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Synthesis, Structure, and Dynamic Properties of Bis(*cis*-(benzylthio)stilbenethiolate) Complexes of Nickel(II), Palladium(II), and Platinum(II) and of Related Compounds

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The products of the reactions of the bis(*cis*-stilbenedithiolates) of Ni(II), Pd(II), and Pt(II) with benzyl halides are shown to be chelates of *cis*-(benzylthio)stilbenethiolate by chemical degradation, independent synthesis, and X-ray structural analyses. The isolated solid trans–anti isomers of M[(PhCH$_2$)$_2$S$_4$C$_4$Ph$_4$] (M = Ni, Pd, Pt) are isomorphous and crystallize in space group $P2_1/c$ with $Z = 2$. For M = Ni, $a = 14.832$ (3) Å, $b = 8.814$ (2) Å, $c = 14.867$ (3) Å, $\beta = 112.69$ (2)°, and $d_{calcd} = 1.344$ (2) g cm^{-3}. For M = Pd, $a = 14.898$ (3) Å, $b = 8.805$ (3) Å, $c = 14.791$ (3) Å, $\beta = 110.98$ (2)°, and $d_{calcd} = 1.42$ g cm^{-3}. For M = Pt, $a = 14.885$ (4) Å, $b = 8.828$ (3) Å, $c = 14.806$ (6) Å, $\beta = 111.04$ (2)°, and $d_{calcd} = 1.58$ g cm^{-3}. The central metal atoms of the nickel complex are in a slightly distorted planar ligand environment. The C–S(CH$_2$Ph) bond lengths of 1.835 (2) Å are longer than normal due to electronic labilization. The complexes show dynamic behavior in solution primarily due to sulfur inversion processes, as evidenced by variable-temperature ^{1}H NMR measurements. The trans–anti and trans–syn isomers are the predominant species in solutions of the nickel complexes. In solutions of the complexes of Pd and Pt, the cis–anti isomers were also detectable; the cis–anti isomer of the Pt complex is more stable than that of Pd and can be isolated. Also synthesized were several aralkyl and substituted-benzyl complexes of the type M[RCH$_2$)$_2$S$_4$C$_4$Ph$_4$], with M = Ni and R = 4-naphthyl, 9-anthracenyl, 4-CH$_3$OC$_6$H$_4$–, and 4-NO$_2$C$_6$H$_4$–H$_4$–. All aralkyl dithiolenes are light-sensitive in solution. In a series of complexes with M = Ni, the rates of photodecomposition, which proceeds with C–S bond homolysis, increase with increasing electronic labilization of the C–S(aralkyl) bonds.

The reaction of the metal bis(*cis*-stilbenedithiolate) anions [M(S$_2$C$_2$Ph$_2$)$_2$]$^{2-}$, with M = Ni(II), Pd(II), or Pt(II), with alkyl and benzyl halides yields[2] complexes of composition M-(R$_2$S$_4$C$_4$Ph$_4$). In a recent paper,[3] we reported the structure of the Ni(II) complex with R = CH$_3$, **1**, and showed that it exhibits dynamic behavior in solution due to sulfur inversion and cis–trans isomerization reactions. With the employment of variable-temperature ^{1}H NMR measurements, evidence for the presence of three isomeric species of **1** was obtained, which are identified in Scheme I.
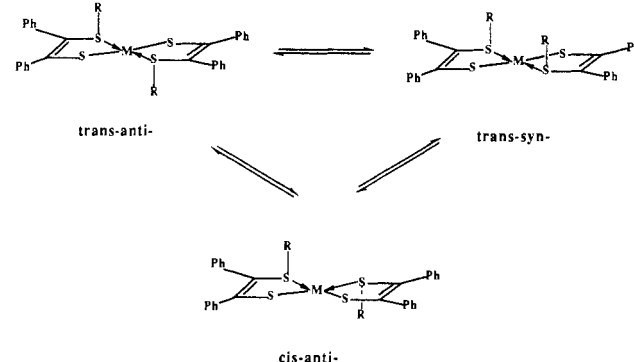
The conformationally most stable trans–anti isomer could be isolated, and its structure was proven by single-crystal X-ray analysis. Two conformationally labile isomers could not be isolated (see Scheme I).

