–S distances, however, lie in the range 215–225 pm, which is typical of diamagnetic Ni(II)–thiolate complexes.[6] The Ni–C1 distance (186.3 (5) pm) is characteristic of Ni(II)–carbene complexes;[7] the C(carbene)–N distances (134.9 (10) and 135.2 (8) pm) are considerably shorter than the N1–C15 (141.7 (10) pm) and N1–C16 (148.3 (7) pm) distances and indicate double-bond character of the C(carbene)–N bonds. Carbene C and N atoms are each surrounded in a trigonal-planar fashion by their neighbor atoms, resulting in absolutely planar five-membered CN_2S_2 rings.

2 is diamagnetic, is stable toward air and temperatures up to 300 °C, and dissolves only in donor solvents such as pyridine, DMF, and DMSO. The NMR spectra of these solutions and, in particular, the number of ^{13}C signals indicate that **2** dissociates into two $[Ni(S_2C)]$ fragments, which possess at least C_s symmetry. The large high-field shift of the ^{13}C(carbene) signal at 184.9 ppm indicates nucleophilic character of the carbene C atom, because carbene ^{13}C shifts are normally found in the range of 250–220 ppm and for electrophilic carbenes even up to 350 ppm.[8,12]

Cleavage of **2** into $[Ni(S_2C)]$ fragments in solution, indicated by NMR spectroscopic evidence, could be experimentally verified. When reacted with nucleophiles L = PMe_3 and CN^- at room temperature or L = PPh_3 in boiling THF, **2** yielded the derivatives $[NiL(S_2C)]$ (**3**) according to eq 2.[9] The neutral complexes **3a** and **3b**, as well as the monoanionic **3c**, precipitated as $[NMe_4]$**3c**, were isolated and completely characterized; X-ray structure analyses of **3a** and **3b** will be reported in a forthcoming paper.

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(4) All operations were carried out under nitrogen by using the Schlenk technique. Solvents were dried and distilled under nitrogen before use. $N_2H_2S_2$-H_2 was prepared as described in the literature.[3] $[Ni(S_2C)]_2$·DMF (**2**): A solution of $N_2H_2S_2$-H_2 (2.76 g, 10.0 mmol) and 10 mL of $CH(OEt)_3$ in 30 mL of DMF was heated under reflux. $NiCl_2$ (1.29 g, 10.0 mmol) in 10 mL of DMF was added dropwise, and the mixture was heated for another 3 h. The resulting deep red reaction mixture was cooled to room temperature, and the precipitated red-brown microcrystalline **2**·DMF was collected, washed with 20 mL of MeOH and 10 mL of Et_2O, and dried under vacuum; yield 3.22 g (47%). Anal. Calcd for $C_{33}H_{31}N_5Ni_2OS_4$ (M_r = 759.33): C, 52.20; H, 4.12; N, 9.22; S, 16.89. Found: C, 52.09; H, 4.05; N, 9.01; S, 16.71. MS (FD): m/z 686 (M^+ − DMF). NMR (pyridine-d_5, δ [ppm]): ^1H NMR (270 MHz), 7.1–7.9 (m, 8 H, C_6H_4), 3.9 (s, 4 H, C_2H_4); $^{13}C\{^1H\}$ NMR (67.94 MHz), 184.9 (carbene C), 143.2, 138.3, 132.1, 125.4, 125.0, 119.5 (C_6H_4), 52.2 (C_2H_4).

(5) Crystal data for $C_{33}H_{31}N_5Ni_2OS_4$ (**2**·DMF): space group $C2/c$, Nicolet R3m/V diffractometer, T = 200 K, Mo Kα radiation, graphite monochromator, ω-scan, $3° < 2\theta < 54°$, the structure was solved by direct methods (SHELXTL-PLUS), 5643 reflections measured, 3418 independent and 2846 with $F > 6\sigma(F)$, non-hydrogen atoms were refined with anisotropic thermal parameters, R = 6.9%, R_w = 5.6%, a = 2338.1 (4) pm, b = 976.5 (4) pm, c = 1613.5 (4) pm, β = 120.98 (1)°, V = 3159 (2) × 10^6 pm^3, Z = 4. Further details of the X-ray crystal structure analysis have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, by citing the deposition number (CSD 320387), the authors, and the reference.

