Figure 3), which is assigned to an increased contribution from the TBP geometry. As the temperature is lowered, however, the equilibrium shifts to favor the lower energy conformation and the resonances merge into two sets of less well defined resonances that we believe correlate to SP geometry. In solvents such as $CH_2Cl_2$ and acetonitrile where no temperature-dependent shifts are observed, one conformer has an energy low enough to generate a single dominant SP structure.

The simple VDW energy calculations have, once again, proven to be very useful in helping us qualitatively understand the various rotational conformations possible and the pathway energetics between them. We consider it very important to gain a firm understanding of the rotational dynamics in open-mode bimetallic $M_2$(eHTP)-type systems so that we can predict when the two metal centers can approach one another to cooperate in the joint activation of a substrate molecule.

The reduction of $Co_2(CO)_4(eHTP)^{2+}$ by naphthalenide anion produces several diamagnetic bimetallic Co(0) complexes involving both carbonyl and phosphine dissociation. On the basis of one- and two-dimensional $^{31}P$ NMR studies, one of the major products can be confidently assigned as the symmetrical Co–Co-bonded dimer $Co_2(CO)_2$(eHTP), the first example of a M–M-bonded eHTP binuclear species. The very reactive nature of this electron-rich species, unfortunately, kept us from isolating and further characterizing it.

**Acknowledgment.** This work was supported by the National Science Foundation (Grants CHE-86-13089 and CHE-88-23041). The Washington University High-Resolution NMR Service Facility was funded in part through NIH Biomedical Research Support Shared Instrument Grant 1-S10-RR02004 and a gift from the Monsanto Co. We would also like to thank Dr. Suzanne E. Saum (Washington University) for assistance in preparing a number of NMR samples and Prof. Leslie Butler (LSU) for helpful suggestions.

**Supplementary Material Available:** Text containing a detailed experimental NMR section and figures of the 300-MHz 2-D $^1H$–$^1H$ *J*-correlated spectrum of **2** in $CD_2Cl_2$ and 500-MHz 2-D $^1H$–$^1H\{^{31}P\}$ *J*-correlated spectrum of **2** in acetone-$d_6$ (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Revelle College, University of California at San Diego, La Jolla, California 92093

# Synthesis, Properties, and Structure of Bis(*cis*-(methylthio)stilbenethiolato)nickel(II) and Bis(*cis*-bis(methylthio)stilbene)nickel(II) Iodide

G. N. Schrauzer,* Cheng Zhang, and E. O. Schlemper*,[†]

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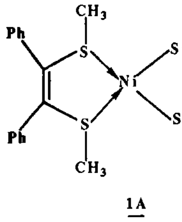
The sulfur atoms in the bis(*cis*-stilbene-1,2-dithiolato)nickel(II) dianion, $[Ni(S_2C_2Ph_2)_2]^{2-} = Ni[S_4C_4Ph_4]^{2-}$, react with alkyl halides to yield unusually stable bis(alkylthio) derivatives of composition $Ni[R_2S_4C_4Ph_4]$, with R = alkyl. The green, diamagnetic complex with $R = CH_3$ crystallizes in space group $P2_1/n$, with unit cell dimensions at 23 °C of $a = 6.127$ (3) Å, $b = 8.001$ (3) Å, $c = 27.663$ (3) Å, $\beta = 93.81$ (2)°, $Z = 2$, and $d_{cald} = 1.407$ g cm$^{-3}$, and is shown to be bis((methylthio)stilbenethiolato)nickel(II), $Ni[PhC(SCH_3){=}C(S)Ph]_2$. The $NiS_4$ moiety is essentially planar with mean Ni–S bond lengths of 2.161 (2) Å. The observed ligand C–S($CH_3$)– and C–S bond lengths of 1.779 (5) and 1.737 (5) Å are in the range of C–S single bonds; the C–C bond distance is 1.352 (7) Å, consistent with an essentially localized electronic structure. The Ni–S–$CH_3$ bond angles of 105.2 (2)° are smaller than expected due to crystal packing forces. In a 1:1 inclusion compound with $CH_2Cl_2$, which crystallizes in space group $P\bar{1}$, with unit cell dimensions $a = 8.424$ (3) Å, $b = 13.461$ (3) Å, $c = 14.745$ (3) Å, $\alpha = 68.93$ (2)°, $\beta = 84.08$ (2)°, $\gamma = 75.10$ (2)°, $Z = 2$, $d_{calc} = 1.45$ g cm$^{-3}$, the lattice expansion causes a normalization of the Ni–S–$CH_3$ angles to 109.2 (2)°. Variable-temperature $^1H$ NMR measurements in solution reveal dynamic equilibria attributed to sulfur inversion and cis–trans isomerization reactions. On heating, decomposition occurs with ligand disproportionation to bis(methylthio)stilbene and nickel(II) stilbenedithiolate, $[Ni(S_2C_2Ph_2)]_x$. The sulfur atoms exhibit residual nucleophilic reactivity on reaction with $CH_3I$, affording a complex of composition $[(CH_3)_2S_2C_2Ph_2]_2NiI_2$, which crystallizes in space group $P2_1/n$, with $a = 8.178$ (3) Å, $b = 11.992$ (3) Å, $c = 18.229$ (5) Å, $\beta = 94.28$ (2)°, $Z = 2$, $d_{calcd} = 1.69$ g cm$^{-3}$. Its structure reveals a linear I–Ni–I moiety with two molecules of symmetrically S-bonded molecules of *cis*-bis(methylthio)stilbene as the ligands in the equatorial positions. The mean Ni–S bond and C–S($CH_3$) bond lengths are 2.379 (9) and 1.803 (4) Å, and the mean Ni–I bond lengths are 2.7989 (2) Å, respectively.

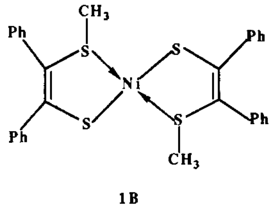
## Introduction

Complexes of transition metals with substituted or unsubstituted *cis*-ethylene-1,2-dithiols of composition $M(S_2C_2R_2)_2 = MS_4C_4R_4$, or $M(S_2C_2R_2)_3 = MS_6C_6R_6$, where R may be H, alkyl, aryl, etc., are commonly known[1,2] as metal dithiolenes. After their discovery in 1960,[3,4] they were widely studied because their spectra and chemical properties suggested a high degree of electronic delocalization and the presence of low-lying unoccupied orbitals, rendering them easily reducible to anionic species.