The inversion of configuration at the sulfur atoms of thioether ligands appears to involve simultaneous bond making and breaking with the free and coordinated sulfur lone pairs and has been investigated in complexes of a limited number of metals and ligands.[5–7] On the basis of studies with a series of unsubstituted and substituted aralkyl dithiolenes of nickel, palladium, and platinum, we will show that the chemical and dynamic properties of complexes of this type are influenced by the nature of the central metal and by steric and electronic effects of the thioether ligand substituents. In addition, the structures of the conformationally most stable isomers of the *S*-benzyl derivatives, M-[(PhCH$_2$)$_2$S$_4$C$_4$Ph$_4$], with Ni, Pd, and Pt will be reported.

Experimental Section

Synthesis of Complexes M(R$_2$S$_4$C$_4$Ph$_4$) (M = Ni, Pd, Pt; R = CH$_2$Ph). **(a) In Methanol.** The reaction of the anions [M(S$_2$C$_2$Ph$_2$)$_2$]$^{2-}$, M = Ni, Pd, and Pt, with 2 equiv of C$_6$H$_5$CH$_2$Br was performed as described in ref 2, affording complexes **2** (M = Ni), **3** (M = Pd), and **4** (M = Pt) in yields ranging from 70 to 80%, based on dithiolene dianion. Anal. Calcd for NiC$_{42}$H$_{34}$S$_4$ (**2**, mp 196 °C): C, 69.53; H, 4.69. Found: C, 69.30; H, 4.71. Calcd for PdC$_{42}$H$_{34}$S$_4$ (**3**, mp 202 °C dec): C, 65.24;

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(2) Schrauzer, G. N.; Rabinowitz, H. N. *J. Am. Chem. Soc.* **1968,** *90*, 4297.
(3) Schrauzer, G. N.; Zhang, C.; Schlemper, E. O. *Inorg. Chem.*, in press.
(4) Miller, T. R.; Dance, I. G. *J. Am. Chem. Soc.* **1973,** *95*, 6970.
(5) (a) Haake, P.; Turley, P. C. *J. Am. Chem. Soc.* **1967,** *89*, 4611. (b) Coletta, F.; Ettore, R.; Gambrano, A. *Inorg. Nucl. Chem. Lett.* **1972,** *8*, 667.
(6) Cross, R. J.; Dalgleish, I. G.; Smith, G. J.; Wardle, R. *J. Chem. Soc., Dalton Trans.* **1972,** 992.
(7) Abel, E. W.; Shamsuddin Ahmed, A. K.; Farrow, G. W.; Orrell, K. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* **1977,** 47.

Scheme I

H, 4.40. Found: C, 65.25; H, 4.55. Calcd for PtC$_{42}$H$_{34}$S$_4$ (**4**, mp 203 °C dec): C, 58.53; H, 3.93. Found: C, 58.25; H, 4.03.

(b) In Anhydrous Tetrahydrofuran (THF). Into a Schlenk tube of 200-mL capacity was suspended 2.0 g (3.68 mmol) of dry Ni[S$_4$C$_4$(C$_6$-H$_5$)$_4$] in 30 mL of THF, and the tube was flushed with dry argon. To the suspension, 6 mL of a 1.25 M solution of CH$_3$MgBr in THF was added dropwise, causing the gradual precipitation of the magnesium salt of the nickel dithiolene dianion. After 30 min, 1.43 g (8.45 mmols) of PhCH$_2$Br was added to the suspension, drop by drop, by means of a syringe. After 12 h, the reaction suspension was evaporated to dryness and the residue extracted with 50 mL of CH$_2$Cl$_2$ from which 1.74 g (65.2%) of **2** was obtained by partial evaporation of CH$_2$Cl$_2$ and addition of *n*-hexane.

(c) Synthesis of Pd[(PhCH$_2$)$_2$S$_4$C$_4$Ph$_4$] (3) from (Benzylthio)stilbenethiol. (Benzylthio)stilbenethiol, 670 mg (2 mmol), was dissolved in 50 mL of C$_2$H$_5$OH. To this a solution of 140 mg of PdCl$_2$ (0.81 mmol) in 15 mL of H$_2$O (containing a small amount of HCl to facilitate solubilization) was added dropwise. A red precipitate formed, which was collected, dried, and recrystallized from CH$_2$Cl$_2$, affording 0.51 g (0.69 mmol) of **3**, corresponding to 85%, based on PdCl$_2$.

(Benzylthio)stilbenethiol (**9**, mp 61 °C) was prepared by the reaction of **2** with alkaline NaCN by using the method described in ref 3. Anal. Calcd for C$_{21}$H$_{18}$S$_2$: C, 75.40; H, 5.42. Found: C, 75.20; H, 5.31. ^{1}H NMR (CDCl$_3$), ppm: phenyl (15 H), 7.11 (m), 7.25 (m); –CH$_2$– (2 H), 3.67; SH (1 H), 4.34.