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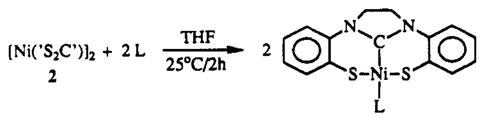
(9) $[Ni(PMe_3)(S_2C)]$ (**3a**): PMe_3 (2.0 mL, 20.00 mmol) was added to a suspension of $[Ni(S_2C)]_2$·DMF (1.50 g, 1.98 mmol) in 30 mL of THF and stirred for 2 h. The resulting deep red solution was filtered and layered with 30 mL of MeOH. Red needles precipitated, which were collected after 3 days, washed with 5 mL of MeOH and 10 mL of Et_2O and dried under vacuum; yield 1.63 g (97%). Anal. Calcd for $C_{18}H_{21}N_2NiPS_2$ (M_r = 419.16): C, 51.58; H, 5.05; N, 6.68; S, 15.30. Found: C, 51.10; H, 5.12; N, 6.30; S, 15.58. MS (FD): m/z 419 (M^+). IR (KBr): δ_{PCH} 950 cm^{-1}. NMR (DMSO-d_6, δ [ppm]): ^1H NMR (270 MHz), 7.5–6.8 (m, 8 H, C_6H_4), 4.3 (s, 4 H, C_2H_4), 1.3 (d, 9 H, $P(CH_3)_3$; $^{13}C\{^1H\}$ NMR (67.94 MHz), 187.0 (d, $^2J(^{31}P^{13}C)$ = 108.7 Hz, carbene C), 140.9, 133.6, 130.1, 123.0, 122.6, 117.5 (C_6H_4), 49.9 (C_2H_4), 11.1 (d, $^1J(^{31}P^{13}C)$ = 40.7 Hz, $P(CH_3)_3$); $^{31}P\{^1H\}$ NMR (109.38 MHz, relative to H_3PO_4), −16.0 (s, $P(CH_3)_3$). $[Ni(PPh_3)(S_2C)]$ (**3b**): PPh_3 (1.4 g, 5.30 mmol) was added to a suspension of $[Ni(S_2C)]_2$·DMF (367 mg, 0.48 mmol) in 50 mL of THF. The mixture was heated under reflux for 1 day, resulting in a red solution. It was cooled to room temperature, filtered, and layered with 20 mL of Et_2O. Red needles and dark green cubes precipitated, which were collected, washed with 5 mL of MeOH and 10 mL of Et_2O, and dried under vacuum. Red needles and dark green cubes proved to be spectroscopically identical; yield 240 mg (41%). Anal. Calcd for $C_{33}H_{27}N_2NiPS_2$ (M_r = 605.44): C, 65.47; H, 4.49; N, 4.63; S, 10.58. Found for green cubes: C, 65.64; H, 4.48; N, 4.45; S, 10.48. Found for red needles: C, 66.00; H, 4.57; N, 4.43; S, 10.39. MS (FD): m/z 605 (M^+). NMR (DMSO-d_6, δ [ppm]): ^1H NMR (270 MHz), 7.5–7.3 (m, 15 H, $P(C_6H_5)_3$), 7.6–6.8 (m, 8 H, C_6H_4), 4.4 (s, 4 H, C_2H_4); $^{13}C\{^1H\}$ NMR (67.94 MHz) (due to low solubility of 4, the ^{13}C(carbene) signal could not be observed), 141.0, 133.6, 130.0, 123.3, 122.8, 117.6 (C_6H_4), 133.8, 129.7, 128.4, 128.3 ($P(C_6H_5)_3$), 50.1 (C_2H_4); $^{31}P\{^1H\}$ NMR (109.38 relative to H_3PO_4), 24.8 (s, 1 P, $P(C_6H_5)_3$). $[NMe_4][Ni(CN)(S_2C)]$ (**3c**): NaCN (340 mg, 0.70 mmol) in 5 mL of H_2O was added to a suspension of $[Ni(S_2C)]_2$·DMF (527 mg, 0.70 mmol) in 25 mL of THF, and the mixture was stirred for 2 h. When stirring was stopped, the THF and H_2O phase separated; the THF phase was removed, filtered, layered with a solution of NMe_4Cl (154 mg, 1.4 mmol) in 5 mL of MeOH, and kept at −30 °C for 3 days. The precipitated orange needles of **5** were collected, washed at −30 °C with 3 mL of MeOH and 10 mL of Et_2O, and dried under vacuum; yield 438 mg (71%). Anal. Calcd for $C_{20}H_{24}N_4NiS_2$ (M_r = 443.16): C, 54.21; H, 5.46; N, 12.64; S, 14.47. Found: C, 53.86; H, 5.48; N, 12.49; S, 14.60. MS (FD): m/z 369 (M^+ − NMe_4). IR (KBr): ν_{CN} = 2110 cm^{-1}. NMR (DMSO-d_6, δ [ppm]): ^1H NMR (270 MHz), 7.4–6.8 (m, 8 H, C_6H_4), 4.2 (s, 4 H, C_2H_4), 3.1 (s, 12 H, $N(CH_3)_4$); $^{13}C\{^1H\}$ NMR (67.94 MHz) 186.8 (carbene C), 140.4, 136.2, 129.8, 122.1, 121.8, 117.4 (C_6H_4), 138.4 (CN), 54.3 ($N(CH_3)_4$), 49.9 (C_2H_4).

