Transition-Metal Complexes with Sulfur Ligands. 94.[1] Synthesis and Reactivity of Nickel, Palladium, and Platinum Complexes with the Thiolate Carbene Ligand 'S_2C'$^{2-}$. X-ray Structure Determinations of [$Ni(PMe_3)$('S_2C')], [$Ni(PPh_3)$('S_2C')], [Ni('SC')$_2$], [$Pt(PMe_3)$('S_2C')], and ('S_2CO')$_2$[†]

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In quest of model compounds for the active sites of CO dehydrogenases, the interaction of the nickel thiolate amine complex [Ni('$N_2H_2S_2$')] ('$N_2H_2S_2$'$^{2-}$ = 1,2-ethanediamine-*N,N'*-bis(2-benzenethiolate)(2–)) with CO and other C_1 sources was investigated. In the course of these investigations, the nickel(II) thiolate carbene complex [Ni('S_2C')]$_2$ (**1**) ('S_2C'$^{2-}$ = 1,3-imidazolidinyl-*N,N'*-bis(2-benzenethiolate)(2–)) was obtained and characterized. Binuclear **1** is cleaved when reacted with pyridine, PMe_3, PPh_3, and CN^- and yields the mononuclear [Ni(py)('S_2C')] (**2**), [$Ni(PMe_3)$('S_2C')] (**3**), [$Ni(PPh_3)$('S_2C')] (**4**), and [NMe_4][Ni(CN)('S_2C')] (**5**). **3** and **4** were characterized by X-ray structure determination. **3**: orthorhombic space group *Pbca*; a = 12.028 (5), b = 16.884 (4), c = 18.008 (3) Å; Z = 8; R/R_w = 5.9/4.1. **4**: triclinic space group $P\bar{1}$; a = 9.597 (5), b = 10.300 (5), c = 15.872 (10) Å; α = 72.41 (5)°, β = 83.39 (5)°, γ = 68.24 (4)°; Z = 2; R/R_w = 5.2/3.9. In both complexes, the Ni(II) centers are coordinated by two thiolate donors, the C(carbene) and one phosphine P atom in distorted square planes. Reaction of **1** with $LiBEt_3H$ yielded the bis(carbene thiolate) complex [Ni('SC')$_2$] (**6**) via partial desulfuration of the 'S_2C'$^{2-}$ ligand and intermolecular ligand transfer ('SC'$^-$ = 1,3-imidazolidinyl-*N*-phenyl-*N'*-(2-benzenethiolate)-(1–)). **6** was characterized by X-ray structure analysis (monoclinic space group *C2/c*; a = 25.070 (9), b = 8.427 (2), c = 12.813 (2) Å; β = 111.44 (2)°; Z = 4; R/R_w = 2.8/2.5) and contains a nickel center which is surrounded by two thiolate donors and two carbene C atoms in a plane. The palladium and platinum complexes [Pd('S_2C')]$_2$ (**7**) and [Pt('S_2C')]$_2$ (**8**) are homologous to **1** and were obtained in one-pot syntheses from [MCl_2(COD)] (M = Pd, Pt), '$N_2H_2S_2$'-H_2, and $CH(OEt)_3$. Reactions with pyridine yielded [Pd(py)('S_2C')] (**9**) and [Pt(py)('S_2C')] (**10**), and the reaction of **8** with PMe_3 gave [$Pt(PMe_3)$('S_2C')] (**11**). **11** was characterized by X-ray structure analysis (orthorhombic space group *Pbca*; a = 12.299 (4), b = 17.265 (5), c = 17.674 (6) Å; Z = 8; R/R_w = 5.0/4.1) and is isomorphic to **3**. Attempts to obtain the free carbene ligand 'S_2C'-H_2 yielded the dimeric ('S_2C'-H_2)$_2$ (**12**) in which both C(carbene) atoms are probably linked by a C=C double bond. Oxidation of **12** by air gave macrocyclic ('S_2CO')$_2$ (**13**) (monoclinic space group $P2_1/c$; a = 12.582 (8), b = 9.450 (5), c = 24.719 (11) Å; β = 102.60 (4); Z = 4; R/R_w = 3.8/3.0). In **13**, the C(carbene) atoms of the 'S_2C'$^{2-}$ ligand are formally oxidized to C=O groups, and two of the resulting ['S_2CO'] fragments are connected to each other via disulfide bridges. The high stability of the [M('S_2C')] fragments in all complexes is attributed to the tridenticity of the 'S_2C'$^{2-}$ ligand, the N substituents at the C(carbene) atom and especially the π-donor properties of the thiolate S atoms. The latter ones increase the electron density at the metal centers such that strong π-back-bonds from the metal to the carbene donor can form.

Introduction

Elucidation of the functions of metal oxidoreductases by means of model complexes is a current topic of coordination chemistry. Such oxidoreductases include the nickel-containing hydrogenases and CO dehydrogenases (CODH), which catalyze H_2/H^+ reactions, or CO_2/CO conversion and acetyl-CoA synthesis from CO, CH_3, and CoA.[2] EXAFS results indicate that the nickel centers of these enzymes are surrounded by sulfur and/or nitrogen donors.[3]

For this reason, nickel complexes with thiolate and amine ligands can be regarded as structural models for the active centers, for example, of CODH. These complexes also become functional models, if they are able to react with CO_2, CO, or CH_3 groups or other related C_1 compounds. In order to find complexes exhibiting the structural *and* functional model character of CODH we had investigated the interaction of CO with the thiolate amine complex [Ni('$N_2H_2S_2$')] ('$N_2H_2S_2$'$^{2-}$ = 1,2-ethanediamine-*N,N'*-bis(2-benzenethiolate)(2–)).[4] Unexpectedly, we obtained the nickel carbene complex [Ni('S_2C')]$_2$·DMF (**1**·DMF) ('S_2C'$^{2-}$ = 1,3-imidazolidinyl-*N,N'*-bis(2-benzenethiolate)(2–)), which was described recently in a preliminary communication.[5] **1** contains the novel tridentate 'S_2C'$^{2-}$ ligand, combining carbene and thiolate functions. The goal of the investigations reported here was to elucidate the reactivity of **1** toward small species such as CO,

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[†] Ligand abbreviations: 'S_2C'$^{2-}$ = 1,3-imidazolidinyl-*N,N'*-bis(2-benzenethiolate)(2–); 'SC'$^-$ = 1,3-imidazolidinyl-*N*-phenyl-*N'*-(2-benzenethiolate)(1–); ('S_2CO')$_2$ = bis(2-oxo-1,3-imidazolidinyl-*N,N'*-bis(2-benzenethiolate)).

(1) Part 93. Sellmann, D.; Hannakam, M.; Knoch, F.; Moll, M. *Inorg. Chim. Acta* **1993**, *205*, 105.

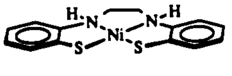
(2) (a) Lancaster, J. R., Jr., Ed. *The Bioinorganic Chemistry of Nickel*; Verlag Chemie: Weinheim, Germany, 1988. (b) Cramer, S. P.; Eidness, M. K.; Pan, W. H.; Morton, T. A.; Ragsdale, S. W.; DerVartanian, D. V.; Ljungdahl, L. G.; Scott, R. A. *Inorg. Chem.* **1987**, *26*, 2477. (c) Ragsdale, S. W.; Wood, H. G. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 6261.

(3) (a) Cammack, R.; Kovacs, K. L.; McCracken, J.; Peisach, J. J. *Eur. J. Biochem.* **1989**, *182*, 363. (b) Maroney, M. J.; Colpas, G. J.; Bagyinka, C. *J. Am. Chem. Soc.* **1990**, *112*, 7067. (c) Teixeira, M.; Moura, I.; Xavier, A. V.; Moura, J. J. G.; LeGall, J.; DerVartanian, D. V.; Peck, H. D.; Huynh, B.-H. *J. Biol. Chem.* **1989**, *264*, 16435. (d) Bastian, N. R.; Diekert, G.; Niederhoffer, E. C.; Teo, B. K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 5581.

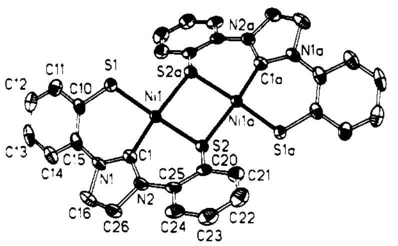
(4) Sellmann, D.; Prechtel, W.; Knoch, F.; Moll, M. *Z. Naturforsch.*, in press.

(5) Sellmann, D.; Prechtel, W.; Knoch, F.; Moll, M. *Organometallics* **1992**, *11*, 2346.

0020-1669/93/1332-0538$04.00/0



$[Ni('N_2H_2S_2')]$



$[Ni('S_2C')]_2\cdot DMF$, **1·DMF**

CH_3^-, H^+, H^-, CN^-, and PMe_3 and to obtain the carbene ligand $'S_2C'-H_2$ in the free state.

Experimental Section

General Methods. Unless noted otherwise, all reactions were carried out under nitrogen at room temperature in dried N_2-saturated solvents by using the Schlenk technique. IR spectra of solutions were recorded in CaF_2 cuvettes with compensation of the solvent bands; solids were measured in KBr pellets. Physical measurements were carried out with the following instruments: IR spectra, Zeiss IMR 16 and Perkin-Elmer 1620 FT IR; NMR spectra, JEOL FT-NMR JNM-GX 270 and EX 270; mass spectra, Varian MAT 212; magnetism (solid samples, 295 K), magnetic susceptibility balance, Johnson Matthey Chemicals Limited; molecular weights, Knauer vapor pressure osmometer; cyclic voltammetry, EG&G potentiostat (Model PAR 264A) equipped with Rotel A (glassy carbon working electrode, Ag/AgCl reference, and Pt counterelectrode; conducting salt, 0.1 m NBu_4ClO_4. Redox potentials are referred to NHE via ferrocene as internal reference).

$'N_2H_2S_2'-H_2$,[6] $[Ni('N_2H_2S_2')]$,[4] PMe_3,[7] $[PdCl_2(COD)]$ (COD = cyclooctadiene),[8] and $[PtCl_2(COD)]$[9] were prepared as described in the literature.