Preparation of Complexes Ni[(RCH$_2$)$_2$S$_4$C$_4$Ph$_4$] with R = 4-CH$_3$OC$_6$H$_4$– (5), 4-NO$_2$C$_6$H$_4$– (6) C$_{10}$H$_7$– (7), and C$_{14}$H$_9$– (8). These complexes were obtained by procedure a in yields averaging 65%. Anal. Calcd for NiC$_{44}$H$_{38}$O$_2$S$_4$ (**5**, mp 180 °C): C, 67.26; H, 4.87. Found: C, 67.33; H, 5.21. Calcd for NiC$_{42}$H$_{32}$N$_2$O$_4$S$_4$ (**6**, mp 182 °C): C, 61.85; H, 3.95. Found: C, 62.20; H, 4.50. Calcd for NiC$_{50}$H$_{38}$S$_4$ (**7**, mp 178 °C): C, 72.27; H, 4.65. Found: C, 72.50; H, 5.23. Calcd for NiC$_{58}$-H$_{42}$S$_4$ (**8**, mp 158 °C (dec)): C, 75.24; H, 4.57. Found: C, 75.86; H, 5.45.

Thermolysis Studies. Powdered samples, 0.2 g each, of complexes **2–8** were placed into a microsublimation apparatus, which was heated to 250 °C in a silicone oil bath after evacuation by means of an oil diffusion pump. From **2**, the sublimate of mp 95–97 °C was identified as (benzylthio)stilbenethiol (**9**), yield 50 mg (0.12 mmol), 54% based on **2**. Anal. Calcd for $C_{28}H_{24}S_2C$: 79.22; H, 5.68. Found: C, 79.53; H, 5.65. ^{1}H NMR (CDCl₃), ppm: phenyl (20 H), 7.57 (m), 7.07 (m), 6.90 (m); –CH₂– (4 H), 4.07. The nonvolatile black residue was identified as $[Ni(S_2C_2Ph_2)]_x$ by its infrared spectrum. The thermolysis of **2** was also conducted in molten 2,2′-bipyridyl (bpy), affording the known[2,4] adduct (bpy)Ni(S₂C₂Ph₂) (**10**). The thioether **9** was also obtained on pyrolyzing complexes **3** and **4**.

The sublimation product formed in the pyrolysis of **8**, mp 78 °C (lit.[8] mp 80 °C), was identified as 9-methylanthracene, yield 26 mg (0.062 mmol), 64% based on **8**. ^{1}H NMR (CDCl₃), ppm: aromatic (9 H), 8.67–7.57; methyl (3 H), 3.10. The thermolysis residue of **8** was dissolved in CH₂Cl₂ and identified as Ni(S₄C₄Ph₄) by its UV–vis absorption spectrum.

Photolysis. Solutions of complexes **2–8** in benzene were placed into Pyrex glass vials and were exposed to light emitted from a 150-W General Electric tungsten projector spot lamp while being air-cooled. The progress of photolysis was followed by measuring the increase of the first allowed low-energy absorption at 800–900 nm. The relative photolysis rates were as follows: **3**, 0.1; **5**, 0.5; **2**, 1.0; **6**, 2.3; **4**, 2.7; **7**, 3.4; **8**, 14.2.

Variable-Temperature ¹H NMR Measurements. The ¹H NMR spectra of complexes **2–8** in CDCl₃ were recorded in sealed tubes at different temperatures with a GE-300 NMR instrument at 300 MHz. ¹H NMR signals, assignment (number) and shift in ppm (multiplicity), *J* values in hertz), for complexes **2–8** at different temperatures are as follows. **2**, +20 °C: phenyl (30 H), 6.94–7.37 (m); –CH₂– (4 H), 3.99 (s). **2**, 0 °C: phenyl (30 H), 6.98–7.47 (m); –CH₂– (4 H), 3.81 (s), 4.07 (s). **2**, –50 °C: phenyl (30 H), 6.90–7.50 (br); –CH₂– (4 H), 3.68 (d, *J* = 13.5), 3.80 (d, *J* = 14.1), 4.02 (d, *J* = 14.4), 4.16 (d, *J* = 13.5).