Organometallics 1992, *11*, 2348–2350



(2)

3 **3a**: L = PMe_3
3b: L = PPh_3 (T = 65°C)
3c: L = CN^-

The retention of the $[Ni(S_2C)]$ core in the course of cleavage reactions according to eq 2 demonstrates the high stability of the Ni–C(carbene) bond. It can be attributed to several facts. The carbene C atom carries two N substituents, as in the case of "Wanzlick"[10] and "Arduengo" carbenes[11] or in Lappert-type carbene complexes.[12] Furthermore, the carbene donor is part of a tridentate ligand, and the Ni center in the $[Ni(S_2C)]$ fragment is coordinated by two thiolate donors. These donors can act, via their lone pairs, as π-donors to the nickel center, increasing the electron density at the nickel and as a consequence thereof also the π-back-bonding from nickel to the carbene ligand. The π-donor bonds from thiolate donors to nickel and the resulting double-bond character of the Ni–S bonds are indicated by the Ni–S distances within the $[Ni(S_2C)]$ fragments, which are relatively short when compared with the Ni–S distances in the thiolate bridges.

Formation of S→Ni π-donor bonds is expected to reduce the Lewis basicity of the thiolate S atoms, and this explains, at least partly, the complete inertness of **2** toward protonic acids. While metal thiolate complexes usually react with protonic acids to decoordinate the thiolate ligands,[13] **2** is stable even toward concentrated H_2SO_4, aqueous HCl, or solutions of gaseous HCl in boiling THF.

The present work has shown that highly stable Ni(II) carbene complexes can formed by reaction of C_1 sources, thiolate amine ligands, and Ni(II) salts. The question as to whether analogous reactions occur in the course of CO_2/CO conversion or CH_4 formation in CO dehydrogenases still remains open. Further investigations have shown that palladium and platinum form analogous complexes.

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Supplementary Material Available: Tables of crystal data and details of the structure solution and refinement, positional and thermal parameters, and bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of the First Diazagermocines

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Summary: New 1,3,2-diazagermines **2**, formed by reaction of 4-amino-1-azabutadienes **1** and diethyl- or diphenylgermanium dichloride, react with dimethyl acetylenedicarboxylate to yield novel 1,5,2-diazagermocines **3** in quantitative yield; the crystal structure of **3a** has been determined. The behavior of **3** toward hydrolysis and heating is also reported.

The chemistry of organosilicon compounds has been widely developed over the last few decades,[1] and the silicon amides in particular represent very useful species in organic synthesis.[2] For instance, we have been able to successfully exploit the reactivity of the nitrogen–silicon bond of 1,3,2-diazasilines toward esters of acetylenedi-

Table I. 1,5,2-Diazagermocines 3 Prepared from 1

compd[a]	R^1	R^2	R^3	R^4	R^5	mp, °C
3a	4-MeC_6H_4	Ph	Me	Ph	Et	126–128[b]
3b	4-MeC_6H_4	Ph	Me	Ph	Ph	158–160[b]
3c	Ph	Ph	Me	c-C_6H_{11}	Et	125–127[b]
3d	4-MeC_6H_4	Ph	Cl	Ph	Et	oil
3e	c-C_6H_{11}	H	H	4-$MeOC_6H_4$	Ph	*c*
3f	Bu	H	H	4-MeC_6H_4	Ph	*c*

[a] For isolated compounds **3a–d** yields from **1** >95% according to NMR spectra of the crude reaction mixtures. [b] Recrystallized from hexane–dichloromethane. [c] Not isolated (see text).

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