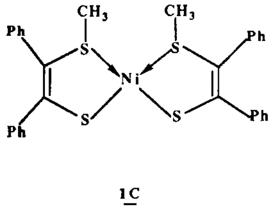
To show that these orbitals were predominantly ligand rather than metal based, as indicated by some of the MO treatments, the dianion $[NiS_4C_4Ph_4]^{2-}$, where Ph = $C_6H_5$, was reacted with alkylating agents. With methyl iodide a neutral dimethyl derivative of composition $Ni[(CH_3)_2S_4C_4Ph_4]$ (**1**) was obtained, for which structures **1A–C** are possible. Structure **1A** was suggested,[5] as bis(methylthio)stilbene (**2**) was formed on thermolysis or on reaction with 2,2′-bipyridyl (eq 1).



1A



1B



1C

In 1978, Eckstein and co-workers[6] suggested that **1** had structure **1B**, since the disulfide $[CH_3S{-}C(Ph){=}C(Ph){-}S]_2$ (**4**)

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[†] Department of Chemistry, The University of Missouri, Columbia, MO 65211.

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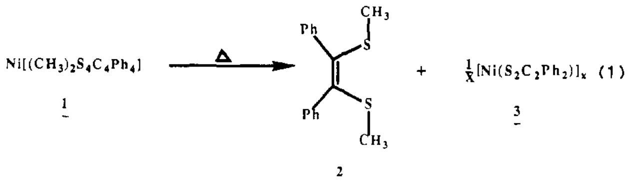

was formed on reaction with $I_2$. However, this evidence was inconclusive as only low yields of **4** were obtained.

In the meantime, our work focused on the preparation and isolation of all possible isomers of **1**, the synthesis of the free ligands, the development of alternative methods of synthesis of **1**, the thermolysis of **1**, and the isolation of single crystals of **1** and of related complexes for X-ray crystallographic structure determinations. In the course of this work, crystals of solvent-free **1** as well as of its 1:1 inclusion compound with $CH_2Cl_2$ were obtained. As the latter is yellow-brown and the former olive green, the structures of both were determined to establish the origin of this striking color difference.

We also determined the structure of a complex of composition $[(CH_3)_2S_2C_2Ph_2]_2NiI_2$ (**5**), the product of the reaction of **1** with $CH_3I$ under conditions of exhaustive methylation. Finally, variable-temperature $^1H$ NMR measurements were performed, which revealed dynamic behavior of **1** in solution due to sulfur-inversion and cis–trans-isomerization processes.

## Experimental Section

**Synthesis of 1 by Methylation of $[Ni(S_2C_2Ph_2)_2]^{2-}$. (a) In Methanol.** The reaction was conducted at $^1/_{10}$ of the scale as described in ref 5, affording 1.80 g of **1** (3.14 mmol), corresponding to 85.3% based on starting complex.

**(b) In Anhydrous Tetrahydrofuran (THF).** Into a Schlenk tube of 200-mL capacity was suspended 2.0 g (3.68 mmol) of dry $NiS_4C_4(C_6H_5)_4$ in 30 mL of THF, and the tube was flushed with dry argon. To the suspension was added 6 mL of a 1.25 M solution of $CH_3MgBr$ in THF dropwise. The reaction proceeded with the evolution of mainly $C_2H_6$ and traces of $CH_4$, as identified by GLPC, and was complete in about 30 min. To the resulting suspension, 0.57 mL (8.45 mmol) of $CH_3I$ was added drop by drop by means of a syringe. After 12 h, the reaction suspension was evaporated to dryness and extracted with *n*-hexane. From the hexane solution, 220 mg (0.7 mmol, yield 19.9%) of a pale yellow crystalline solid was obtained, mp 94–95 °C, which was identified as *cis*-bis(methylthio)stilbene (**2**) by $^1H$ NMR and mass spectroscopy. The residue was treated with $CH_2Cl_2$ and on recrystallization afforded 2.06 g of yellow crystals identified as a 1:1 $CH_2Cl_2$ adduct of **1**, mp ca. 100 °C dec. Anal. Calcd for $C_{31}H_{28}S_4Cl_2Ni$: C, 56.54; H, 4.28; Ni, 8.91. Found: C, 56.45; H, 4.35; Ni, 8.99. Recrystallization of from toluene/hexane afforded olive green crystals of **1**, 1.72 g (3.0 mmol), 81.5% based on $NiS_4C_4(C_6H_5)_4$. Anal. Calcd for $C_{30}H_{26}S_4Ni$: C, 62.82; H, 4.57; Ni, 10.24. Found: C, 62.78; H, 4.60; Ni, 10.33. From the $CH_2Cl_2$ filtrates, 210 mg (0.613 mmol, yield 16.6%) of $[Ni(S_2C_2Ph_2)]_x$ (**3**), mp 350 °C, precipitated upon the addition of *n*-hexane. Anal. Calcd for $C_{14}H_{10}S_2Ni$: C, 55.85; H, 3.34. Found: C, 55.80; H, 3.25.

**(c) From (Methylthio)stilbenethiol.** (Methylthio)stilbenethiol, 130 mg (0.50 mmol), prepared from **1** by alkaline degradation with KCN (see below), was dissolved in 100 mL of $C_2H_5OH$ and added slowly to 10 mL of an aqueous solution of 61 mg (0.257 mmol) of $NiCl_2 \cdot 6H_2O$. A green precipitate formed, which was collected, dried, and recrystallized from toluene/hexane, affording 131 mg (0.23 mmol) of **1**, corresponding to a yield of 92% based on the thiol, mp 257 °C dec.

**Thermolysis of 1.** Complex **1**, 0.50 g (0.87 mmol), was placed into a micro sublimation apparatus. After evacuation by means of an oil diffusion pump, the complex was slowly heated in a silicone bath to 225 °C. After 30 min the temperature was raised to 250 °C. The olive green crystals first turned greenish brown and without melting began to slowly release a volatile product that condensed in the form of faintly yellow crystals on the cold finger. After 90 min of continuous heating the thermolysis was terminated to yield 0.219 g of crystals identified by melting point and $^1H$ NMR and mass spectroscopy as a 3:1 mixture of *cis*- and *trans*-bis(methylthio)stilbene (**2**), corresponding to a yield of 91%, based on **1** (see eq 1).

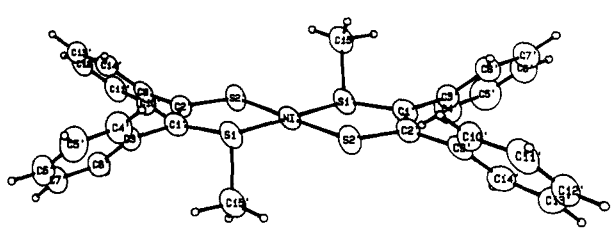

**Figure 1.** Perspective view of the anti isomer of complex **1B** with atoms numbered.

**Exhaustive Methylation of 1.** Complex **1**, 1.0 g (1.74 mmol), was heated in 10 mL of a 1:2 (v/v) mixture of $CH_3I$ and $CH_2Cl_2$ in a sealed tube for 40 min at 75 °C. After cooling, the tube was opened and all volatiles were evaporated under reduced pressure. The residue was recrystallized from $CH_2Cl_2$, affording purple crystals. These contain $CH_2Cl_2$ of crystallization, which was removed by heating to 60 °C under reduced pressure. Anal. Calcd for $C_{32}H_{32}S_4I_2Ni$ (**5**): C, 44.83; H, 3.76; I, 29.60. Found: C, 44.78; H, 3.61; I, 29.70. $^1H$ NMR ($CDCl_3$): 8.40 ppm (20), broad, phenyl H; 2.17 ppm (12), $CH_3$.