X-ray Structure Analyses of $[Ni(PMe_3)('S_2C')]$ (3), $[Ni(PPh_3)('S_2C')]$ (4), $[Ni('SC')_2]$ (6), $[Pt(PMe_3)('S_2C')]$ (11) and $('S_2CO')_2$ (13). Red needles of $[Ni(PMe_3)('S_2C')]$ (**3**), green prisms of $[Ni(PPh_3)('S_2C')]$ (**4**), and yellow plates of $[Pt(PMe_3)('S_2C')]$ (**11**) were grown from saturated THF solutions, which were layered with Et_2O. Red-brown single crystals of $[Ni('SC')_2]$ (**6**) were obtained from the reaction mixture. Colorless needles of $('S_2CO')_2$ (**13**) precipitated in the course of 3 weeks from a toluene solution of $('S_2C')_2$ (**12**), which had been heated under reflux, cooled to room temperature, and filtered. The solution was kept at room temperature in a Schlenk tube which was plugged with a rubber stopper in order to allow the solvent slowly to evaporate by diffusion.

Suitable single crystals were selected, sealed in glass capillaries, and mounted on the diffractometer. For **11**, a semiempiric absorption correction was carried out. Structures were solved by direct methods (SHELXTL-PLUS); non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms with a common isotropic thermal parameter. Aromatic hydrogen atoms were placed at calculated positions and refined as rigid groups; methyl (**3**, **11**) and methylene hydrogen atoms were placed at ideal tetrahedral positions and allowed to rotate around their central carbon atom during refinement.

Tables I–VI contain selected crystallographic data, fractional atomic coordinates, and equivalent isotropic thermal parameters of **3**, **4**, **11**, **6**, and **13**, respectively.

Preparation of Compounds. $[Ni('S_2C')]_2\cdot DMF$ (1·DMF). To a boiling 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 added dropwise $NiCl_2$ (1.29 g, 10.0 mmol) in 10 mL of DMF. The resulting deep red reaction mixture was kept boiling for 3 h and cooled to room temperature. Red-brown microcrystalline **1**·DMF precipitated, which 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). ^1H NMR (pyridine-d_5, δ (ppm), 270 MHz): 8.1 (s, 1 H, DMF), 7.9–7.1 (m, 8 H, C_6H_4), 3.9 (s, 4 H, C_2H_4), 2.7 (s, 3 H, DMF), 2.6 (s, 3 H, DMF). $^{13}C\{^1H\}$ NMR (pyridine-d_5 δ (ppm), 67.94 MHz): 184.9 (carbene C), 164.2 (DMF), 143.2, 138.3, 132.1, 125.4, 125.0, 119.5 (C_6H_4), 52.2 (C_2H_4), 38.3, 32.1 (DMF).

$[Ni(py)('S_2C')]$ (2). A suspension of $[Ni('S_2C')]_2\cdot DMF$ (1.48 g, 1.95 mmol) in 30 mL of pyridine was heated under reflux for 1 h. The resulting orange-yellow solution was filtered hot and cooled to –20 °C. Precipitated orange microcrystalline **2** was collected by filtration after 3 d, washed with 5 mL of MeOH and 10 mL of Et_2O, and dried under vacuum. Layering the filtered solution with 15 mL of MeOH yielded additional product. Yield: 1.30 g (79%). Anal. Calcd for $C_{20}H_{17}N_3NiS_2$ (M_r = 422.19): C, 56.90; H, 4.06; N, 9.95; S, 15.19. Found: C, 56.78; H, 4.02; N, 9.77; S, 14.85. MS (FD): m/z 343 (M^+ – py). ^1H NMR (pyridine-d_5, δ (ppm), 270 MHz): 7.1–7.9 (m, 8 H, C_6H_4), 3.9 (s, 4 H, C_2H_4). $^{13}C\{^1H\}$ NMR (pyridine-d_5 δ (ppm), 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).

$[Ni(PMe_3)('S_2C')]$ (3). PMe_3 (2.0 mL, 20.00 mmol) was added to a suspension of $[Ni('S_2C')]_2\cdot DMF$ (1.50 g, 1.98 mmol) in 30 mL of THF and stirred for 1 d. The resulting deep red solution was filtered and layered with 30 mL of MeOH. Red needles precipitated which were collected after 3 d, 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_{PC} = 950 cm^{-1}. ^1H NMR (DMSO-d_6, δ (ppm), 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 (DMSO-d_6, δ (ppm), 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 (DMSO-d_6, δ (ppm), 109.38 MHz, rel H_3PO_4): –16.0 (s, $P(CH_3)_3$.

$[Ni(PPh_3)('S_2C')]$ (4). PPh_3 (1.4 g, 5.30 mmol) was added to a suspension of $[Ni('S_2C')]_2\cdot DMF$ (367 mg, 0.48 mmol) in 50 mL of THF. When the mixture was heated under reflux for 1 d, a red solution resulted which 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: C, 65.64; H, 4.48; N, 4.45; S, 10.48 (green cubes); C, 66.00; H, 4.57; N, 4.43; S, 10.39 (red needles). MS (FD): m/z 605 (M^+). ^1H NMR (DMSO-d_6, δ (ppm), 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 (DMSO-d_6, δ (ppm), 67.94 MHz): (due to low solubility of **4**, the ^{13}C 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 DMSO-d_6, δ (ppm), 109.38 MHz, rel H_3PO_4): 24.8 (s, $P(C_6H_5)_3$).

$[NMe_4][Ni(CN)('S_2C')]$ (5). NaCN (340 mg, 0.70 mmol) in 5 mL of H_2O was added to a suspension of $[Ni('S_2C')]_2\cdot DMF$ (527 mg, 0.70 mmol) in 25 mL of THF and stirred for 2 h. When stirring was stopped, THF and H_2O phases 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 d. 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}. ^1H NMR (DMSO-d_6, δ (ppm), 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 (DMSO-d_6, δ (ppm), 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).

$[Ni('SC')_2]$ (6). $LiBEt_3H$ (2.00 mmol, 2.0 mL of a 1 M solution in THF) was added to a suspension of $[Ni('S_2C')]_2\cdot DMF$ (343 mg, 0.50 mmol) in 30 mL of THF and stirred for 5 h. The resulting dark brown suspension was evaporated to dryness and the residue redissolved in 20 mL of THF. The solution was filtered, layered with 5 mL of Et_2O, and kept at –30 °C for 5 d. Precipitated red crystals were collected, washed with 10 mL of Et_2O, and dried under vacuum. Yield: 122 mg (43%). Anal. Calcd for $C_{30}H_{26}N_4NiS_2$ (M_r = 565.38): C, 63.73; H, 4.63; N, 9.91; S, 11.34. Found: C, 64.08; H, 4.80; N, 9.74; S, 11.15. MS (FD): m/z 565 (M^+). ^1H NMR (DMSO-d_6, δ (ppm), 270 MHz): 8.0–6.4 (m, 18 H, C_6H_4), 4.2–3.4 (m, 8 H, C_2H_4). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ (ppm), 67.94 MHz): 194.3 (carbene C), 142.2, 139.8, 134.7, 129.6, 128.7, 125.4, 122.9, 122.3, 121.4, 118.1 (C_6H_4, C_6H_5), 49.7, 48.2 (C_2H_4).

$[Pd('S_2C')]_2\cdot DMF$ (7·DMF). A boiling solution of $'N_2H_2S_2'-H_2$ (440 mg, 1.60 mmol) and 5 mL of $CH(OEt)_3$ in 8 mL of DMF was combined

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(6) (a) Corbin, J. L.; Work, D. E. *Can. J. Chem.* **1974**, *52*, 1054. (b) Sellmann, D.; Käppler, O. *Z. Naturforsch.* **1987**, *42B*, 1291.

(7) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1975**, *4*, 149.

(8) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 52.

(9) Dermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

Table I. Crystallographic Data for [Ni(PMe$_3$)('S$_2$C')] (**3**) [Ni(PPh$_3$)('S$_2$C')] (**4**), [Pt(PMe$_3$)('S$_2$C')] (**11**), [Ni('SC')$_2$] (**6**), and ('S$_2$CO')$_2$ (**13**)

compd	**3**	**4**	**11**	**6**	**13**
chem form	$C_{18}H_{21}N_2NiPS_2$	$C_{33}H_{27}N_2NiPS_2$	$C_{18}H_{21}N_2PPtS_2$	$C_{30}H_{26}N_4NiS_2$	$C_{30}H_{24}N_4O_2S_4$
form wt	419.16	605.44	555.55	565.38	600.78
space gp	*Pbca*	$P\bar{1}$	*Pbca*	$C2/c$	$P2_1/c$
a (Å)	12.028 (5)	9.597 (5)	12.299 (4)	25.070 (9)	12.582 (8)
b (Å)	16.884 (4)	10.300 (5)	17.265 (5)	8.427 (2)	9.450 (5)
c (Å)	18.008 (3)	15.872 (10)	17.674 (6)	12.813 (2)	24.719 (11)
α (deg)	90.00 (0)	72.41 (5)	90.00 (0)	90.00 (0)	90.00 (0)
β (deg)	90.00 (0)	83.39 (5)	90.00 (0)	111.44 (2)	102.60 (4)
γ (deg)	90.00 (0)	68.24 (4)	90.00 (0)	90.00 (0)	90.00 (0)
Z	8	2	8	4	4
cell vol (Å^3)	3656 (2)	1389 (2)	3753 (2)	2519 (1)	2868 (3)
d_{calc} (g/cm^3)	1.52	1.45	1.97	1.49	1.39
μ (cm^{-1})	13.7	9.27	78.5	9.62	3.67
radiation (Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
meas temp (K)	200	293	293	173	293
R; R_w (%)[a]	5.9; 4.1	5.2; 3.9	5.0; 4.1	2.8; 2.5	3.8; 3.0

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$; $R_w = \sum\sqrt{w}\|F_o| - |F_c\|/\sum\sqrt{w}|F_o|$; $w = 1/\sigma^2(F_o)$.

