The Methylene Adduct of Bis(1,2-diphenyl-1,2-ethylenedithiolato)nickel(II): A Nickel(II) Complex of *cis*-(Methylenethio)stilbenethiol Which Cyclodimerizes to 4,5,9,10-Tetraphenyl-1,3,6,8-tetrathia-4,9-cyclodecadiene

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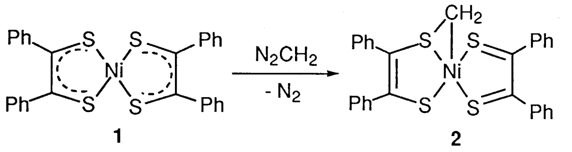
The reaction of bis(1,2-diphenyl-1,2-ethylenedithiolato)-nickel(II), $Ni(S_2C_2Ph_2)_2$, with diazomethane affords a 1:1 methylene adduct, $Ni[CH_2(S_2C_2Ph_2)_2]$ (**2**), which is identified as a nickel(II) complex of *cis*-(methylenethio)stilbenethiol (**3**). Ligand **3** cyclodimerizes, on decomposition of **2** or by reaction of **2** with 2,2'-bipyridyl, to yield 4,5,9,10-tetraphenyl-1,3,6,8-tetrathia-4,9-cyclodecadiene.

The metal-sulfur bonds in a variety of derivatives of (η^5-cyclopentadienyl)(ethylene-1,2-dithiolato)cobalt(III) complexes, $CpCo(S_2C_2R_2)$ ($Cp = \eta^5\text{-}C_5H_5$; $R = CO_2Me$, Ph, H, CN), have previously been shown[1] to react with diazomethane to yield unusual methylene adducts with evolution of N_2 containing a C-Co-S three-membered ring which decompose photochemically or thermally in cyclohexene to give the parent complex $CpCo(S_2C_2R_2)$ and methylene addition- and insertion-products[1a] similar to those resulting from the thermal decomposition or direct photolysis of N_2CH_2 in cyclohexene.[2] In view of these results we investigated the reaction of the planar Ni(II) derivative of *cis*-stilbene-1,2-dithiol,[3] $Ni(S_2C_2Ph_2)_2$ (**1**), with N_2CH_2. Nickel complexes such as **1**, in contrast to dithiolene derivatives of CoCp, possess an *electronically delocalized ground state* and a high residual electron affinity which renders them comparable to quinones.[3] We will show in the following that a typical complex of this type forms a methylene adduct exhibiting properties substantially different from the previously reported CoCp dithiolene derivatives.

A solution of N_2CH_2 (0.60 g, 14.3 mmol) in diethylether (100 ml) was added to a solution of complex **1** (2.60 g, 4.78 mmol) in dichloromethane (1000 cm^3) at 0 °C. The color changed from green to green-black and the reaction mixture was stirred for 5 min. The solvent was removed under reduced pressure. The crude product was purified by dissolving in 50 ml of benzene/dichloromethane (1:1) at 0 °C and reprecipitating with hexane.[4]



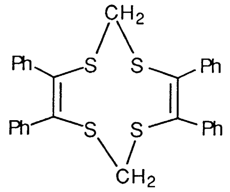
1 2 (1)

The structure of **2** was determined on the basis of the similarity of its physical and spectroscopic properties with the previously described alkylidene derivatives of CoCp,[1] and which contains a C-S-Ni three-membered ring. The structure of **2** is also consistent with its deep black color in the solid state, its uv-vis absorption spectra in solution, and its reaction with HI in THF which leads to quantitative recovery of **1** and the formation of CH_3I.

The mechanism of the addition reaction in eq 1 can be elucidated in the same way as CoCp complexes;[1] the reaction should be initiated by the nucleophilic attack of diazomethane at nickel atom of **1** followed by the elimination of N_2. On the other hand and unlike to the behavior of the CoCp complexes, **2** does not release the methylene moiety to any appreciable extent on thermolysis and photolysis. In the mass spectrum (EI) of **2**, the first and most prominent primary fragment has the mass of 256, corresponding to $CH_2S_2C_2Ph_2$, indicating that **2** thus could also be described as a complex having the hypothetical ligand, *cis*-(methylenethio)stilbenethiol (**3**), formally best written as a 1,5-dipole, $^{(+)}CH_2\text{-}S\text{-}C(Ph)\text{=}C(Ph)\text{-}S^{(-)}$.

Although **2** is stable in the solid state, it was found to decompose spontaneously in solvents such as benzene, dichloromethane, toluene or tetrachloroethane, according to eq 2.[5]

$$2 \longrightarrow 1/2$$



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$$+\ 1/2\ \mathbf{1}\ +\ 1/2\ [\mathrm{Ni}] \qquad (2)$$

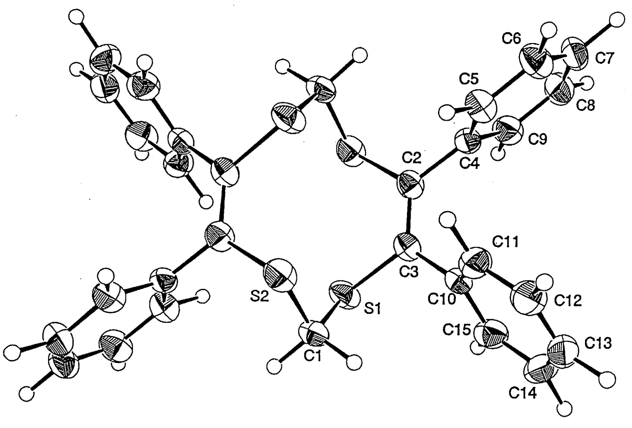


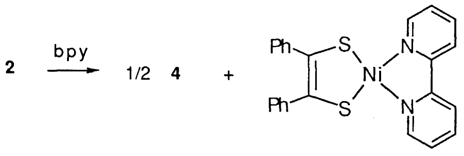
Figure 1. Molecular structure of **4**.
Selected bond lengths (Å) and angles (deg) are as follows: S(1)-C(1) 1.807(2), S(1)-C(3) 1.775(2), S(2)-C(1) 1.816(2), C(2)-C(3) 1.343(3), C(3)-C(10) 1.489(3), S(1)-C(1)-S(2) 113.8(1), C(1)-S(1)-C(3) 100.1(1), S(1)-C(3)-C(10) 115.0(1).