Complex **5** decomposed on contact with aqueous methanol to produce a faintly yellow, crystalline solid, mp 95 °C, identified by $^1H$ NMR as *cis*-1,2-bis(methylthio)stilbene.

**Reaction of 1 with Concentrated $H_2SO_4$.** Complex **1**, 100 mg, was dissolved in 10 mL of anhydrous $H_2SO_4$ at room temperature. After 30 min, **1** was recovered in virtually quantitative yield by pouring the solution into 100 mL of water. The recovered complex was identified by $^1H$ NMR.

**Degradation with Alkaline Cyanide.** Complex **1**, 0.5 g (0.87 mmol), was placed into a tube of 75-mL capacity. After the addition of 25 mL of $CH_3OH$ and 2 mL of a solution of 0.98 g of NaCN (20 mmol) in 1 m aqueous NaOH, the tube was sealed and heated to 75 °C for 2 h. After cooling, the tube was opened with appropriate precautions against the possible release of gaseous HCN in a vented hood and the reaction solution was neutralized with acetic acid. The reaction mixture was then transferred into a separatory funnel of 500-mL capacity, diluted with 150 mL of $H_2O$, and extracted with 100 mL of diethyl ether. The aqueous phase was shown spectroscopically to contain the ion $Ni(CN)_4^{2-}$ and was discarded. The yellow ether phase was washed three times with 50-mL portions of water, dried with $MgSO_4$, and evaporated to dryness, affording 0.33 g (1.24 mmol) of (methylthio)stilbenethiol (**6**), mp 67–68 °C, after recrystallization from hexane/$CH_2Cl_2$, corresponding to a yield of 70% based on **1**. Anal. Calcd for $C_{15}H_{14}S_2$: C, 69.72; H, 5.46; S, 24.82 (MW 258.39). Found: C, 69.50; H, 5.35; S, 24.6 (MW (by MS) 258). $^1H$ NMR (25 °C; $CDCl_3$): cis isomer, 7.09 (10), phenyl H, 4.22 (1), S–H, 1.98 ppm (3), $CH_3$; trans isomer, 7.42 (10), phenyl H, 3.13 (1), S–H, 1.74 ppm (3), $CH_3$. The cis–trans ratio was ca. 10:1.

**Variable-Temperature $^1H$ NMR Measurements.** The $^1H$ NMR spectra of **1** in $CDCl_3$ were recorded at different temperatures by using a GE QE-300 NMR instrument at 300 MHz. $^1H$ NMR ($CDCl_3$): at 50 °C (coalescence temperature), 7.24–7.27 and 7.11–7.17 (10), phenyl H, 2.38 ppm (6), $CH_3$, (s); at 0 °C, 7.24–7.26 and 7.10–7.17 (10), phenyl H, 2.36 (s) and 2.38 (sh) ppm (6), $CH_3$; at −50 °C, 7.25–7.26 and 7.10–7.19 (10), phenyl H, 2.28, 2.36, and 2.46 ppm (7:1:11) (6), $CH_3$.

**Structural Studies.** The crystals of **1** were obtained from toluene/hexane. The crystals of the $CH_2Cl_2$ inclusion compound **1**, and those of complex **2**, were grown from $CH_2Cl_2$. The crystals of the latter contain $CH_2Cl_2$, which is slowly lost on storage and during X-ray analysis. When the $CH_2Cl_2$ inclusion compound of **1** was exposed to air over a prolonged period up to several months, the loss of $CH_2Cl_2$ was also observed.

An outline of crystallographic data collection parameters is given in Table I. The crystals were mounted on an Enraf-Nonius CAD4 automated diffractometer for data collection. The unit cells were determined by automatic search and centering of 25 reflections on the diffractometer. The intensity data were measured at 23 °C by the $\theta/2\theta$ step-scan technique with Mo K$\alpha$ radiation from a graphite monochromator. The intensities of three standard reflections, measured after each 7200 s of X-ray exposure, showed no systematic changes during data collection. Orientation was maintained by checking the centering of three reflections after every 200 reflections, recentering 25 reflections, and calculating a new orientation matrix if any of the three were significantly off center. The structures were solved by Patterson and Fourier methods. Least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o/[\sigma_{count}{}^2$

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(1) (a) Schrauzer, G. N. *Transition Met. Chem.* **1968**, *4*, 299. (b) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49.

(2) Mueller-Westerhoff, U. T.; Vance, B. *Comprehensive Coordination Chemistry*; Wilkinson, G., et al., Eds.; Pergamon: Oxford, England, 1987; Vol. 2, p 595.

(3) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1968**, *84*, 3201.

(4) Gray, H. B.; Williams, R.; Bernal, I.; Billig, E. *J. Am. Chem. Soc.* **1963**, *85*, 2029.

(5) Schrauzer, G. N.; Rabinowitz, H. N. *J. Am. Chem. Soc.* **1968**, *90*, 4297.

(6) Eckstein, P. E.; Heber, R.; Reinhold, J.; Hoyer, E. *Z. Anorg. Allg. Chem.* **1978**, *440*, 253.

**Table I.** Crystallographic Data Collection Parameters of Complexes *anti*-**1B**, *anti*-**1B**·$CH_2Cl_2$, and **5**

| | *anti*-**1B** | *anti*-**1B**·$CH_2Cl_2$ | **5** |
|---|---|---|---|
| formula | $Ni[(CH_3)_2S_4C_4Ph_4]$ | $Ni[(CH_3)_2S_4C_4Ph_4]\cdot CH_2Cl_2$ | $[(CH_3)_2S_2C_2Ph_2]_2NiI_2$ |
| space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ |
| $a$, Å | 6.127 (3) | 8.424 (3) | 8.178 (3) |
| $b$, Å | 8.001 (3) | 13.461 (3) | 11.992 (3) |
| $c$, Å | 27.663 (3) | 14.745 (3) | 18.229 (5) |
| $\alpha$, deg | | 68.93 (3) | |
| $\beta$, deg | 93.81 (2) | 84.08 (3) | 94.29 (2) |
| $\gamma$, deg | | 75.10 (3) | |
| $V$, Å$^3$ | 1353.17 (9) | 1507.7 (8) | 1782.9 (3) |
| $T$, °C | 23 | 23 | -110 |
| $d_{calcd}$, g/cm$^3$ | 1.407 | 1.450 | 1.69 |
| $Z$ | 2 | 2 | 2 |
| fw | 573.51 | 658.44 | 908.88 |
| range of transm | 0.729–1.00 | 0.89–1.00 | 0.90–1.00 |
| λ, Å (Mo K$\alpha$) | 0.71073 | 0.71073 | 0.71073 |
| $\mu$, cm$^{-1}$ | 10.3 | 11.107 | 25.8 |
| $R(F_o)$ | 0.054 | 0.037 | 0.033 |
| $R_w(F_o)$ | 0.063 | 0.048 | 0.044 |