Table II. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (10^{-1} pm^2) of [Ni(PMe$_3$)('S$_2$C')] (**3**)

	x	*y*	*z*	*U*(eq)[a]
Ni(1)	2287 (1)	3850 (1)	3814 (1)	19 (1)
P(1)	1487 (1)	3088 (1)	2962 (1)	21 (1)
C(2)	1566 (5)	3388 (3)	1988 (3)	36 (2)
C(3)	14 (5)	3066 (4)	3128 (4)	37 (2)
C(4)	1852 (5)	2058 (3)	2905 (4)	36 (2)
S(1)	1919 (1)	2933 (1)	4633 (1)	26 (1)
S(2)	3008 (1)	4592 (1)	2974 (1)	26 (1)
C(1)	2474 (5)	4614 (3)	4581 (3)	19 (2)
N(1)	1780 (4)	4676 (3)	5172 (3)	18 (2)
N(2)	3204 (4)	5223 (3)	4615 (3)	17 (2)
C(15)	918 (5)	4170 (3)	5406 (3)	20 (2)
C(14)	96 (5)	4458 (4)	5863 (3)	23 (2)
C(13)	−730 (5)	3969 (4)	6140 (3)	28 (2)
C(12)	−723 (5)	3177 (4)	5956 (3)	27 (2)
C(11)	63 (5)	2889 (4)	5485 (3)	26 (2)
C(10)	912 (5)	3359 (3)	5206 (3)	18 (2)
C(25)	4107 (5)	5383 (3)	4138 (3)	18 (2)
C(24)	4975 (5)	5842 (3)	4390 (3)	23 (2)
C(23)	5859 (5)	6037 (4)	3944 (3)	31 (2)
C(22)	5873 (5)	5766 (4)	3225 (4)	28 (2)
C(21)	5015 (5)	5311 (3)	2957 (3)	26 (2)
C(20)	4093 (5)	5113 (3)	3387 (3)	19 (2)
C(16)	1940 (5)	5438 (3)	5574 (3)	24 (2)
C(26)	3065 (5)	5694 (3)	5295 (3)	23 (2)

[a] Equivalent isotropic *U*(eq) defined as one-third of the trace of the orthogonalized U_{ij} tensors.

Table III. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (10^{-1} pm^2) of [Ni(PPh$_3$)('S$_2$C')] (**4**)

	x	*y*	*z*	*U*(eq)[a]
Ni(1)	2526 (1)	352 (1)	2982 (1)	38 (1)
P(1)	1537 (1)	86 (1)	1863 (1)	38 (1)
S(1)	3516 (2)	−2009 (1)	3510 (1)	47 (1)
S(2)	2286 (2)	2559 (1)	2276 (1)	51 (1)
C(1)	2765 (5)	553 (5)	4087 (3)	36 (2)
N(1)	2318 (4)	−232 (4)	4860 (2)	38 (2)
N(2)	3181 (4)	1541 (4)	4282 (2)	42 (2)
C(15)	1904 (5)	−1461 (5)	5009 (3)	38 (2)
C(14)	1051 (5)	−1819 (5)	5751 (3)	47 (2)
C(13)	721 (6)	−3061 (5)	5947 (3)	52 (2)
C(12)	1224 (6)	−3970 (5)	5407 (3)	55 (3)
C(11)	2059 (6)	−3625 (5)	4661 (3)	50 (2)
C(10)	2418 (5)	−2367 (5)	4450 (3)	40 (2)
C(25)	3765 (5)	2565 (5)	3693 (3)	41 (2)
C(24)	4633 (5)	3102 (5)	4038 (3)	50 (2)
C(23)	5195 (6)	4124 (6)	3501 (4)	62 (3)
C(22)	4902 (6)	4612 (6)	2614 (4)	67 (3)
C(21)	4039 (6)	4100 (5)	2261 (3)	58 (3)
C(20)	3445 (6)	3062 (5)	2790 (3)	46 (2)
C(16)	2227 (5)	402 (5)	5591 (3)	47 (2)
C(26)	3081 (6)	1418 (5)	5237 (3)	49 (2)
C(35)	−708 (6)	2835 (6)	1426 (3)	53 (3)
C(34)	−1602 (6)	4118 (6)	876 (3)	61 (3)
C(33)	−1382 (7)	4388 (6)	−27 (4)	70 (3)
C(32)	−283 (7)	3371 (6)	−370 (3)	62 (3)
C(31)	587 (6)	2077 (5)	180 (3)	48 (2)
C(30)	402 (5)	1776 (5)	1088 (3)	40 (2)
C(45)	4421 (6)	−1042 (6)	1275 (3)	54 (3)
C(44)	5520 (7)	−1748 (6)	748 (4)	72 (3)
C(43)	5177 (8)	−2271 (7)	147 (4)	82 (4)
C(42)	3730 (8)	−2139 (6)	70 (4)	76 (4)
C(41)	2605 (6)	−1464 (6)	597 (3)	58 (3)
C(40)	2950 (5)	−890 (5)	1196 (3)	41 (2)
C(55)	858 (6)	−2467 (6)	2481 (3)	57 (3)
C(54)	−89 (8)	−3250 (7)	2734 (3)	71 (3)
C(53)	−1614 (8)	−2569 (8)	2704 (3)	80 (4)
C(52)	−2207 (7)	−1085 (8)	2414 (3)	72 (4)
C(51)	−1294 (6)	−260 (6)	2151 (3)	58 (3)
C(50)	260 (6)	−953 (6)	2180 (3)	42 (2)

[a] Equivalent isotropic *U*(eq) defined as one-third of the trace of the orthogonalized U_{ij} tensors.

dropwise with [PdCl$_2$(COD)] (455 mg, 1.60 mmol) in 8 mL of DMF, kept boiling for 3 h, and cooled to room temperature. Precipitated green **7**·DMF was collected, washed with 5 mL of MeOH and 10 mL of Et$_2$O, and dried under vacuum. Yield: 448 mg (65%). Anal. Calcd for $C_{33}H_{31}N_5OPd_2S_4$ (M_r = 854.80): C, 46.37; H, 3.66; N, 8.19; S, 15.00. Found: C, 46.29; H, 4.19; N, 8.66; S, 14.19. MS (FD): *m/z* 781 (M$^+$ − DMF). ^{1}H NMR (pyridine-d_5, δ (ppm), 270 MHz): 8.1 (s, 1 H, DMF), 8.0–7.0 (m, 8 H, C$_6$*H*$_4$), 4.1 (s, 4 H, C$_2$*H*$_4$), 2.7 (s, 3 H, DMF), 2.6 (s, 3 H, DMF). ^{13}C{^{1}H} NMR (pyridine-d_5, δ (ppm), 67.94 MHz): 183.6 (carbene C), 141.7, 164.2 (DMF), 138.4, 131.4, 124.4, 123.9, 118.8 (*C*$_6$H$_4$), 51.4 (*C*$_2$H$_4$), 38.3, 32.1 (DMF).

[Pt('S$_2$C')]$_2$·DMF (8·DMF). A boiling solution of 'N$_2$H$_2$S$_2$'-H$_2$ (567 mg, 2.10 mmol) and 5 mL of CH(OEt)$_3$ in 10 mL of DMF was combined dropwise with [PtCl$_2$(COD)] (767 mg, 2.10 mmol) in 5 mL of DMF, kept boiling for 2 h, and cooled to room temperature. Green **8**·DMF precipitated, was collected, washed with 2 mL of DMF, 5 mL of MeOH, and 10 mL of Et$_2$O, and dried under vacuum. Yield: 740 mg (70%). Anal. Calcd for $C_{33}H_{31}N_5OPt_2S_4$ (M_r = 1032.18): C, 38.40; H, 3.03; N, 6.78; S, 12.42. Found: C, 38.32; H, 2.77; N, 6.03; S, 12.39. MS (FD): *m/z* 959 (M$^+$ − DMF). ^{1}H NMR (pyridine-d_5, δ (ppm), 270 MHz): 8.1 (s, 1 H, DMF), 8.0–6.6 (m, 8 H, C$_6$*H*$_4$), 4.0 (s, 4 H, C$_2$*H*$_4$), 2.7 (s, 3 H, DMF), 2.6 (s, 3 H, DMF). ^{13}C{^{1}H} NMR (pyridine-d_5, δ (ppm), 67.94 MHz): 168.5 (carbene C), 164.2 (DMF), 141.5, 137.1, 131.4, 124.3, 123.9, 118.8 (*C*$_6$H$_4$), 50.5 (*C*$_2$H$_4$), 38.3, 32.1 (DMF).

[Pd(py)('S$_2$C')] (9). A suspension of [Pd('S$_2$C')]$_2$·DMF (205 mg, 0.24 mmol) in 10 mL of pyridine was stirred for 1 d and filtered, and the filtered solution was layered with 10 mL of Et$_2$O. Precipitating yellow microcrystals of **8** were collected after 5 d, washed with 5 mL of Et$_2$O, and dried under vacuum. Yield: 129 mg (57%). Anal. Calcd for $C_{20}H_{17}N_3PdS_2$ (M_r = 469.89): C, 51.12; H, 3.65; N, 8.94; S, 13.6. Found: C, 50.94; H, 3.77; N, 8.85; S, 12.95. MS (FD): *m/z* 390 (M$^+$ − py). ^{1}H NMR (pyridine-d_5, δ (ppm), 270 MHz): 8.1–7.0 (m, 8 H, C$_6$*H*$_4$), 4.1 (s, 4 H, C$_2$*H*$_4$). ^{13}C{^{1}H} NMR (pyridine-d_5, δ (ppm), 67.94 MHz): 183.6 (carbene C), 141.7, 138.4, 131.4, 124.4, 123.9, 118.8 (*C*$_6$H$_4$), 51.4 (*C*$_2$H$_4$).

[Pt(py)('S$_2$C')] (10). [Pt('S$_2$C')]$_2$·DMF (228 mg, 0.24 mmol) was dissolved in 20 mL of pyridine and stirred for 1 d. The resulting dark green solution was filtered and layered with 10 mL of Et$_2$O. Precipitated

Table IV. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (10^{-1} pm^2) of [Pt(PMe$_3$)('S$_2$C')] (**11**)

	x	*y*	*z*	*U*(eq)[a]
Pt(1)	2399 (1)	3835 (1)	1254 (1)	25 (1)
S(1)	1887 (4)	2915 (2)	382 (2)	44 (1)
S(2)	3027 (3)	4756 (2)	2096 (2)	35 (1)
N(1)	1791 (9)	4670 (6)	−188 (5)	27 (3)
N(2)	3173 (9)	5247 (7)	376 (5)	28 (3)
C(1)	2479 (12)	4637 (8)	424 (6)	38 (5)
P(1)	2084 (3)	3022 (2)	2268 (2)	33 (1)
C(2)	3241 (13)	2819 (9)	2908 (8)	59 (6)
C(3)	1595 (15)	2075 (8)	2111 (8)	54 (6)
C(4)	1089 (13)	3437 (11)	2891 (9)	61 (7)
C(15)	945 (11)	4164 (8)	−396 (6)	26 (4)
C(14)	109 (11)	4455 (8)	−854 (7)	34 (5)
C(13)	−725 (11)	3980 (9)	−1114 (6)	42 (5)
C(12)	−725 (13)	3223 (10)	−911 (8)	47 (5)
C(11)	50 (13)	2929 (9)	−442 (8)	45 (6)
C(10)	899 (12)	3382 (8)	−187 (7)	33 (5)
C(25)	4073 (11)	5417 (7)	852 (7)	28 (4)
C(24)	4941 (12)	5837 (8)	547 (7)	31 (4)
C(23)	5807 (12)	6044 (9)	970 (7)	38 (5)
C(22)	5873 (12)	5794 (9)	1716 (8)	42 (5)
C(21)	5032 (12)	5384 (8)	2016 (7)	38 (5)
C(20)	4104 (11)	5181 (7)	1613 (7)	28 (4)
C(16)	1923 (12)	5413 (7)	−602 (6)	33 (4)
C(26)	3035 (12)	5683 (8)	−324 (6)	37 (5)

[a] Equivalent isotropic *U*(eq) defined as one-third of the trace of the orthogonalized U_{ij} tensors.