3, +50 °C: phenyl (30 H), 6.99–7.29 (m); –CH₂– (4 H), 3.79 (s, br). **3**, +20 °C: phenyl (30 H), 6.99–7.30 (m); –CH₂– (4 H), 3.78 (s, br), 4.09 (s, br). **3**, 0 °C: phenyl (30 H), 7.00–7.31 (m); –CH₂– (4 H), 3.61 (s, br), 3.80 (s, br), 4.04 (s, br), 4.10 (s, br). **3**, –50 °C: phenyl (30 H), 6.98–7.30 (m); –CH₂– (4 H), 3.50 (d, *J* = 12.3), 3.77 (d, *J* = 12.3), 3.89 (d, *J* = 13.5), 3.98 (s), 4.03 (s), 4.06 (s), 4.11 (s), 4.15 (s).

4, trans isomer, +50 °C: phenyl (30 H), 6.98–7.28 (m); –CH₂– (4 H), 4.19 (s), 4.27 (s). **4**, trans isomer +20 °C: phenyl (30 H), 6.99–7.26 (m); –CH₂– (4 H), 4.16 (s, br), 4.20 (s, br), 4.24 (s, br), 4.28 (s, br). **4**, trans 0 °C: phenyl (30 H), 6.98–7.27 (m); –CH₂– (4 H), 4.14 (s), 4.19 (s), 4.22 (s), 4.25 (s). **4**, trans isomer, –50 °C: phenyl (30 H), 6.97–7.27 (m); –CH₂– (4 H), 4.13 (s), 4.18 (s), 4.20 (s), 4.22 (s), 4.24 (s), 4.28 (s). **4**, cis isomer, +50 °C: phenyl (30 H), 6.94–7.37 (m); –CH₂– (4 H), 3.97 (s, br), 3.90 (s). **4**, cis isomer, +20 °C: phenyl (30 H), 6.95–7.38 (m); –CH₂– (4 H), 3.82 (s), 3.86 (s), 3.94 (s), 3.99 (s). **4**, cis isomer, 0 °C: phenyl (30 H), 6.96–7.33 (m); –CH₂– (4 H), 3.80 (s), 3.84 (s), 3.92 (s), 3.96 (s). **4**, cis isomer, –50 °C: phenyl (30 H), 6.94–7.36 (m); –CH₂– (4 H), 3.78 (s), 3.83 (s), 3.89 (s), 3.94 (s).

5, +20 °C: phenyl (28 H), 6.74–7.27 (m); Ph–OCH₃ (6 H), 3.80 (s); –CH₂– (4 H), 3.96 (s). **5**, –50 °C: phenyl (28 H), 6.79–7.36 (m); Ph–OCH₃ (6 H), 3.83 (s); –CH₂– (4 H), 3.51 (d, *J* = 12.6), 3.70 (d, *J* = 14.1), 3.98 (d, *J* = 12.9), 4.15 (d, *J* = 13.5).

6, +20 °C: phenyl (28 H), 7.11–8.16 (m); –CH₂– (4 H), 3.96 (br). **6**, –50 °C: phenyl (28 H), 7.10–8.12 (m); –CH₂– (4 H), 3.82 (d, *J* = 13.5), 3.95 (d, *J* = 13.5), 4.08 (d, *J* = 14.1), 4.16 (d, *J* = 13.5).

7, +20 °C: phenyl (20 H) and naphthyl (14 H), 6.66–8.33 (m); –CH₂– (4 H), 4.40 (s). **7**, –50 °C: phenyl (20 H) and naphthyl (14 H), 6.63–8.36 (m); –CH₂– (4 H), 3.75 (d, *J* = 11.7), 4.04 (d, *J* = 18.6), 4.62 (d, *J* = 13.5), 4.31 (d, *J* = 12.0).

8, +20 °C: phenyl (20 H) and anthracenyl (18 H), 6.45–8.40 (m); –CH₂– (4 H), 4.12 (s, br), 4.90 (s, br). **8**, –50 °C: phenyl (20 H), anthracenyl (18 H), 6.43–8.50 (m); –CH₂– (4 H), 3.96 (d, *J* = 12.0), 4.87 (d, *J* = 12.0).

X-ray Crystallographic Studies. Crystals of complexes **2–4** were obtained from CH₂Cl₂. They were mounted on Enraf-Nonius CAD-4 automated diffractometer.