**Table II.** Positional Parameters and Their Estimated Standard Deviations of *anti*-**1B**

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Ni | 0.000 | 0.000 | 0.000 | 2.65 (2) |
| S1 | 0.0741 (3) | 0.1218 (2) | 0.06888 (6) | 2.91 (4) |
| S2 | 0.2299 (3) | -0.1973 (2) | 0.01980 (7) | 3.40 (4) |
| C1 | 0.261 (1) | -0.0117 (9) | 0.1022 (2) | 2.6 (1) |
| C2 | 0.324 (1) | -0.1506 (8) | 0.0789 (2) | 2.3 (1) |
| C3 | 0.332 (1) | 0.0452 (8) | 0.1517 (2) | 2.4 (1) |
| C4 | 0.184 (1) | 0.122 (1) | 0.1810 (2) | 3.2 (2) |
| C5 | 0.246 (1) | 0.175 (1) | 0.2271 (3) | 3.8 (2) |
| C6 | 0.458 (1) | 0.154 (1) | 0.2463 (3) | 3.8 (2) |
| C7 | 0.606 (1) | 0.077 (1) | 0.2178 (3) | 3.6 (2) |
| C8 | 0.547 (1) | 0.0270 (9) | 0.1710 (2) | 3.1 (2) |
| C9 | 0.471 (1) | -0.2774 (8) | 0.1026 (2) | 2.5 (1) |
| C10 | 0.412 (1) | -0.365 (1) | 0.1425 (3) | 3.7 (2) |
| C11 | 0.552 (1) | -0.484 (1) | 0.1635 (3) | 4.5 (2) |
| C12 | 0.750 (1) | -0.517 (1) | 0.1447 (3) | 5.6 (2) |
| C13 | 0.808 (1) | -0.430 (1) | 0.1048 (3) | 5.8 (2) |
| C14 | 0.669 (1) | -0.312 (1) | 0.0829 (3) | 4.1 (2) |
| C15 | 0.256 (1) | 0.293 (1) | 0.0560 (3) | 3.9 (2) |

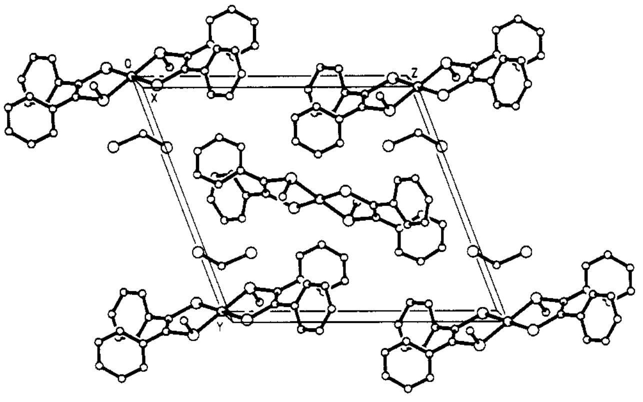

**Figure 2.** Perspective view of the unit cell of the $CH_2Cl_2$ inclusion compound of the anti isomer of **1B**.

+ $(0.040F_o^2)]^2$. Hydrogen atoms were located and held near "ideal" X-ray positions. Atomic scattering factors were taken from ref 7. Final atomic positional parameters are given in Tables II–IV. Selected interatomic distances and angles are summarized in Tables V–VII.

## Results

Complex **1** of composition $Ni[(CH_3)_2S_4C_4Ph_4]$ was obtained by several methods and was characterized by variable-temperature $^1H$ NMR measurements and by X-ray crystallographic structure analysis.

The structures of the 1:1 $CH_2Cl_2$ inclusion compound of **1** and of a complex of composition $[(CH_3)_2S_2C_2Ph_2]_2NiI_2$ (**5**), a product

**Table III.** Positional Parameters and Their Estimated Standard Deviations of *anti*-**1b**·$CH_2Cl_2$

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Ni | 0.000 | 0.000 | 0.000 | 2.96 (2) |
| Ni′ | 0.500 | 0.500 | 0.500 | 3.03 (2) |
| Cl1 | 0.6074 (3) | 0.7179 (2) | 0.9812 (2) | 10.40 (8) |
| Cl2 | 0.5349 (4) | 0.7246 (2) | 1.1754 (2) | 10.67 (9) |
| S1 | -0.0909 (2) | -0.0951 (1) | 0.1380 (1) | 3.08 (3) |
| S1′ | 0.3459 (2) | 0.5968 (1) | 0.5793 (1) | 3.35 (4) |
| S2 | 0.1832 (2) | 0.0275 (1) | 0.0754 (1) | 3.73 (4) |
| S2′ | 0.6985 (2) | 0.4550 (1) | 0.6002 (1) | 3.57 (4) |
| C1 | 0.0175 (6) | -0.0855 (4) | 0.2303 (4) | 2.9 (1) |
| C1′ | 0.4636 (6) | 0.5793 (4) | 0.6800 (4) | 3.2 (1) |
| C2 | 0.1452 (6) | -0.0378 (4) | 0.1997 (4) | 3.0 (1) |
| C2′ | 0.6193 (6) | 0.5207 (4) | 0.6842 (4) | 3.1 (1) |
| C3 | -0.0381 (6) | -0.1340 (4) | 0.3316 (4) | 3.2 (1) |
| C3′ | 0.3723 (6) | 0.6302 (4) | 0.7510 (4) | 3.1 (1) |
| C4 | -0.0825 (7) | -0.2334 (4) | 0.3634 (4) | 4.1 (2) |
| C4′ | 0.2723 (7) | 0.7358 (4) | 0.7191 (4) | 4.3 (2) |
| C5 | -0.1322 (7) | -0.2780 (5) | 0.4599 (5) | 5.3 (2) |
| C5′ | 0.1858 (8) | 0.7797 (4) | 0.7873 (5) | 5.3 (2) |
| C6 | -0.1368 (8) | -0.2224 (6) | 0.5234 (4) | 5.8 (2) |
| C6′ | 0.1978 (7) | 0.7212 (4) | 0.8842 (4) | 4.9 (2) |
| C7 | -0.0957 (8) | -0.1247 (5) | 0.4922 (4) | 5.6 (2) |
| C7′ | 0.2958 (7) | 0.6171 (4) | 0.9161 (4) | 4.2 (2) |
| C8 | -0.0465 (7) | -0.0801 (4) | 0.3980 (4) | 4.2 (2) |
| C8′ | 0.3830 (7) | 0.5712 (4) | 0.8502 (4) | 3.6 (1) |
| C9 | 0.2644 (6) | -0.0356 (4) | 0.2662 (4) | 3.3 (1) |
| C9′ | 0.7420 (6) | 0.5067 (4) | 0.7558 (4) | 3.1 (1) |
| C10 | 0.3390 (7) | -0.1314 (5) | 0.3392 (4) | 4.5 (2) |
| C10′ | 0.8459 (6) | 0.4042 (4) | 0.8003 (4) | 3.5 (1) |
| C11 | 0.4483 (7) | -0.1292 (5) | 0.3997 (4) | 5.3 (2) |
| C11′ | 0.9649 (7) | 0.3910 (5) | 0.8637 (4) | 4.4 (2) |
| C12 | 0.4871 (7) | -0.0332 (6) | 0.3905 (4) | 5.8 (2) |
| C12′ | 0.9873 (7) | 0.4799 (5) | 0.8825 (4) | 4.5 (2) |
| C13 | 0.4141 (7) | 0.0637 (5) | 0.3184 (4) | 5.4 (2) |
| C13′ | 0.8863 (7) | 0.5810 (4) | 0.8395 (4) | 4.4 (2) |
| C14 | 0.3042 (7) | 0.0624 (4) | 0.2557 (4) | 4.1 (2) |
| C14′ | 0.7630 (7) | 0.5961 (4) | 0.7769 (4) | 3.8 (1) |
| C15 | -0.2991 (7) | -0.0248 (5) | 0.1582 (4) | 4.7 (2) |
| C15′ | 0.1851 (7) | 0.5272 (5) | 0.6390 (4) | 4.8 (2) |
| C16 | 0.506 (1) | 0.7815 (8) | 1.0500 (7) | 13.9 (4) |