Table V. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (10^{-1} pm^2) of [Ni('SC')$_2$] (**6**)

	x	*y*	*z*	*U*(eq)[a]
Ni(1)	5000	824 (1)	2500	19 (1)
S(1)	5489 (1)	2705 (1)	2103 (1)	27 (1)
C(1)	5364 (1)	−698 (3)	1922 (2)	20 (1)
N(1)	5925 (1)	−755 (2)	2040 (2)	22 (1)
N(2)	5107 (1)	−1978 (2)	1321 (2)	22 (1)
C(15)	6345 (1)	410 (3)	2508 (2)	23 (1)
C(14)	6919 (1)	−22 (3)	2889 (2)	31 (1)
C(13)	7347 (1)	1100 (4)	3271 (2)	38 (1)
C(12)	7206 (1)	2682 (4)	3275 (2)	40 (1)
C(11)	6637 (1)	3124 (3)	2908 (2)	33 (1)
C(10)	6194 (1)	2016 (3)	2523 (2)	24 (1)
C(25)	4506 (1)	−2265 (3)	873 (2)	23 (1)
C(24)	4309 (1)	−3810 (3)	827 (2)	31 (1)
C(23)	3728 (1)	−4096 (4)	363 (2)	40 (1)
C(22)	3344 (1)	−2870 (4)	−35 (2)	42 (1)
C(21)	3541 (1)	−1326 (4)	15 (2)	34 (1)
C(20)	4125 (1)	−1025 (3)	453 (2)	27 (1)
C(16)	6074 (1)	−2275 (3)	1641 (2)	29 (1)
C(26)	5495 (1)	−3003 (3)	992 (2)	30 (1)

[a] Equivalent isotropic *U*(eq) defined as one-third of the trace of the orthogonalized U_{ij} tensors.

Table VI. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (10^{-1} pm^2) of ('S$_2$CO')$_2$ (**13**)

	x	*y*	*z*	*U*(eq)[a]
S(1)	6659 (2)	1555 (2)	1567 (1)	64 (1)
S(2)	7143 (2)	2789 (2)	3150 (1)	58 (1)
S(3)	6262 (2)	4078 (2)	3553 (1)	65 (1)
S(4)	5509 (2)	2266 (2)	897 (1)	71 (1)
N(1)	9042 (4)	2197 (6)	2010 (2)	46 (3)
N(2)	9350 (5)	2374 (7)	2917 (2)	52 (3)
C(1)	8784 (6)	1598 (9)	2481 (3)	43 (3)
O(1)	8212 (4)	584 (5)	2499 (2)	50 (2)
C(15)	8815 (7)	1522 (8)	1496 (3)	52 (4)
C(14)	9644 (6)	1231 (8)	1220 (3)	65 (4)
C(13)	9450 (8)	514 (9)	723 (3)	80 (5)
C(12)	8411 (8)	65 (10)	498 (3)	93 (5)
C(11)	7575 (7)	346 (8)	746 (3)	79 (5)
C(10)	7752 (7)	1077 (8)	1248 (3)	54 (4)
C(25)	9285 (6)	2120 (8)	3478 (3)	46 (3)
C(24)	10213 (6)	1692 (8)	3850 (3)	67 (4)
C(23)	10180 (7)	1471 (9)	4396 (3)	82 (4)
C(22)	9247 (8)	1721 (9)	4576 (3)	74 (4)
C(21)	8310 (7)	2133 (8)	4213 (3)	62 (4)
C(20)	8338 (5)	2343 (7)	3663 (3)	43 (3)
C(16)	9897 (6)	3278 (8)	2161 (3)	74 (4)
C(26)	9946 (6)	3568 (8)	2758 (3)	66 (4)
N(3)	6319 (5)	5760 (6)	2472 (3)	55 (3)
N(4)	6093 (5)	5095 (7)	1587 (3)	56 (3)
C(2)	6859 (7)	5652 (8)	2024 (3)	53 (4)
O(2)	7786 (4)	5968 (6)	2044 (2)	63 (2)
C(35)	6799 (6)	6438 (9)	2980 (3)	44 (3)
C(34)	7232 (6)	7779 (9)	2957 (3)	51 (3)
C(33)	7710 (6)	8461 (9)	3450 (4)	66 (4)
C(32)	7736 (6)	7826 (10)	3946 (3)	66 (4)
C(31)	7291 (6)	6495 (10)	3961 (3)	64 (4)
C(30)	6814 (5)	5771 (7)	3487 (3)	46 (3)
C(45)	6271 (6)	5086 (9)	1035 (3)	51 (4)
C(44)	6648 (6)	6327 (9)	837 (3)	64 (4)
C(43)	6791 (6)	6333 (10)	298 (3)	74 (4)
C(42)	6582 (6)	5182 (11)	−27 (3)	68 (4)
C(41)	6212 (6)	3930 (9)	163 (3)	64 (4)
C(40)	6052 (5)	3884 (8)	705 (3)	52 (3)
C(36)	5180 (6)	5297 (10)	2304 (3)	87 (4)
C(46)	5013 (6)	4997 (9)	1702 (3)	83 (4)

[a] Equivalent isotropic *U*(eq) defined as one-third of the trace of the orthogonalized U_{ij} tensors.

green microcrystals of **10** were collected after 4 d, washed with 5 mL of Et$_2$O, and dried under vacuum. Yield: 166 mg (62%). Anal. Calcd for $C_{20}H_{17}N_3PtS_2$ (M_r = 558.58): C, 43.01; H, 3.07; N, 7.52; S, 11.48. Found: C, 43.17; H, 3.22; N, 7.13; S, 10.82. MS (FD): *m/z* 479 (M$^+$ − py). ^{1}H NMR (pyridine-d_5, δ (ppm), 270 MHz): 8.0–6.6 (m, 8 H, C$_6$*H*$_4$), 4.0 (s, 4 H, C$_2$*H*$_4$). ^{13}C{^{1}H} NMR (pyridine-d_5, δ (ppm), 67.94 MHz): 168.5 (carbene C), 141.5, 137.1, 131.4, 124.3, 123.9, 118.8 (*C*$_6$H$_4$), 50.5 (*C*$_2$H$_4$).

[Pt(PMe$_3$)('S$_2$C')] (11). PMe$_3$ (0.5 mL, 5.00 mmol) was added to a suspension of [Pt('S$_2$C')]$_2$·DMF (497 mg, 0.48 mmol) in 20 mL of THF and heated under reflux for 2 h. The resulting solution was filtered, cooled to room temperature, and layered with 15 mL of Et$_2$O. Yellow **11** precipitated and was collected after 2 d, washed with 10 mL of Et$_2$O, and dried under vacuum. Yield: 355 mg (67%). Anal. Calcd for $C_{18}H_{21}N_2PPtS_2$ (M_r = 555.55): C, 38.91; H, 3.81; N, 5.04; S, 11.54. Found: C, 39.22; H, 3.75; N, 4.75; S, 11.35. MS (FD): *m/z* 555 (M$^+$). IR (KBr): δ_{PC} = 950 cm^{-1}. ^{1}H NMR (CDCl$_3$, δ (ppm), 270 MHz): 7.7–6.8 (m, 8 H, C$_6$*H*$_4$), 4.3 (s, 4 H, C$_2$*H*$_4$), 1.5 (d, 9 H, P(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ (ppm), 67.94 MHz): 186.6 (dd, $^1J(^{195}Pt^{13}C)$ = 1236.1 Hz; $^2J(^{31}P^{13}C)$ = 147.5, carbene C), 141.6, 135.8, 132.6, 124.3, 124.1, 118.5 (*C*$_6$H$_4$), 51.0 (dd, $^3J(^{195}Pt^{13}C)$ = 34.3 Hz; $^4J(^{31}P^{13}C)$ = 5.1 Hz, *C*$_2$H$_4$), 12.8 (dd, $^1J(^{31}P^{13}C)$ = 36.0 Hz; $^2J(^{195}Pt^{13}C)$ = 68.6 Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$, δ (ppm), 109.38 MHz, rel H$_3$PO$_4$): −26.7 (t, $^1J(^{195}Pt^{31}P)$ = 2490.3 Hz, *P*(CH$_3$)$_3$). ^{195}Pt NMR (CDCl$_3$, δ (ppm), 57.81 MHz, rel [Pt(CN)$_4$]$^{2-}$): 317.7 (d, $^1J(^{195}Pt^{31}P)$ = 2490.3 Hz).

('S$_2$C'-H$_2$)$_2$ (12). A yellow suspension of 'N$_2$H$_2$S$_2$'-H$_2$ (5.1 g, 18.45 mmol) in 20 mL of CH(OEt)$_3$ was heated under reflux for 3 h, in the course of which it became a clear solution, from which a yellow-green powder started precipitating. The reaction mixture was cooled to room temperature; the precipitated powder was collected, washed with 30 mL of Et$_2$O, and dried under vacuum. Yield: 2.9 g (55%). Anal. Calcd for $C_{30}H_{28}N_4S_4$ (M_r = 572.78): C, 62.91; H, 4.92; N, 9.78; S, 22.39. Found: C, 63.15; H, 4.38; N, 9.41; S, 22.60. MS (FD): *m/z* 286 (M$^+$), 572 (2M$^+$). ^{1}H NMR (DMSO-d_6, δ (ppm), 270 MHz): 7.3–6.8 (m, 8 H, C$_6$*H*$_4$), 6.7–6.6 (s, 2 H, S*H*), 3.6 (s, 4 H, C$_2$*H*$_4$). ^{13}C{^{1}H} NMR (DMSO-d_6, δ (ppm), 67.94 MHz): 144.1, 128.3, 125.7, 122.5, 120.3, 114.1 (*C*$_6$H$_4$), 119.9 (carbene C), 51.9 (*C*$_2$H$_4$).