The unit cell of **2** was determined by automatic search and centering of 25 reflections on the diffractometer. The intensity data were measured by the θ/2θ step–scan technique with Mo Kα radiation from a graphite monochromator. The data were reduced with correction for background, *Lp*, and absorption effects (Enraf-Nonius SDP programs). The structure was solved by Patterson and Fourier methods; least-squares refinement minimized $\sum w(|F_o| - |F_o|)^2$, where $w = 4F_o/[\sigma^2_{counting} + (0.040F_o^2)]^2$.

(8) (a) Sieglitz, A. *Ber. Dtsch. Chem. Ges.* **1923**, *56*, 1619. (b) Merritt, C.; Braun, C. E. *Organic Syntheses*; J. Wiley and Sons: New York, 1963; Collect. Vol. IV, p 8.

Table I. Crystallographic Data Collection Parameters for *anti-2*, *anti-3*, and *anti-4*

	anti-2	*anti-3*	*anti-4*
formula	$C_{42}H_{34}S_4Ni$	$C_{42}H_{34}S_4Pd$	$C_{42}H_{34}S_4Pt$
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	14.832 (3)	14.898 (3)	14.885 (4)
b, Å	8.814 (2)	8.805 (3)	8.828 (3)
c, Å	14.867 (3)	14.791 (3)	14.806 (6)
β, deg.	112.69 (2)	110.98 (2)	111.04 (2)
V, Å³	1793 (1)	1811.6	1815.8
T, K	295	295	295
ρ, g/cm³ (calcd)	1.344	1.42	1.576
Z	2	2	2
fw	725.7	773.40	862.06
range of transm	0.786–1.00	0.418–1.00	0.781–1.00
λ, Å (Mo Kα)	0.7107	0.7107	0.7107
μ, cm⁻¹	7.95	7.50	
$R(F_o)$	0.031	0.041	
$R_w(F_o)$	0.041	0.034	

Table II. Selected Geometric Data for *anti-2*

Distances (Å)			
Ni–S(1)	2.1711 (6)	S(2)–C(2)	1.753 (2)
Ni–S(2)	2.1593 (6)	C(1)–C(2)	1.339 (3)
S(1)–C(1)	1.775 (2)	C(1)–C(3)	1.482 (3)
S(1)–C(15)	1.835 (2)	C(2)–C(9)	1.488 (3)

Angles (deg)			
S(1)–Ni–S(1)	180	S(1)–C(1)–C(2)	115.4 (2)
S(1)–Ni–S(2)	90.73 (2)	S(1)–C(1)–C(3)	116.0 (2)
S(1)–Ni–S(2)	89.27 (2)	C(2)–C(1)–C(3)	128.6 (2)
S(2)–Ni–S(2)	180	S(2)–C(2)–C(1)	122.2 (2)
Ni–S(1)–C(1)	106.80 (8)	S(2)–C(2)–C(9)	113.3 (2)
Ni–S(1)–C(15)	109.31 (8)	C(1)–C(2)–C(9)	124.4 (2)
C(1)–S(1)–C(15)	101.9 (1)	C(1)–C(3)–C(4)	120.4 (2)
Ni–S(2)–C(2)	105.11 (7)	C(1)–C(3)–C(8)	121.7 (2)

Table III. Selected Geometric Data for *anti-3*

Distances (Å)			
Pd–S(1)	2.2861 (4)	S(2)–C(2)	1.749 (2)
Pd–S(2)	2.2939 (4)	C(1)–C(2)	1.347 (2)
S(1)–C(1)	1.782 (2)	C(1)–C(3)	1.476 (2)
S(1)–C(15)	1.835 (2)	C(2)–C(9)	1.490 (2)

Angles (deg)			
S(1)–Pd–S(1)	180	S(1)–C(1)–C(2)	117.3 (1)
S(1)–Pd–S(2)	86.88 (1)	S(1)–C(1)–C(3)	115.3 (1)
S(1)–Pd–S(2)	93.12 (1)	C(2)–C(1)–C(3)	127.3 (1)
S(2)–Pd–S(2)	180	S(2)–C(2)–C(1)	124.0 (1)
Pd–S(1)–C(1)	106.19 (5)	C(2)–C(2)–C(9)	112.6 (1)
Pd–S(1)–C(15)	108.08 (6)	C(1)–C(2)C(9)	123.4 (1)
C(1)–S(1)–C(15)	102.47 (7)	C(1)–C(3)–C(4)	120.5 (1)
Pd–S(2)–C(2)	104.46 (6)	C(1)–C(3)–C(8)	121.8 (1)

Hydrogen atoms were located and held in near-"ideal" X-ray positions. Atomic scattering factors were taken from the literature.[9,10]

The structure of **3** was solved by using Patterson and Fourier methods. Hydrogen atoms were located, and their positions and thermal parameters were refined. The structures of **3** was refined in full-matrix least squares. Scattering factors were taken from ref 10. Anomalous dispersion effects were included in F_c; the values for *f′* and *f″* were those of Cromer.[11] All calculations were performed on a VAX computer using SDP/VAX.[12] The structure of **4** was not solved, but unit cell dimensions are included in Table I.