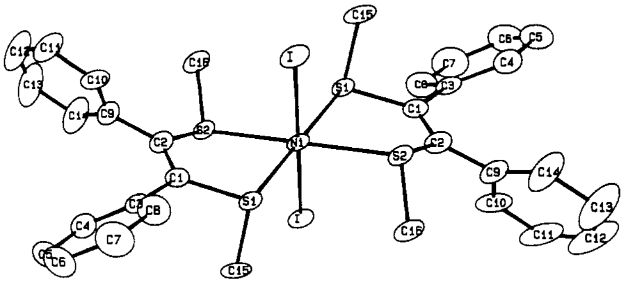

**Figure 3.** Perspective view of **5** with atoms numbered.

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(7) *International Tables for Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

**Table IV**. Positional Parameters and Their Standard Estimated Deviations of **5**

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| I | 0.25216 (3) | 0.14368 (2) | 0.05220 (2) | 1.819 (7) |
| Ni | 0.000 | 0.000 | 0.000 | 1.36 (2) |
| Cl1 | 0.6146 (7) | 0.4604 (4) | 0.0598 (3) | 3.0* |
| Cl2 | −0.0638 (5) | 0.1069 (3) | 0.5121 (2) | 3.0* |
| S1 | 0.1368 (1) | −0.1708 (1) | 0.03243 (6) | 1.52 (2) |
| S2 | −0.0836 (1) | −0.0087 (1) | 0.12166 (6) | 1.57 (2) |
| C1 | −0.0343 (6) | 0.2183 (4) | −0.1094 (3) | 1.76 (9) |
| C2 | 0.0744 (6) | 0.1538 (4) | −0.1414 (3) | 1.9 (1) |
| C3 | −0.0829 (6) | 0.3319 (4) | −0.1353 (3) | 1.9 (1) |
| C4 | −0.1253 (6) | 0.3530 (4) | −0.2094 (3) | 2.3 (1) |
| C5 | −0.1817 (7) | 0.4561 (5) | −0.2333 (3) | 3.1 (1) |
| C6 | −0.1940 (7) | 0.5419 (4) | −0.1835 (3) | 3.4 (1) |
| C7 | −0.1515 (8) | 0.5237 (4) | −0.1095 (4) | 3.5 (1) |
| C8 | −0.0978 (7) | 0.4203 (4) | −0.0851 (3) | 2.7 (1) |
| C9 | 0.1890 (6) | 0.1956 (4) | −0.1943 (3) | 2.5 (1) |
| C10 | 0.2940 (6) | 0.2820 (5) | −0.1732 (3) | 3.4 (1) |
| C11 | 0.4134 (7) | 0.3177 (5) | −0.2175 (4) | 4.7 (1) |
| C12 | 0.4290 (8) | 0.2650 (5) | −0.2839 (4) | 6.1 (1) |
| C13 | 0.3245 (9) | 0.1805 (6) | −0.3072 (4) | 5.8 (2) |
| C14 | 0.2011 (8) | 0.1443 (5) | −0.2609 (4) | 4.4 (1) |
| C15 | 0.3423 (6) | −0.1575 (4) | 0.0743 (3) | 2.5 (1) |
| C16 | −0.2991 (6) | 0.0248 (4) | 0.1216 (3) | 2.2 (1) |
| C17 | 0.475 (1) | 0.4298 (9) | −0.0086 (6) | 3.0* |
| C18 | 0.111 (1) | −0.020 (1) | 0.5655 (7) | 3.0* |
| C19 | 0.043 (1) | 0.0838 (7) | 0.5249 (5) | 3.0* |
| C20 | −0.094 (1) | −0.0925 (7) | 0.4367 (4) | 3.0* |

[a] Starred *B* values for atoms that were refined isotropically.

**Table V**. Selected Geometrical Data for *anti*-**1B**

| | | | |
|---|---|---|---|
| | Distances (Å) | | |
| Ni–S1 | 2.161 (1) | S2–C2 | 1.737 (5) |
| Ni–S2 | 2.162 (1) | C1–C2 | 1.352 (7) |
| S1–C1 | 1.779 (5) | C1–C3 | 1.480 (7) |
| S1–C15 | 1.815 (6) | C2–C9 | 1.484 (7) |
| | Angles (deg) | | |
| S1–Ni–S1 | 180 | S1–C1–C3 | 115.7 (4) |
| S1–Ni–S2 | 89.38 (5) | C2–C1–C3 | 128.2 (5) |
| S1–Ni–S2 | 90.62 (5) | S2–C2–C1 | 122.6 (4) |
| Ni–S1–C1 | 106.0 (2) | S2–C2–C9 | 115.0 (4) |
| Ni–S1–C15 | 105.2 (2) | C1–C2–C9 | 122.3 (4) |
| C1–S1–C15 | 99.8 (3) | C1–C3–C4 | 120.8 (4) |
| Ni–S2–C2 | 104.5 (2) | C1–C3–C8 | 122.2 (4) |
| S1–C1–C2 | 116.1 (4) | | |