('S$_2$CO')$_2$ (13). A suspension of ('S$_2$C'-H$_2$)$_2$ (165 mg, 0.29 mmol) in 10 mL of THF was heated under reflux in air for 6 h, cooled to room temperature, and filtered, and the resulting orange solution was layered with 20 mL of Et$_2$O. The precipitated light brown ('S$_2$CO')$_2$ was collected, washed with 5 mL of Et$_2$O, and dried under vacuum. Yield: 52 mg (30%). Anal. Calcd for $C_{30}H_{24}N_4O_2S_4$ (M_r = 600.78): C, 59.98; H, 4.03. Found: C, 60.09; H, 3.80. MS (FD): *m/z* 600 (M$^+$). IR (KBr): ν_{CO} = 1700 cm^{-1}. ^{1}H NMR (DMSO-d_6, δ (ppm), 270 MHz): 7.9–6.8 (m, 16 H, C$_6$H$_4$), 3.9 (s, 8 H, C$_2$H$_4$). ^{13}C{^{1}H} NMR (DMSO-d_6, δ (ppm), 67.94 MHz): 156.8 (C=O), 137.9, 135.8, 129.1, 128.2, 126.4, 125.3 (C$_6$H$_4$), 45.1 (C$_2$H$_4$).

Results

Synthesis and Reactions of [M('S₂C')] Complexes. Formation of 1·DMF in minor yields was observed for the first time when Ni('N$_2$H$_2$S$_2$')] was recrystallized from hot DMF. Detailed investigations showed that **1** also forms in small yields from [Ni('N$_2$H$_2$S$_2$')] and formic acid and can be obtained in preparative amounts by the one-pot synthesis according to eq 1.[5] **1** proved

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

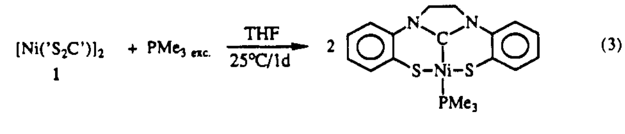
to be unexpectedly stable toward protonic acids such as concentrated H_2SO_4 or HCl. This is remarkable, because thiolate metal complexes usually react with protonic acids under decoordination of the thiolate ligands.[10]

In contrast to its high stability toward electrophilic reagents such as H^+, **1** readily reacts with nucleophiles. Cleavage of binuclear **1** into mononuclear complexes takes place when **1** is dissolved in pyridine, and accordingly, recrystallization of **1** from refluxing pyridine yielded [Ni(py)('S$_2$C')] (**2**) (eq 2). Orange,

$$\underset{\mathbf{1}}{[Ni('S_2C')]_2} \xrightarrow[105\ °C/1\ h]{pyridine} \underset{\mathbf{2}}{2[Ni(py)('S_2C')]} \quad (2)$$

microcrystalline **2** is soluble without decomposition only in pyridine. In all other solvents, e.g., THF, acetone, or DMF, **2** splits off the pyridine ligand and regenerates **1**.

Cleavage of **1** occurred also in reactions with the nucleophiles PMe$_3$, PPh$_3$, and CN$^-$. The PMe$_3$ adduct [Ni(PMe$_3$)('S$_2$C')] (**3**) formed with an excess of PMe$_3$ according to eq 3. **3** crystallizes



[Ni(PMe$_3$)('S$_2$C')], **3**

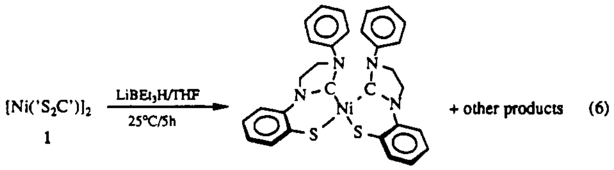
in red needles and readily dissolves in THF, acetone, CH$_2$Cl$_2$, CHCl$_3$, DMF, and DMSO. Like **2**, **4**, and **5**, **3** is diamagnetic and stable toward air at room temperature. In refluxing THF, **3** dissociates PMe$_3$ and regenerates the binuclear **1**. Cleavage of **1** by the bulkier PPh$_3$ required heating and an excess of PPh$_3$ according to eq 4. The resulting [Ni(PPh$_3$)('S$_2$C')] (**4**) crystallized in red needles and dark green prisms which proved to exhibit identical ^1H, ^{13}C, and ^{31}P NMR spectra in solution. The molecular structure of the dark green prisms was elucidated by X-ray structure analysis. The reaction of **1** with NaCN in aqueous THF yielded the [Ni(CN)('S$_2$C')]$^-$ anion, which was isolated as [NMe$_4$][Ni(CN)('S$_2$C')] (**5**) according to eq 5. Orange **5** dissolves in THF, CH$_2$Cl$_2$, acetone, DMF, and DMSO, but not in H$_2$O, MeOH, or Et$_2$O. Suitable single crystals for X-ray structure determination of **5** or other salts of the [Ni(CN)('S$_2$C')]$^-$ anion could not be obtained.

$$\underset{\mathbf{1}}{[Ni('S_2C')]_2} + PPh_{3\,exc} \xrightarrow[65\ °C/1\ d]{THF} \underset{\mathbf{4}}{2[Ni(PPh_3)('S_2C')]} \quad (4)$$

$$\underset{\mathbf{1}}{[Ni('S_2C')]_2} + 2NaCN \xrightarrow[25\ °C/2\ h\ +\ NMe_4^+]{THF/H_2O} \underset{\mathbf{5}}{2[NMe_4][Ni(CN)('S_2C')]} \quad (5)$$

With respect to the nickel centers of CODH, the reactivity of **1** toward species such as CO, CH$_3^-$, H$_2$, and H$^-$ was of special interest. At −30 °C, addition of LiCH$_3$ to the red-brown suspensions of **1** in THF yielded red solutions which were extremely sensitive toward moisture and air, changed color to dark brown at temperatures around 0 °C, and could not be characterized more closely. Attempts to precipitate a potentially formed [Ni(CH$_3$)('S$_2$C')]$^-$ anion by addition of NMe$_4$Cl or AsPh$_4$Cl failed. No reaction was observed between **1** in THF and H$_2$ (150 bar), but with CO (150 bar), deep red solutions formed which contained a very labile species. When the autoclave was opened, these solutions immediately started evolving gas and **1** precipitated as microcrystalline and analytically pure powder.

In order to obtain hydride complexes, **1** was reacted with NaBH$_4$ in THF or MeOH and with LiBEt$_3$H in THF. No reaction took place with NaBH$_4$; with LiBEt$_3$H, however, the nickel biscarbene complex [Ni('SC')$_2$] (**6**) formed in the completely unexpected reaction according to eq 6. Formation of **6** from **1** requires partial desulfuration of the 'S$_2$C'$^{2-}$ ligand and intermolecular transfer of the resulting 'SC'$^-$ ligand ('SC'$^-$ = 1,3-imidazolidinyl-*N*-phenyl-*N*'-(2-benzenethiolate)(1−)). Diamagnetic **6** crystallizes in red-brown prisms and is soluble in THF, DMF, and DMSO.



[Ni('SC')$_2$], **6**

Formation of other metal complexes with the novel 'S$_2$C' ligand was investigated with palladium and platinum. [Pd('S$_2$C')]$_2$·DMF (**7**·DMF) and [Pt('S$_2$C')]$_2$·DMF (**8**·DMF) formed in the one-pot syntheses according to eq 7, where M = Pd (**7**·DMF) or Pt (**8**·DMF). **7**·DMF and **8**·DMF were isolated as olive-green microcrystals and exhibit properties and reactivity similar to **1**. For instance, they are soluble only in donor solvents such as pyridine, by which they are cleaved to give the mononuclear pyridine complexes [Pd(py)('S$_2$C')], (**9**) and [Pt(py)('S$_2$C')] (**10**) according to eq 8, **9** and **10** crystallize in yellow plates and are labile. When dissolved in THF, they lose pyridine and yield the binuclear starting complexes **7** and **8**. **8** was also reacted with PMe$_3$ according to eq 9. Like the analogous **3**, the resulting yellow [Pt(PMe$_3$)('S$_2$C')] (**11**) is diamagnetic, stable toward air, and exhibits comparable solubilities. **11** was characterized by X-ray structure analysis and is isomorphic to **3**.

$$2[MCl_2(COD)] + 2'N_2H_2S_2'\text{-}H_2 + 2CH(OEt)_3 \xrightarrow[153\ °C/3\ h]{DMF} [M('S_2C')]_2\cdot DMF + \text{other products} \quad (7)$$

$$\underset{M\ =\ Pd\ (\mathbf{7})\ or\ Pt\ (\mathbf{8})}{[M('S_2C')]_2} \xrightarrow[25\ °C]{pyridine} \underset{M\ =\ Pd\ (\mathbf{9})\ or\ Pt\ (\mathbf{10})}{2[M(py)('S_2C')]} \quad (8)$$

$$\underset{\mathbf{8}}{[Pt('S_2C')]_2} + PMe_{3\,exc} \xrightarrow[65\ °C/2\ h]{THF} \underset{\mathbf{11}}{2[Pt(PMe_3)('S_2C')]} \quad (9)$$

Spectra and Cyclic Voltammetry of the Complexes. All [M('S$_2$C')] complexes exhibit similar IR (KBr) spectra in the range of 4000–600 cm^{-1}. Characteristic of the [M('S$_2$C')] fragment is an intensive and sharp band at 1300 cm^{-1}. In addition, the PMe$_3$ complexes **3** and **11** show characteristic δ_{PCH} bands at

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(10) (a) Sellmann, D.; Reisser, W. *Z. Naturforsch.* **1984**, *39B*, 1268. (b) Sellmann, D.; Reisser, W. *J. Organomet. Chem.* **1985**, *294*, 333.

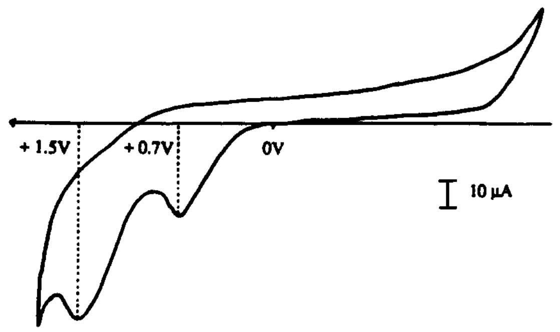


Figure 1. Cyclic voltammogram of **2** (pyridine, 100 mV/s, potentials vs NHE).

950 cm^{-1}, the PPh$_3$ complex **4** shows an intensive band at 700 cm^{-1}, and the cyano complex **5** shows the ν_{CN} band at 2110 cm^{-1}. In the FD mass spectra, the molecular ions could be observed for **1**, **3**, **4**, **6**–**8**, and **11**, whereas the spectra of the pyridine complexes **2**, **9**, and **10** and of the salt **5** exhibited only the fragment ions [M('S$_2$C')]$^+$ (M = Ni, Pd, Pt), and the [Ni(CN)('S$_2$C')]$^+$ ion.