Results

The results of the chemical studies and of the variable-temperature ¹H NMR measurements on complexes **2–8** are outlined in the Experimental Section. The structural data for complexes

(9) Cromer, D. T.; Waber, J. T. *International Tables of X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(10) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(11) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(12) Cruickshank, D. W. J. *Acta Crystallogr.* **1949**, *2*, 154.

Table IV. Positional Parameters of *anti*-3 and Their Estimated Standard Deviations

| atom	x	y	z	B, Å^2
Pd	0.000	0.000	0.000	2.831 (3)
S(1)	0.06512 (3)	0.03307 (5)	0.16402 (3)	2.815 (7)
S(2)	0.15357 (3)	0.01960 (6)	0.00009 (3)	3.76 (1)
C(1)	0.1922 (1)	0.0220 (2)	0.1956 (1)	2.66 (3)
C(2)	0.2263 (1)	0.0248 (2)	0.1227 (1)	2.75 (3)
C(3)	0.2485 (1)	0.0185 (2)	0.3005 (1)	2.79 (3)
C(4)	0.3255 (1)	-0.0823 (2)	0.3380 (1)	3.52 (4)
C(5)	0.3795 (1)	-0.0845 (3)	0.4353 (1)	4.70 (5)
C(6)	0.3580 (2)	0.0121 (3)	0.4989 (2)	5.54 (6)
C(7)	0.2813 (2)	0.1096 (3)	0.4630 (1)	5.32 (5)
C(8)	0.2272 (1)	0.1134 (2)	0.3652 (1)	3.88 (4)
C(9)	0.3304 (1)	0.0364 (2)	0.1380 (1)	2.91 (3)
C(10)	0.3886 (1)	0.1470 (2)	0.1971 (1)	3.88 (4)
C(11)	0.4843 (1)	0.1576 (3)	0.2085 (2)	4.97 (5)
C(12)	0.5239 (1)	0.0585 (3)	0.1612 (2)	5.05 (5)
C(13)	0.4676 (1)	-0.0516 (3)	0.1021 (1)	4.64 (4)
C(14)	0.3714 (1)	-0.0625 (2)	0.0898 (1)	3.76 (4)
C(15)	0.0390 (1)	-0.1371 (2)	0.2218 (1)	3.59 (4)
C(16)	0.0873 (1)	-0.2790 (2)	0.2071 (1)	3.55 (4)
C(17)	0.1543 (1)	-0.3501 (2)	0.2860 (1)	4.31 (4)
C(18)	0.1991 (2)	-0.4814 (2)	0.2751 (2)	5.46 (6)
C(19)	0.1788 (2)	-0.5430 (3)	0.1858 (2)	6.66 (6)
C(20)	0.1127 (3)	-0.4735 (3)	0.1056 (2)	8.25 (9)
C(21)	0.0665 (2)	-0.3427 (3)	0.1173 (2)	6.19 (6)
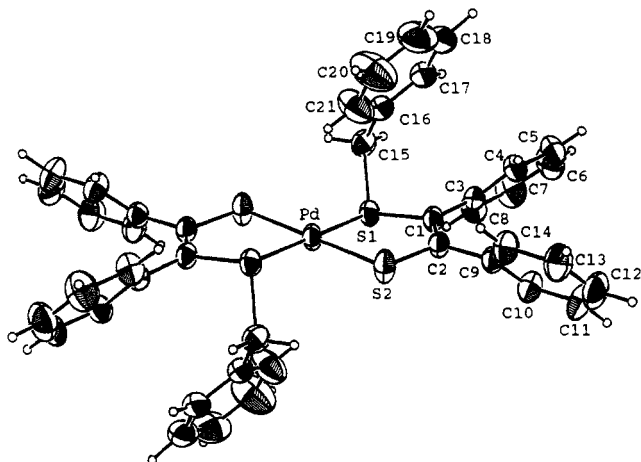
Figure 1. Perspective drawing of the structure of the anti isomer of **3** with numbering of atoms other than hydrogen.