**Table VI**. Selected Geometrical Data for *anti*-**1B**·$CH_2Cl_2$

| | | | |
|---|---|---|---|
| | Distances (Å) | | |
| Ni–S1 | 2.163 (1) | S2–C2 | 1.761 (4) |
| Ni–S2 | 2.167 (1) | S2′–C2′ | 1.754 (4) |
| Ni′–S1′ | 2.160 (1) | C1–C2 | 1.349 (5) |
| Ni′–S2′ | 2.166 (1) | C1–C3 | 1.480 (6) |
| S1–C1 | 1.773 (4) | C1′–C2′ | 1.340 (6) |
| S1–C15 | 1.816 (5) | C1′–C3′ | 1.495 (6) |
| S1′–C1′ | 1.781 (5) | C2–C9 | 1.488 (6) |
| S1′–C15′ | 1.817 (5) | C2′–C9′ | 1.484 (6) |
| | Angles (deg) | | |
| S1–Ni–S1 | 180 | S1′–C1′–C3′ | 114.8 (3) |
| S1–Ni–S2 | 90.27 (4) | C2′–C1′–C3′ | 128.4 (4) |
| S1–Ni–S2 | 89.73 (4) | S2–C2–C1 | 121.7 (3) |
| S2–Ni–S2 | 180 | S2–C2–C9 | 114.6 (3) |
| S1′–Ni′–S1′ | 180 | C1–C2–C9 | 123.8 (4) |
| S1′–Ni′–S2′ | 90.35 (4) | S2′–C2′–C1′ | 121.6 (4) |
| S1′–Ni′–S2′ | 89.65 (4) | S2′–C2′–C9′ | 113.3 (3) |
| S2′–Ni′–S2′ | 180 | C1′–C2′–C9′ | 125.1 (4) |
| Ni–S1–C1 | 107.2 (1) | C1–C3–C4 | 121.3 (4) |
| Ni–S1–C15 | 109.2 (2) | Ni′–S2′–C2′ | 104.8 (2) |
| C1–S1–C15 | 101.7 (2) | S1–C1–C2 | 115.8 (3) |
| Ni′–S1′–C1′ | 106.1 (2) | S1–C1–C3 | 116.6 (3) |
| Ni′–S1′–C15′ | 107.2 (2) | C2–C1–C3 | 127.6 (4) |
| C1′–S1′–C15′ | 101.9 (2) | S1′–C1′–C2′ | 116.9 (4) |
| Ni–S2–C2 | 105.0 (2) | | |

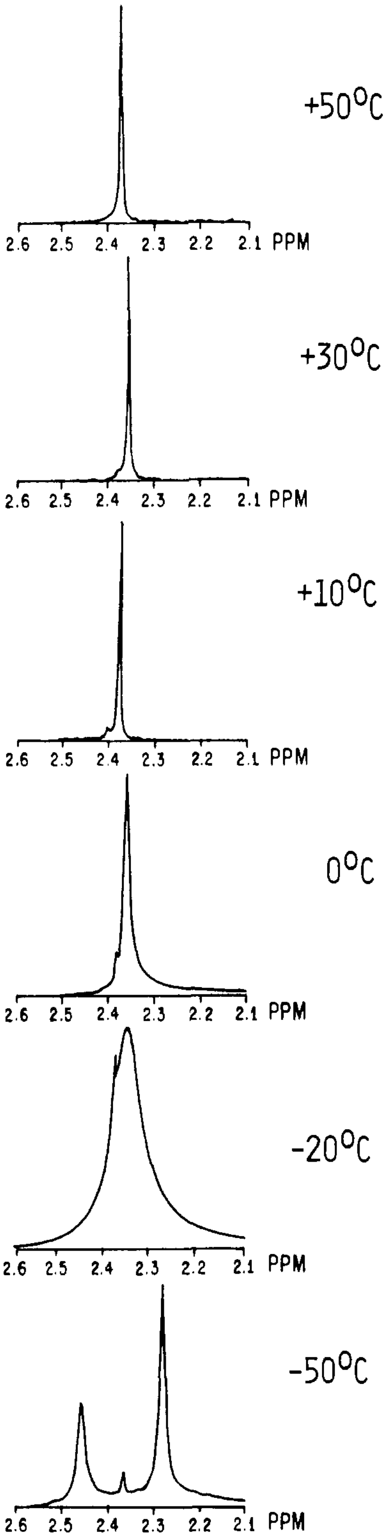
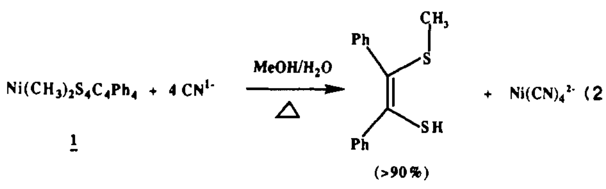


**Figure 4.** $^1H$ NMR signals of the methyl group protons of the anti and syn isomers of **1B** and **1C** in $CDCl_3$ at different temperatures (scan range 2.10–2.60 ppm).

of the exhaustive methylation of **1**, were also determined. The chemical methods employed are outlined in the Experimental Section; the results of the structure determinations and of the $^1H$ NMR measurements are summarized in Figures 1–4 and Tables I–VII.

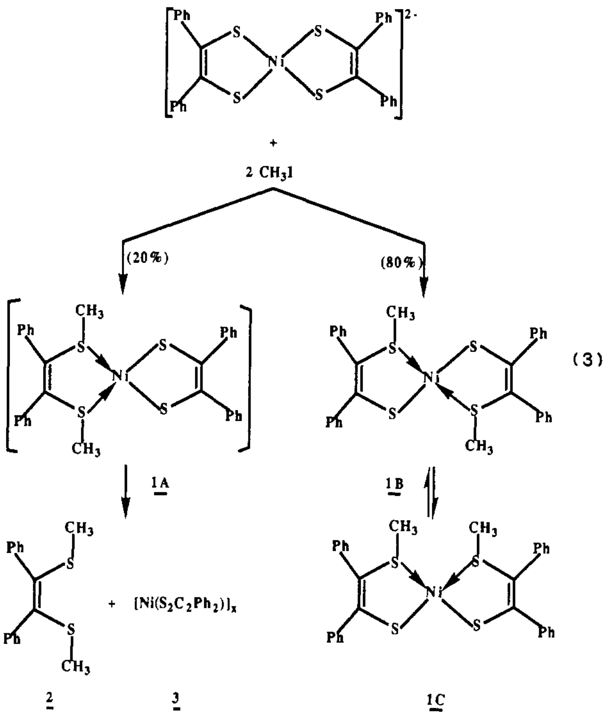
## Discussion

**Chemical Studies.** Although complex **1** is remarkably stable to mineral acids, it is degraded on heating with aqueous–alcoholic NaCN under pressure, affording the free ligand, *cis*-(methylthio)stilbenethiol (**6**), and complex cyanides of nickel(II) according to eq 2.