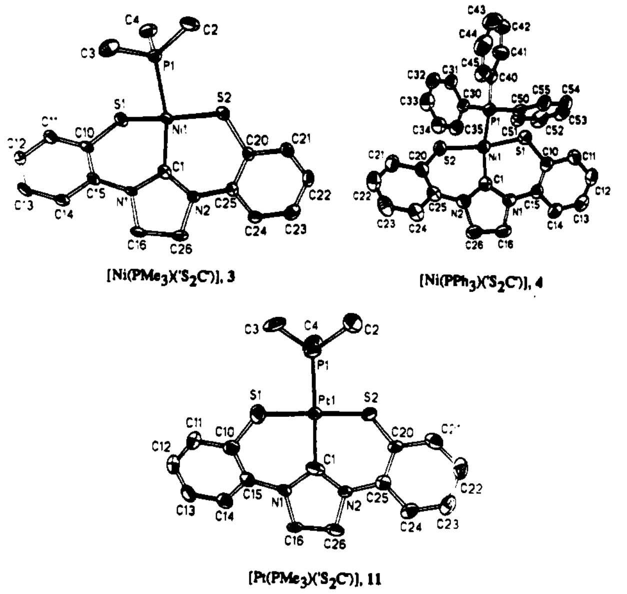
Cyclic voltammograms (CV) were recorded of **2** in pyridine and of **3** and **5** in THF. The CVs were nearly identical and each exhibited only two irreversible oxidation waves at about +0.7 and +1.5 V. Figure 1 displays the CV of **2**.

These results showed that the carbene complexes are inert in the redox range of nickel enzymes at about –0.4 V[3c] and, with respect to electrochemistry, rather behave like the Ni(II)–thioether–thiolate complexes [Ni('S$_4$-C$_5$')] or [Ni('OS$_4$')]$_2$ ('S$_4$-C$_5$'$^{2-}$ = 1,5-bis((2-mercaptophenyl)thio)propanato(2–), 'OS$_4$'$^{2-}$ = bis(2-((2-mercaptophenyl)thio)ethyl)etherato(2–)).[11]

NMR Spectra. Because the binuclear [M('S$_2$C')]$_2$ complexes **1** (Ni), **7** (Pd), and **8** (Pt) dissolve only in donor solvents such as pyridine yielding the mononuclear [M(py)('S$_2$C')] complexes **2**, **9**, and **10**, [M('S$_2$C')]$_2$ and [M(py)('S$_2$C')] complexes each show identical NMR spectra in pyridine. In the ^{1}H NMR spectra, all complexes exhibit nearly the same splitting of C$_6$H$_4$ and C$_2$H$_4$ protons of the 'S$_2$C'$^{2-}$ ligand, and only the biscarbene complex **6** showed a different pattern.

The same holds for the ^{13}C NMR spectra. The ^{13}C NMR spectra of **1**, **7**, and **8** in pyridine unambiguously indicate that the binuclear complexes having C_i symmetry are cleaved into mononuclear complexes possessing C_s symmetry, because the 12 aromatic C atoms of the [M('S$_2$C')] units give rise to only six ^{13}C NMR signals. The ^{13}C C(carbene) signals of the nickel complexes **2**, **3**, and **5** are found in the narrow range of 187.0–184.9 ppm and demonstrate that coordination of electronically different ligands such as py, PMe$_3$, and CN$^-$ in trans position to the C(carbene) atom has practically no influence on the ^{13}C NMR shift of the C(carbene) atom. This may be traced back to the geometrically rigid structure of the [Ni('S$_2$C')] fragment and the fact that the electron density at the nickel center is mainly determined by the thiolate ligands which are electron rich and possess σ-donor/π-donor properties.

In this context the ^{13}C C(carbene) shift of **10** (168.5 ppm) is to be noted. When compared with the ^{13}C C(carbene) shift of **2** (184.9 ppm), it is shifted about 15 ppm to higher field and possibly indicates that **10** in pyridine coordinates one additional pyridine molecule yielding [Pt(py)$_2$('S$_2$C')] with five-coordinate platinum. In all cases, the large ^{13}C C(carbene) highfield shifts characterize the carbene ligands as nucleophilic. Carbene complexes normally exhibit ^{13}C NMR shifts in the range of 250–220 ppm, and the so-called electrophilic carbene complexes even in the range up to 350 ppm.[12,20] In this respect, it is surprising that so far no reaction of [Ni('S$_2$C')]$_2$ with protons could be observed.



[Ni(PMe$_3$)('S$_2$C')], 3 [Ni(PPh$_3$)('S$_2$C')], 4

[Pt(PMe$_3$)('S$_2$C')], 11

Figure 2. Molecular structures of (a) [Ni(PMe$_3$)('S$_2$C')] (**3**), (b) [Ni(PPh$_3$)('S$_2$C')] (**4**), and (c) [Pt(PMe$_3$)('S$_2$C')] (**11**) (H atoms omitted).

X-ray Structure Determination of 3, 4, 6, and 11. The molecular structures of **3**, **4**, and **11** are shown in Figure 2; selected distances and angles are listed in Tables VII–IX, respectively. **3**, **4** and **11** have nearly identical structures. In all three complexes, the metal centers are coordinated by two sulfur, one phosphorus, and one C(carbene) donor in a distorted plane. The metal and 'S$_2$C'$^{2-}$ donors form planes from which the P donors deviate 106 pm in **3**, 119 pm in **4**, and 48 pm in **11**.

Ni–S distances (214–218 pm) and Ni–P distances (222–224 ppm) in **3** and **4** are typical of planar low-spin Ni(II)–thiolate or phosphine complexes.[11,13] Due to the larger radius of platinum, the average M–S distances in the platinum complex **11** (230.1 (4), 231.1 (4) pm) are longer than in the nickel complexes **3** and **4**.[14] The nickel–C(carbene) distances in the binuclear **1**·DMF (186.3 (5) pm), in **3** (190.3 (6) pm), and in **4** (187.6 (5) pm) are

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(11) (a) Sellmann, D.; Fünfgelder, S.; Pöhlmann, G.; Knoch, F.; Moll, M. *Inorg. Chem.* **1990**, *29*, 4772. (b) Sellmann, D.; Fünfgelder, S.; Knoch, F.; Moll. M. *Z. Naturforsch.* **1991**, *46B*, 1601.

(12) (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983. (c) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121.

(13) (a) Sellmann, D.; Schillinger, H.; Knoch, F.; Moll, M. *Z. Naturforsch.* **1992**, *47B*, 748. (b) Krüger, T.; Krebs, B.; Henkel, G. *Angew. Chem.* **1992**, *104*, 71; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 54.

(14) Cardin, D. J.; Cetinkaya, B.; Cetinkaya, E.; Lappert, M. F.; Manojlovic-Muir, J. *J. Organomet. Chem.* **1972**, *44*, C59.

(15) (a) Dean, W. K.; Charles, R. S.; VanDerVeer, D. G. *Inorg. Chem.* **1977**, *16*, 3328. (b) Miki, K.; Taniguchi, H.; Kai, Y.; Kasai, N.; Nishiwaki, K.; Wada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1178.

(16) (a) Dong, D. F.; Hoyano, J. K.; Graham, W. A. G. *Can. J. Chem.* **1981**, *59*, 1455. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (c) Wassermann, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294. (d) Kubas, G. J. *Acc. Chem. Res.* **1988**, *23*, 120.

(17) (a) Regitz, M. *Angew. Chem.* **1991**, *103*, 691; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674. (b) Hoffmann, R. W. *Angew. Chem.* **1968**, *80*, 823; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 754. (c) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(18) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(19) (a) Wanzlick, H.-W. *Angew. Chem.* **1962**, *74*, 129. (b) Cetinkaya, E.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Spyropoulos, K. *J. Chem. Soc., Perkin Trans. 1* **1992**, 561.

(20) (a) Lappert, M. F.; Dye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172. (b) Lappert, M. F. *J. Organomet. Chem.* **1975**, *100*, 139. (c) Coleman, A. W.; Hitchcock, P. B.; Lappert, M. F.; Maskell, R. K.; Müller, J. C. *J. Organomet. Chem.* **1985**, *296*, 173. (d) Davie, C. H.; Game, C. H.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 357. (e) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545.

Table VII. Selected Distances (pm) and Angles (deg) of $[Ni(PMe_3)(`S_2C')]$ (**3**)

	Distances		
Ni(1)–P(1)	222.2 (2)	Ni(1)–S(1)	218.3 (2)
Ni(1)–S(2)	214.6 (2)	Ni(1)–C(1)	190.3 (6)
S(2)–C(10)	174.7 (6)	C(1)–N(1)	135.7 (7)
C(1)–N(2)	135.2 (7)	N(1)–C(15)	140.8 (8)
N(1)–C(16)	149.0 (7)	N(2)–C(25)	141.2 (7)
N(2)–C(26)	147.1 (7)	C(16)–C(26)	150.7 (8)
	Angles		
P(1)–Ni(1)–S(1)	88.1 (1)	P(1)–Ni(1)–S(2)	91.5 (1)
S(1)–Ni(1)–S(2)	166.2 (1)	P(1)–Ni(1)–C(1)	160.9 (2)
S(1)–Ni(1)–C(1)	90.8 (2)	S(2)–Ni(1)–C(1)	93.9 (2)
Ni(1)–C(1)–N(1)	123.3 (4)	Ni(1)–C(1)–N(2)	128.6 (4)
N(1)–C(1)–N(2)	107.8 (5)	C(1)–N(1)–C(15)	129.9 (5)
C(1)–N(1)–C(16)	111.6 (4)	C(15)–N(1)–C(16)	118.4 (4)
C(1)–N(2)–C(25)	128.2 (5)	C(1)–N(2)–C(26)	112.1 (4)
C(25)–N(2)–C(26)	119.3 (4)	N(1)–C(16)–C(26)	101.6 (4)
N(2)–C(26)–C(16)	102.9 (4)		

Table VIII. Selected Distances (pm) and Angles (deg) of $[Ni(PPh_3)(`S_2C')]$ (**4**)