2-4 are given in Tables I–IV; a perspective view of the structure of **3** is provided in Figure 1.

Discussion

Structural Studies. The complexes M[(PhCH$_2$)$_2$S$_4$C$_4$Ph$_4$], with M = Ni, Pd, and Pt, are isomorphous. As the unit cell dimensions of **3** and **4** are almost identical (see Table I), only the structures of **2** and **3** were solved, and only the structure of **2** is shown (see Figure 1). The structure of **2** also resembles that of **1**, although the C–S(benzyl) bond of 1.835 (5) Å in **2** is significantly longer than the C–S(CH$_3$) bond of 1.779 (5) Å in **1**. This suggests that the C–S(benzyl) bonds are labilized due to a combination of steric and electronic effects. The Ni–S–C(benzyl) bond angle in **2** [109.31 (8)°] is also significantly wider than the Ni–S–C(CH$_3$) bond angle in **1** [105.2 (2)°], revealing the absence of lattice compression effects. Such effects are also absent in **3**, as evidenced by the observed Pd–S–C(benzyl) bond angle of 108.8 (8)°. The MS$_4$ moieties in the complexes are essentially coplanar. Although the Ni–S(1) bond in **2** appears to be longer than Ni–S(2) in **4**, the Pd–S(1) bond is slightly shorter than Pd–S(2). In both cases, the differences are only about 0.01 Å (see Table II). The phenyl rings of the benzyl groups are in a near parallel arrangement with the nearest phenyl group of the dithiolene ligand, suggesting a possible interaction between the aromatic π-electrons.

Dynamic Properties in Solution. The dynamic behavior of complexes **2–8** reflects influences of the central metal and the
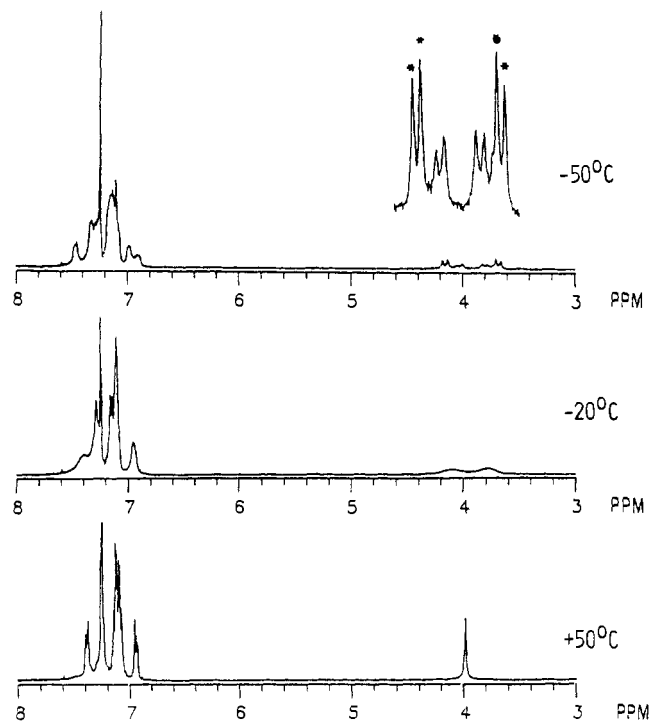
Figure 2. ^{1}H NMR spectra of **2** in CDCl$_3$ at different temperatures, showing the trans–anti isomer (at –50 °C, signals with asterisks) and the trans–syn isomer, generated by sulfur inversion.