6

A complex identical in every respect with the product of the reaction of $[Ni(S_2C_2Ph_2)_2]^{2-}$ with $CH_3I$ was also obtained by reacting **6** with nickel salts, which is thus identified as bis((methylthio)stilbenethiolato)nickel(II): its structure could be either **1B** or **1C**. As will be shown below, the X-ray structural analysis revealed that the isolated complex is the anti isomer of **1B**, while $^1H$ NMR measurements indicate that isomers **1B** and **1C** are at equilibrium in solution. Mixtures of **1B** and **1C** are presumably formed in the reaction of $[Ni(S_2C_2Ph_2)_2]^{2-}$ with $CH_3I$ in combined yields of 80%. Approximately 20% of the dithiolene dianion reacts with $CH_3I$ to yield *cis*-bis(methylthio)stilbene (**2**) and nickel(II) stilbenedithiolate (**3**) in equimolar amounts. This suggests that isomer **1A** is formed in about 20% yield, but it is unstable and decomposes into the isolated products **2** and **3** (eq 3).



As **2** and **3** are also formed on thermolysis of **1B**, it must be assumed that a ligand disproportionation reaction with methyl group transfer occurs as formulated in eq 4.

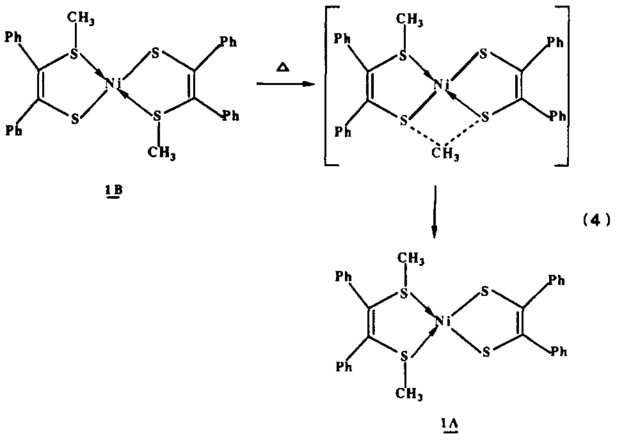
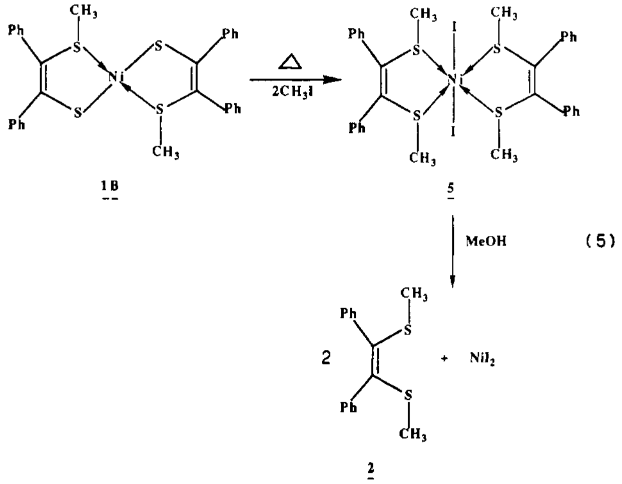


Table VII. Selected Geometrical Data for 5

| | | | |
|---|---|---|---|
| | Distances (Å) | | |
| I-Ni | 2.7989 (2) | S2-C2 | 1.777 (4) |
| Ni-S1 | 2.3870 (9) | S2-C16 | 1.807 (4) |
| Ni-S2 | 2.3717 (9) | C1-C2 | 1.344 (5) |
| S1-C1 | 1.781 (4) | C1-C3 | 1.486 (5) |
| S1-C15 | 1.800 (4) | C2-C9 | 1.483 (5) |
| | Angles (Å) | | |
| I-Ni-I | 180 | S2-C2-C9 | 116.3 (3) |
| I-Ni-S1 | 97.15 (2) | C1-C2-C9 | 123.9 (3) |
| I-Ni-S1 | 82.85 (2) | C1-C3-C4 | 121.0 (4) |
| I-Ni-S2 | 88.06 (2) | C1-C3-C8 | 121.1 (3) |
| I-Ni-S2 | 91.94 (2) | C4-C3-C8 | 117.7 (4) |
| S1-Ni-S1 | 180 | Ni-S2-C2 | 102.8 (1) |
| S1-Ni-S2 | 83.87 (3) | Ni-S2-C16 | 109.8 (1) |
| S1-Ni-S2 | 96.13 (3) | C2-S2-C16 | 104.2 (2) |
| S2-Ni-S2 | 180 | S1-C1-C2 | 121.5 (3) |
| Ni-S1-C1 | 103.3 (1) | S1-C1-C3 | 114.4 (3) |
| Ni-S1-C15 | 115.7 (1) | C2-C1-C3 | 124.1 (3) |
| C1-S1-C15 | 100.0 (2) | S2-C2-C1 | 119.7 (3) |

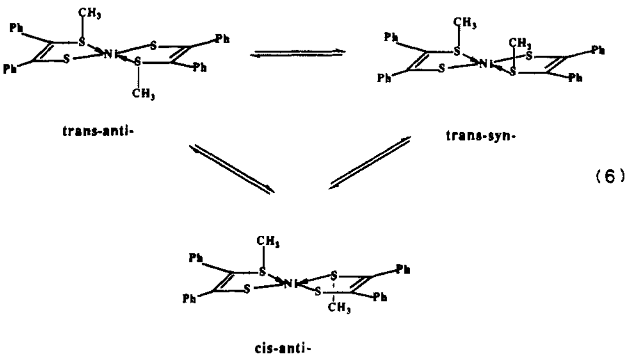
Under vigorous conditions (sealed tube at 75 °C), complex **1B** reacts with alkyl iodides, in contrast to previous claims of Eckstein et al.[6] On reaction with $CH_3I$, the diamagnetic complex **5** was obtained according to eq 5. Complex **5** is relatively labile, decomposing on contact with protic solvents to **2** and a solution of nickelous iodide.