	Distances		
Ni(1)–P(1)	223.6 (2)	Ni(1)–S(1)	218.1 (2)
Ni(1)–S(2)	214.8 (2)	Ni(1)–C(1)	187.6 (5)
S(2)–C(10)	175.1 (5)	C(1)–N(1)	137.1 (5)
C(1)–N(2)	134.5 (7)	N(1)–C(15)	141.0 (7)
N(1)–C(16)	147.4 (7)	N(2)–C(25)	142.2 (6)
N(2)–C(26)	147.8 (6)	C(16)–C(26)	150.3 (8)
	Angles		
P(1)–Ni(1)–S(1)	90.2 (1)	P(1)–Ni(1)–S(2)	91.8 (1)
S(1)–Ni(1)–S(2)	160.8 (1)	P(1)–Ni(1)–C(1)	161.6 (2)
S(1)–Ni(1)–C(1)	89.6 (1)	S(2)–Ni(1)–C(1)	94.4 (1)
Ni(1)–C(1)–N(1)	122.4 (4)	Ni(1)–C(1)–N(2)	129.6 (3)
N(1)–C(1)–N(2)	107.4 (4)	C(1)–N(1)–C(15)	128.8 (4)
C(1)–N(1)–C(16)	111.6 (4)	C(15)–N(1)–C(16)	119.5 (4)
C(1)–N(2)–C(25)	127.5 (4)	C(1)–N(2)–C(26)	112.7 (4)
C(25)–N(2)–C(26)	119.6 (5)	N(1)–C(16)–C(26)	102.9 (4)
N(2)–C(26)–C(16)	102.7 (5)		

Table IX. Selected Distances (pm) and Angles (deg) of $[Pt(PMe_3)(`S_2C')]$ (**11**)

	Distances		
Pt(1)–S(1)	230.1 (4)	Pt(1)–S(2)	231.1 (4)
Pt(1)–C(1)	202.0 (13)	Pt(1)–P(1)	230.9 (4)
S(1)–C(10)	177.1 (14)	S(2)–C(20)	173.9 (14)
N(1)–C(1)	137.4 (16)	N(1)–C(15)	140.7 (17)
N(1)–C(16)	148.6 (15)	N(2)–C(1)	135.7 (18)
N(2)–C(25)	142.1 (17)	N(2)–C(26)	145.8 (15)
C(16)–C(26)	152.6 (20)		
	Angles		
S(1)–Pt(1)–S(2)	176.2 (2)	S(1)–Pt(1)–C(1)	90.0 (4)
S(2)–Pt(1)–C(1)	88.8 (4)	S(1)–Pt(1)–P(1)	93.1 (1)
S(2)–Pt(1)–P(1)	88.5 (1)	C(1)–Pt(1)–P(1)	171.4 (4)
C(1)–N(1)–C(15)	129.4 (10)	C(1)–N(1)–C(16)	110.9 (10)
C(15)–N(1)–C(16)	119.2 (10)	C(1)–N(2)–C(25)	127.8 (10)
C(1)–N(2)–C(26)	112.4 (10)	C(25)–N(2)–C(26)	119.1 (11)
Pt(1)–C(1)–N(1)	124.7 (10)	Pt(1)–C(1)–N(2)	127.4 (9)
N(1)–C(1)–N(2)	107.8 (10)	N(1)–C(16)–C(26)	101.7 (10)
N(2)–C(26)–C(16)	102.7 (10)		

only slightly different and characteristic of Ni(II)–carbene complexes.[15] As discussed above, the Ni–C bond is little influenced only by the different trans ligands such as thiolates in **1** or phosphines in **3** and **4**. The platinum–C(carbene) distance in **11** (202.0 (13) pm) is longer than in nickel complexes, but also not unusual.[14]

In the five-membered C(carbene)N_2C_2 rings, the average distances between C(carbene) atoms and N substituents in **3** (135.5 pm), **4** (135.8 pm), and **11** (136.5 pm) each are considerably shorter than the remaining two C–N distances (N(1)–C(16), N(2)–C(26)), which average 148.0 pm in **3**, 147.6 pm in **4**, and 147.2 pm in **11**. In addition, the C(carbene) atoms and their N substituents each are surrounded trigonally planar by their neighbor atoms such that planar five-membered CN_2C_2 rings result. These findings indicate sp^2 hybridization of the N atoms and double-bond character of the C(carbene)–N bonds.

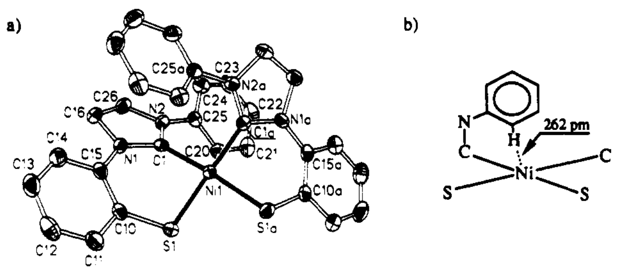


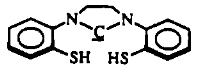
Figure 3. (a) Molecular structure of $[Ni(`SC')_2]$ (**6**) (H atoms omitted). (b) Potential agostic interactions between nickel and the ortho-positioned H atoms of the C_6H_5 rings.

Table X. Selected Distances (pm) and Angles (deg) of $[Ni(`SC')_2]$ (**6**)

	Distances		
Ni(1)–S(1)	217.4 (1)	Ni(1)–C(1)	187.5 (3)
S(1)–C(10)	174.8 (3)	C(1)–N(1)	135.9 (3)
C(1)–N(2)	134.6 (3)	N(1)–C(15)	140.4 (3)
N(1)–C(16)	147.8 (4)	N(2)–C(25)	142.3 (3)
N(2)–C(26)	147.2 (4)	C(16)–C(26)	151.4 (4)
	Angles		
S(1)–Ni(1)–C(1)	90.5 (1)	S(1)–Ni(1)–S(1A)	86.4 (1)
C(1)–Ni(1)–S(1A)	171.0 (1)	C(1)–Ni(1)–C(1A)	93.7 (2)
Ni(1)–S(1)–C(10)	106.2 (1)	Ni(1)–C(1)–N(1)	127.8 (2)
Ni(1)–C(1)–N(2)	125.1 (2)	N(1)–C(1)–N(2)	107.1 (2)
C(1)–N(1)–C(15)	127.4 (2)	C(1)–N(1)–C(16)	112.0 (2)
C(15)–N(1)–C(16)	120.5 (2)	C(1)–N(2)–C(25)	125.5 (2)
C(1)–N(2)–C(26)	114.0 (2)	C(25)–N(2)–C(26)	119.8 (2)
N(1)–C(16)–C(26)	103.2 (2)	N(2)–C(26)–C(16)	101.9 (2)

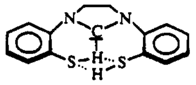
Planar five-membered CN_2C_2 rings also exist in the biscarbene complex **6**. Figure 3a shows the molecular structure; Table X contains selected distances and angles. **6** exhibits a crystallographically imposed C_2 axis. In a distorted plane, the Ni atom is surrounded by two cis thiolate and two cis C(carbene) donors. The resulting trans coordination of thiolate and carbene donors can be attributed to the π-acceptor carbene ligands, which prefer π-donor ligands such as thiolate in trans position, even if a considerable steric hindrance of both C_6H_5 substituents such as in **6** is the consequence. This hindrance is diminished by a propeller-like distortion of both phenyl groups. Possibly this distortion leads to remarkably short distances of 308 pm between the nickel center and the ortho C atoms C(20) and C(20a) such that the corresponding Ni(1)–H(20) and Ni(1)–H(20a) distances are 262 pm, which is only slightly more than the sum of the atomic and van der Waals radii of Ni (125 pm) and hydrogen (120 pm).[16] Ni–S distances (217.4 (1) pm) and Ni–C(carbene) distances (187.5 (3) pm) in **6** correspond with those found in **1**, **3**, or **4**.

Synthesis of $(`S_2C'-H_2)_2$. Carbenes which can be isolated at standard conditions are extraordinarily rare. One example is the recently described "Arduengo" carbene, whose C(carbene) atom is stabilized through steric protection and electron-donating N substituents.[17,18] Thus, it was tempting to obtain the free carbene ligand $`S_2C'-H_2$ (**12a**) whose C(carbene) atom could be potentially



12a

12b



12c

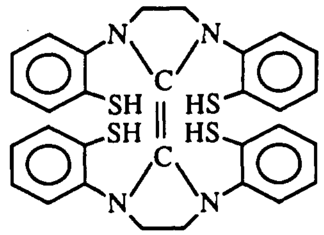
stabilized by the lone pairs of the thiolate atoms via σ–π-donor bonds (**12b**), by intramolecular H bridges (**12c**), or by both effects.

As mentioned above, the $`S_2C'^{2-}$ ligand could not be decoordinated from **1**, either by hydrolysis with strong protonic acids or by reaction with an excess of NaCN. Thus we have tried to obtain it in a direct synthesis according to eq 10. A yellowish

$$2\text{'N}_2\text{H}_2\text{S}_2\text{'-H}_2 + 2\text{CH(OEt)}_3 \xrightarrow[153\ ^\circ\text{C}/3\ \text{h}]{\text{DMF}} \underset{\mathbf{12}}{(\text{'S}_2\text{C'-H}_2)_2} + 6\text{EtOH} \quad (10)$$

powder, **12**, formed which is air sensitive and soluble in common solvents such as THF, CH_2Cl_2, or toluene. Its elemental analysis, mass spectra, and ^{1}H NMR as well as ^{13}C NMR spectra were compatible with the wanted carbene 'S$_2$C'-H$_2$. In addition to a signal at m/z 286 for the molecular ion ['S$_2$C'-H$_2$]$^+$, however, the mass spectra also exhibited a signal at m/z 572 corresponding to the dimeric ion [('S$_2$C'-H$_2$)$_2$]$^+$. Osmometric determination of the molecular mass of **12** in DMF yielded a mass of 571 and finally proved unambigously that **12** in solution had to be formulated as dimeric species ('S$_2$C'-H$_2$)$_2$.

^{1}H NMR and ^{13}C NMR spectra did not allow differentiation between a monomeric and dimeric species. The ^{1}H NMR spectrum of **12** displayed a broad SH signal at 6.6 ppm, a multiplet for the aromatic protons in the typical range of 7.3–6.8 ppm, and a sharp singlet for the C_2H_4 protons at 3.6 ppm. This singlet indicated that **12** possesses at least twofold symmetry, which was corroborated by the number of signals observed in the ^{13}C NMR spectrum. The ^{13}C signal at 119.9 ppm was compatible with a C(carbene) atom such as in **12a** as well as with an olefinic C atom such as in **12d**. Distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR spectra proved that the C atom giving rise to the ^{13}C NMR signal at 119.9 ppm binds no H atom.