A solution of **2** (50.0 mg, 0.0897 mmol) in C_6H_6/CH_2Cl_2 (1 ml, 1:1) was kept for 72 hours in the dark at room temperature. The color of the solution changed from black to green. After filtration of the reaction mixture[6] and removal of the solvent at reduced pressure, the residue was chromatographed on silica-gel

(Merck, silica gel 60; Eluent: CH_2Cl_2/n-Hexane) to afford the dimer of **3**, 4,5,9,10-tetraphenyl-1,3,6,8-tetrathia-4,9-cyclodecadiene (**4**), as a colorless crystalline solid in 88.3% yield (20.3 mg, 0.0396 mmol) and parent complex **1** in 87.6% (21.4 mg, 0.0393 mmol).[7] The structure of **4** was confirmed by x-ray structural analysis (Figure 1).[8]

The tendency of **2** to cause ligand-cyclodimerization rather than release its methylene fragment suggests that the Ni-C bond in **2** undergoes heterolytic cleavage with electrons being transferred into the $NiS_2C_2Ph_2$ moiety, a reaction enabled by the electron deficient nature of the Ni-bound $S_2C_2Ph_2$ ligand.[3] A similar driving force is absent in the corresponding methylene adducts of the CoCp dithiolenes which release the methylene fragment instead.[1a]

The cyclic thioether **4**, together with the known[9] complex (bpy)$Ni(S_2C_2Ph_2)$ (**5**), are also quantitatively formed on reaction of **2** with excess 2,2'-bipyridyl (bpy), according to eq 3. Mixture of **2** (50.0 mg, 0.0897 mmol) and 2,2'-bipyridyl (250 mg, 1.60 mmol) was heated to 150°C. After 15 minutes the melt was dissolved in CH_2Cl_2. Chromatography on silica gel (Merck, silica gel 60; Eluent: CH_2Cl_2/n-Hexane) afforded **4** in 95.7% (22.0 mg, 0.0429 mmol) and **5** in 68.8 % yield (28.2 mg, 0.0617 mmol) which is identical by comparison with authentic sample.[9]



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(3)

References and Notes

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4 $Ni[CH_2(S_2C_2Ph_2)_2]$ (**2**): black solid, 38.7% yield (1.03 g, 1.85 mmol). mp 199-202 °C (Decomp.). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 2.53 (1 H, d, J_{HH} = 14.5 Hz, CH_2), 3.00 (1 H, d, J_{HH} = 14.5 Hz, CH_2), and 6.77 -7.69 (20 H, m, Aromatic Protons). MS (EI): *m/z* (relative intensity) 256 (100, $Ph_2C_2S_2CH_2$), 210 (40, Ph_2C_2S),178 (56, Ph_2C_2), and 165 (35, PhC_2S_2). IR (KBr): 1585 (w), 1475 (w), 1460 (w), 1430 (m), 1350 (W), 1165 (m), 1060 (W), 1020 (m), 855 (W), 800 (m), 750 (m), 735 (m), 720 (W) and 685 (s) cm^{-1}. UV/VIS (CH_2Cl_2): λ_{max} (ε) 781 nm (2274). Anal. Found: C, 62.56; H, 4.05; S, 24.92; Ni, 10.49%. Calcd for $C_{29}H_{22}S_4Ni$ (557.22): C, 62.49; H, 3.98; S, 23.01; Ni, 10.53%.

5 All the attempts to make the single crystal of **2** for x-ray analysis in these solvents had actually afforded the products according to eq 2. The decomposition of **2** in the solutions is significantly promoted by photo-irradiation or in the presence of an acid.

6 Filtration of the reaction mixture gave brown, mainly nickel-containing residue. The nickel was quantitatively detected with dimethylglyoxime after treatment with acid.

7 **4**: mp 280 °C (decomp.). ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 3.56 (4 H, s, CH_2) and 7.1-7.4 (20 H, m, Aromatic Protons). MS (EI): *m/z* (relative intensity) 512 (4, M^+), 256 (100, $Ph_2C_2S_2CH_2$), 210 (36, Ph_2C_2S), 178 (45, Ph_2C_2), 165 (24, PhC_2S_2), and 121 (35, PhCS). IR (KBr): 1465 (m), 1430 (m), 1365 (m), 1185 (m), 1060 (w), 1020(m), 805 (m), 750 (m), 720 (s), and 685 (s) cm^{-1}. Anal. Found: C, 70.22; H, 4.13; S, 25.23%. Calcd for $C_{30}H_{24}S_4$ (512.53): C, 70.27; H, 4.72; S, 25.01%.

8 Crystal data for **4**: $C_{30}H_{24}S_4$ (F.W. = 512.76), triclinic, space group P1, a = 6.183(1) Å, b = 8.612(1) Å, c = 12.243(2) Å, α = 82.57(1)°, β = 86.14(1)°, γ = 73.56(1)°, V = 619.7(2) Å^3, Z = 1, D_c = 1.374 g.cm^{-3}, μ = 3.59 mm^{-1}. F_{000} = 268.00, R = 0.034 (Rw = 0.063) for 1736 observed reflections [$I > 2\sigma(I)$].

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