**Structural Studies.** The X-ray structural analysis of the isolable isomer of **1** and of its $CH_2Cl_2$ inclusion compound identifies the complex as the trans-anti isomer of bis(dithiobenzoin)nickel; see Figures 1 and 2. The structure reveals a centrosymmetric, essentially square-planar $NiS_4$ moiety with Ni–S bond lengths of 2.161 (1) Å. The $C-S(CH_3)$ bond of 1.779 (5) Å is longer than the C–S(2) bond of 1.737 (5) Å, both of which are clearly in the range of C–S single bonds, while the bond distance between C(1) and C(2) of 1.352 (7) Å is normal for a C=C bond. This is consistent with an electronically localized ground-state structure. While all other bond angles are within normal ranges (see Table IV), the $Ni-S-CH_3$ angles of 105.2° deviate significantly from the ideal value of 109.5°. This is attributed to crystal packing effects, since the corresponding angles in the $CH_2Cl_2$ inclusion compound, which crystallizes with a larger unit cell, are relaxed to 109.2 (2)°. This structural difference is probably responsibie for the yellow-brown color of the $CH_2Cl_2$ inclusion compound as even small changes of the $Ni-S-CH_3$ bond angles are expected to affect the energies and intensities of the $n_{-S(CH_3)} \rightarrow \pi^*$ transitions. The structure of the $CH_2Cl_2$ inclusion compound otherwise reveals no unusual features; the molecules of solvent occupy interstitial positions without involving charge transfer or other types of bonding interactions with the molecules of the host complex.

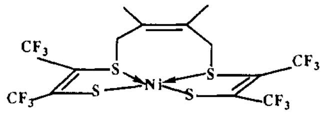
The structure of **5** in Figure 3 presents a 6-coordinated Ni(II) ion equatorially coordinated by two molecules of *cis*-bis(methylthio)stilbene. The mean Ni–I bond lengths of 2.7989 (2) Å are slightly shorter than the sum of the ionic radii, the Ni–S bond lengths of 2.380 (9) Å are longer than those in **1B**, and the C–S bond lengths of 1.792 (4) Å are normal for C–S single bonds. The S1–Ni–S2 bond angles are 83.87 and 96.13°, respectively, indicating a distorted square-planar structure.

**Variable-Temperature $^1$H NMR Measurements.** In the $^1$H NMR spectrum of **1B** in $CDCl_3$ at 50 °C, the signal of the methyl group protons appears as a single peak at 2.38 ppm. On cooling, the signal broadens, develops a shoulder, and at −50 °C splits into three signals at 2.28, 1.36, and 2.46 ppm with relative intensities of 7:1:11. This indicates the presence of dynamic equilibria involving three isomers. The two major signals at 2.28 and 2.48 ppm coalesce at 20 °C and are assigned to the syn- and anti-trans isomers of **1B**, which are interconvertible by sulfur inversion (eq 6).



(6)

The third signal at 2.36 ppm, which remains observable up to 30 °C, is assigned to the cis-anti isomer of **1C**, generated by a backbone isomerization process (see Figure 4 and eq 5). The cis-anti isomer could not be isolated in the solid state. Furthermore, no signal attributable to the presence of the cis-syn isomer was obtained. Its formation either by sulfur inversion or backbone isomerization is apparently sterically unfavorable. This could be due to the shortness of the Ni–S bonds. In **5**, two molecules of *cis*-1,2-bis(methylthio)stilbene are present in a cis-syn arrangement, but in this case the Ni–S bonds are longer by 0.22 Å. A cis-syn arrangement of two C–S bonds is also present in the cycloaddition product of $NiS_4C_4(CF_3)_4$ with 2,3-dimethylbutadiene (**7**).[8] In this complex, the two types of Ni–S bonds



**7**

have the lengths of 2.156 (7) and 2.183 (8) Å. Here the steric obstruction is offset primarily by the formation of a macrocycle. As the conformational stabilities of individual isomers of organodithiolene complexes are evidently difficult to predict, further studies with series of analogous complexes of different metals, e.g. of Ni(II), Pd(II), and Pt(II), are now in progress and will be reported in a forthcoming paper.

**Acknowledgment.** This work was supported by Grant CHE-84-14567 of the National Science Foundation.

**Supplementary Material Available:** For complexes *anti*-**1B**, *anti*-**1B**·$CH_2Cl_2$, and **5**, tables of equivalent positions, scattering factors, least-squares parameters, positional parameters, torsion angles, least-squares planes, thermal parameters, bond distances and bond angles, and crystallographic details (33 pages); listings of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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(8) Herman, A.; Wing, R. M. *J. Organomet. Chem.* **1973**, *63*, 441.

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Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

# Pentacoordinate $Fe(CO)_3$ Complexes of Diphosphine Ligands with Bite Angles Greater Than 120°

Charles P. Casey,* Gregory T. Whiteker, Charles F. Campana,[1] and Douglas R. Powell

*Received November 21, 1989*

The reaction of (benzylideneacetone)tricarbonyliron and *trans*-1,2-bis((diphenylphosphino)methyl)cyclopropane (**1**) in toluene produced [*trans*-1,2-bis((diphenylphosphino)methyl)cyclopropane]tricarbonyliron (**3**) in 24% yield. Crystals of **3** are orthorhombic with space group *Pcba*, $a = 16.359$ (5) Å, $b = 16.711$ (5) Å, $c = 21.057$ (6) Å, $V = 5757$ (3) Å$^3$, and $Z = 8$. The X-ray crystal structure of **3** reveals a trigonal-bipyramidal geometry about the iron atom with diequatorial chelation by diphosphine **1** (P–Fe–P = 123.9 (1)°). The reaction of (benzylideneacetone)tricarbonyliron with 2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl (**2**) formed [2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl]tricarbonyliron (**5**) in 7% yield. Crystals of **5**·$CH_2Cl_2$ are monoclinic with space group $P2_1/n$, $a = 12.863$ (3) Å, $b = 15.173$ (3) Å, $c = 18.753$ (4) Å, $\beta = 95.51$ (3)°, $V = 3643.1$ (13) Å$^3$, and $Z = 4$. The X-ray structure of **5** exhibits a distorted-square-pyramidal geometry with an apical carbonyl ligand. The P–Fe–P angle is 152.0 (1)°; the basal carbonyls form a OC–Fe–CO angle of 141.8 (4)°.

## Introduction

We have recently become interested in the synthesis of transition-metal complexes of chelating diphosphines with large P–M–P bite angles of greater than 120°. Diphosphines with bite angles near 90° are very common and have been useful in studying metal complexes with phosphines locked into cis positions in octahedral and square-planar complexes. Venanzi, Shaw, and Takeuchi have developed unusual chelating diphosphines capable of spanning trans sites.[2] However, few chelating diphosphines with a preferred bite angle near 120° have been available for studying metal complexes with phosphines locked into diequatorial sites in trigonal bipyramids. Such 120° chelating diphosphines are particularly interesting in relation to intermediates in rho-

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(1) Current address: Siemens Analytical X-Ray Instruments, Inc., 6300 Enterprise Lane, Madison, WI 53719.

(2) (a) Camalli, M.; Caruso, F.; Chaloupka, S.; Kapoor, P. N.; Pregosin, P. S.; Venanzi, L. M. *Helv. Chim. Acta* **1984**, *67*, 1603. (b) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59. (c) Leising, R. A.; Grzybowski, J. J.; Takeuchi, K. J. *Inorg. Chem.* **1988**, *27*, 1020 and references therein.

0020-1669/90/1329-3376$02.50/0