('S$_2$C'-H$_2$)$_2$, **12d**

In conclusion, all results indicate the olefin structure **12d** of ('S$_2$C'-H$_2$)$_2$; however, they do not completely exclude minor dissociation of **12d** into **12a** according to

$$(\text{'S}_2\text{C'-H}_2)_2 \rightleftharpoons 2\text{'S}_2\text{C'-H}_2 \quad (11)$$

Such a dissociation may be deduced from the reaction according to eq 12, which gave **1** in high yields. In order to elucidate the molecular structure of **12**, we tried to obtain single crystals by recrystallizing **12** from refluxing toluene. These attempts so far yielded **12** only as fine powder; in one experiment, however, crystals of ('S$_2$CO')$_2$ (**13**) were obtained which had formed through unintentional oxidation of **12** by air. **13** was characterized by X-ray structure analysis, Figure 4 shows its molecular structure, and Table XI contains selected distances and angles. **13** formally derives from two molecules of **12a** via formation of two disulfide bridges and oxygenation of the C(carbene) atoms. Figure 5 schematically displays another view of **13** showing the strongly bent shape of **13** and demonstrating that the geometry of the 'S$_2$CO' units totally differs from the geometry of the ('S$_2$C')$^{2-}$ ligands in [M('S$_2$C')] complexes.

$$2\text{NiCl}_2 + \underset{\mathbf{12}}{(\text{'S}_2\text{C'-H}_2)_2} \xrightarrow[153\ ^\circ\text{C}/3\ \text{h}]{\text{DMF}} \underset{\mathbf{1\cdot DMF}}{[\text{Ni('S}_2\text{C')}]_2\cdot\text{DMF}} + 4\text{HCl} \quad (12)$$

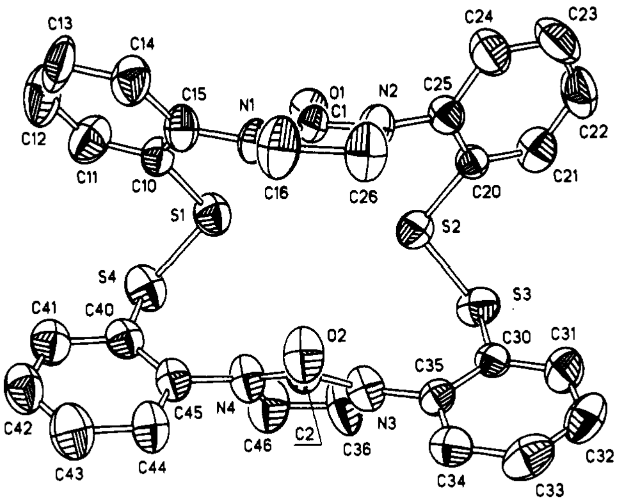


Figure 4. Molecular structure of ('S$_2$CO')$_2$ (**13**) (H atoms omitted).

Table XI. Selected Distances (pm) and Angles (deg) of ('S$_2$CO')$_2$ (**13**)

Distances			
S(1)–S(4)	205.9 (3)	S(1)–C(10)	178.6 (9)
S(2)–S(3)	204.7 (3)	S(2)–C(20)	179.3 (6)
N(1)–C(1)	139.4 (10)	N(1)–C(15)	139.6 (9)
N(1)–C(16)	147.2 (9)	N(2)–C(1)	136.8 (9)
N(2)–C(25)	142.8 (9)	N(2)–C(26)	145.6 (10)
C(1)–O(1)	120.6 (9)	C(16)–C(26)	149.1 (10)
Angles			
S(4)–S(1)–C(10)	101.6 (3)	S(3)–S(2)–C(20)	104.8 (2)
S(2)–S(3)–C(30)	103.2 (3)	S(1)–S(4)–C(40)	104.6 (2)
C(1)–N(1)–C(15)	122.5 (6)	C(1)–N(1)–C(16)	111.2 (5)
C(15)–N(1)–C(16)	122.7 (6)	C(1)–N(2)–C(25)	123.1 (6)
C(1)–N(2)–C(26)	114.4 (6)	C(25)–N(2)–C(26)	122.2 (6)
N(1)–C(1)–N(2)	105.4 (6)	N(1)–C(1)–O(1)	127.1 (6)
N(2)–C(1)–O(1)	127.5 (7)	N(1)–C(16)–C(26)	104.4 (6)
N(2)–C(26)–C(16)	102.2 (6)		

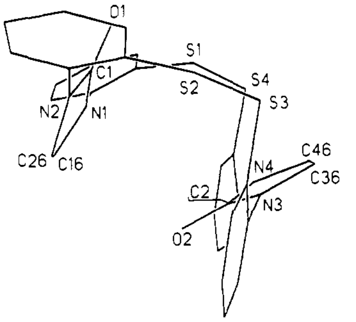


Figure 5. Schematic side view of the molecular structure of ('S$_2$CO')$_2$ (**13**).

The five-membered CN_2C_2 rings of the 'S$_2$CO' units are also planar, but they are no longer coplanar to the phenyl groups. Distances and angles of **13** exhibit no anomalies.[21]

Summary and Discussion

The highly stable nickel thiolate carbene complex **1** was obtained in a one-pot synthesis from $NiCl_2$, 'N$_2$H$_2$S$_2$'-H$_2$, and CH(OEt)$_3$. The reaction mechanism remains open, but the reaction between 'N$_2$H$_2$S$_2$'-H$_2$ and CH(OEt)$_3$ yielding **12**, which subsequently gave **1** when reacted with $NiCl_2$, allows the assumption that primarily the ligand forms.

1 was obtained in minor amounts for the first time when [Ni('N$_2$H$_2$S$_2$')] was recrystallized from DMF. Subsequently, we found that **1** forms from [Ni('N$_2$H$_2$S$_2$')] and formic acid, but in minor yields only.[5] These results allow us to suggest an

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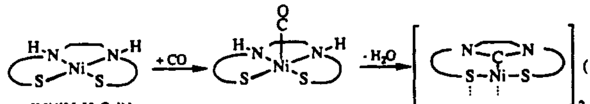
(21) (a) Müller, A.; Pohl, S.; Dartmann, M. *Z. Naturforsch.* **1979**, *34B*, 434. (b) Akbar Ali, M.; Livingstone, S. E. *Coord. Chem. Rev.* **1974**, *13*, 101.

alternative mechanism. DMF or formic acid serve as C_1 sources, releasing CO which coordinates to [Ni('$N_2H_2S_2$')] and inserts into the Ni–N bonds under elimination of H_2O according to eq 13.



[Ni('$N_2H_2S_2$')] [Ni('S_2C')]$_2$, **1**

(13)

C = C_6H_4

Regardless of which mechanism comes true, however, **1** always forms from Ni(II) salts, the thiolate amine ligand '$N_2H_2S_2$'-H_2, and C_1 components such as DMF, HCOOH, or $CH(OEt)_3$. The general applicability of the synthesis involving $CH(OEt)_3$ was proved by the synthesis of homologous palladium and platinum complexes.

One of the most remarkable features of the [M('S_2C')] fragments is their extraordinary stability. While thiolate metal complexes usually decoordinate their thiolate ligands when treated with strong protonic acids, **1** proved to be absolutely stable toward hydrochloric acid.

The high stability of [M('S_2C')] fragments also became apparent in the reactions of the binuclear [M('S_2C')]$_2$ complexes with nucleophiles such as pyridine, PMe_3, PPh_3, and even cyanide. Cleavage into mononuclear [M(L)('S_2C')] complexes always took place but decoordination of the 'S_2C'$^{2-}$ ligand did not, even when, for instance, **1** was reacted with an excess of NaCN.

A change of the [M('S_2C')] fragment was observed only when **1** was reacted with $LiBEt_3H$. The 'S_2C'$^{2-}$ ligands were partially desulfurated to give 'SC'$^-$ ligands, and in a completely unexpected way, the bis(carbene) complex **6** formed. The primary step of this reaction may be cleavage of **1** and formation of the mononuclear nickel hydride complex [Ni(H)('S_2C')]$^-$, which undergoes subsequent reactions including intermolecular ligand-transfer processes.

Despite the sterical hindrance caused by the phenyl substituents, cis coordination of the two carbene ligands in **6** is preferred and can be traced back to the different donor character of carbene and thiolate ligands. In addition, the sterical hindrance is decreased by a propeller-like distortion of the phenyl substituents which simultaneously leads to very short Ni–H–C distances.

The stability of the [M('S_2C')] fragments is attributed to several facts: (1) Two-electron-donating N substituents stabilize the electron-deficient C(carbene) atom as in the comparable "Wanzlick"[19] or "Arduengo"[18] carbenes, or the large number of "Lappert-type" carbene complexes.[20] This effect is indicated by the double-bond character of the respective CN bonds, which can be deduced from the distances. (2) The 'S_2C'$^{2-}$ ligand is tridentate and functions as chelate. (3) Via their lone pairs, the thiolate donors of the 'S_2C'$^{2-}$ ligand form π-donor bonds to the metal center, increase the electron density at the metal, and indirectly strengthen the π-back-bonding from metal to carbene ligand. (4) As a further consequence of thiolate metal π-donor bonds, the Lewis basicity of the thiolate S atoms is reduced such that, at least partly, the inertness of [M('S_2C')] units toward protonic acids can be rationalized.

Attempts to obtain the free 'S_2C'$^{2-}$-H_2 carbene lead to isolation of dimeric **12**. Its properties indicate that it is an olefin in which both C(carbene) atoms of the 'S_2C'$^{2-}$ ligand are linked by a C=C double bond. Oxidation of **12** with oxygen yielded **13**. **13** formally derives from the monomeric 'S_2C'$^{2-}$ ligand by formation of two disulfide bridges and oxygenation of the C(carbene) atom.

The described complexes probably cannot be regarded as model compounds for the active sites in nickel enzymes, but the formation and cleavage of Ni–C bonds in nickel sulfur centers, which were observed here, also represent essential steps of the reactions which are catalyzed by CO dehydrogenases.[3]

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Supplementary Material Available: Listing of crystallographic data and data collection parameters, all bond lengths and bond angles, anisotropic thermal parameters, and fractional coordinates of hydrogen atoms for **3**, **5**, **11**, **6**, and **13** (19 pages). Ordering information is given on any current masthead page. Further details of X-ray crystal structure analyses have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe, W-7514 Eggenstein-Leopoldshafen 2, Germany, by citing the deposition numbers CSD-320451 ([Ni(PMe_3)('S_2C')]), CSD-320449 ([Ni(PPh_3)('S_2C')]), CDS-320447 ([Ni('SC')$_2$]), CSD-320450 ([Pt(PMe_3)('S_2C')]), and CSD-320448 (('S_2CO')$_2$), the authors, and the reference.