aralkyl substituents. Whereas the ^{1}H NMR analysis of solutions of **1** had previously shown[3] the presence of trans–anti, trans–syn, and small amounts of the cis–anti isomers, the spectra of solutions of complexes **2**, **5**, **6**, and **7** consistently revealed the presence of only the trans–anti or the trans–anti and trans–syn isomers. For example, at –50 °C, the signals of the benzyl CH$_2$ protons in **2** appear as two sets of a doublet of doublets (see Figure 2). This pattern is due to sulfur-inversion equilibria involving only the trans–anti and trans–cis isomers. The ratio between the trans–anti and the trans–syn isomers at –50 °C is about 3:1, consistent with the higher stability of the trans–anti isomer, whose J value of the methylene protons is 14.1 Hz, while the J value of the trans–syn isomer is 13.5 Hz. At higher temperatures, the increased rates of the sulfur-inversion processes cause the signal first to broaden to a doublet at 0 °C and ultimately to a singlet at about 5 °C (see Figure 2). However, the NMR spectra of unrecrystallized samples of **3**, prepared by the standard method of reacting [Pd-(S$_4$C$_4$Ph$_4$)]$^{2-}$ with benzyl bromide, show signals consistent with the presence of three species, the trans–anti, trans–syn and cis–anti isomers, at approximate ratios of 1.5:1.0:1.5. This assignment is supported by the fact that the intensities of the signals assigned to the cis–anti isomer are greatly reduced in recrystallized samples of **3**, known to be the trans–anti isomer by X-ray structural analysis. The different isomeric composition of unrecrystallized **3** suggests that the benzylation of [Pd(S$_4$C$_4$Ph$_4$)]$^{2-}$ initially produces a mixture of the cis and the trans isomers. Due to slow racemization processes in solution, the trans–anti isomer accumulates and is isolated; the cis–anti isomer cannot be isolated. Moreover, ^{1}H NMR analyses of solutions of **3** prepared from the pure trans–anti isomer invariably revealed the presence of signals of the cis isomer at concentrations of about 5% (see Figure 3), which presumably represents the equilibrium concentration. The NMR signals of the trans–anti, trans–syn, and cis–anti isomers were also detected in the NMR spectra of the unrecrystallized platinum complex **4** (see Figure 4). In this case, separation of the trans and the cis isomers was possible because the cis isomer of **4** is conformationally sufficiently stable and more soluble in CH$_2$Cl$_2$ than the trans isomer. The spectra of both isolated isomers are also shown in Figure 4.

In contrast to complexes **2**, **5**, **6**, and **7**, the ^{1}H NMR spectra of the anthracenyl complex **8** revealed the presence of only one isomer at –50 °C, which was assigned to the trans–anti isomer.
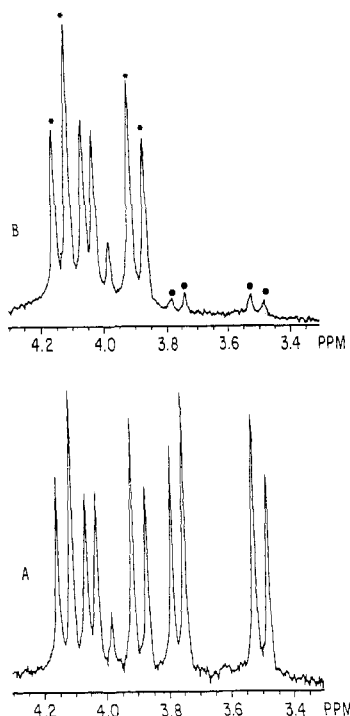
Figure 3. ¹H NMR spectra of **3**: (A) signals of unrecrystallized **3**; (B) signals of the anti isomer of **3**, showing the equilibrium concentrations of the trans-anti (signals with asterisks), trans-syn (unmarked), and cis-anti isomers (signals with ●), in CDCl₃ at –50 °C.

The sulfur-inversion processes are in this case apparently blocked due to steric effects or possibly by interactions of the anthracenyl and the phenyl substituents.

Chemical Properties. All aralkyl dithiolene complexes are water-insoluble and air-stable, just as the corresponding dialkyl dithiolenes. Complex **2** on heating decomposes with ligand disproportionation (eq 1).
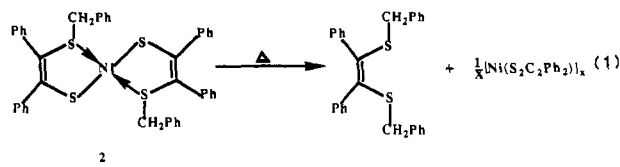
However, the 9-methylene anthracenyl derivative **8**, in contrast, decomposes by way of C–S bond homolysis (eq 2).

(R= 9-methylene anthracenyl)

8
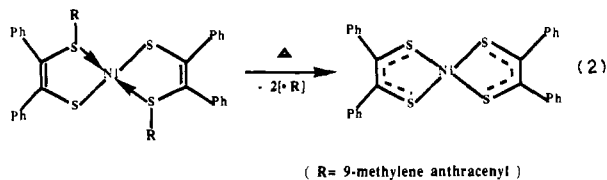
Complex **8** is thermally significantly less stable (mp 158 °C dec) due to the electronic labilization of the C–S(anthracenylmethyl) bonds. Complex **8** is also the most light-sensitive of all the aralkyl dithiolenes of d⁸ metals that have thus far been synthesized. The photolysis of the complexes proceeds more rapidly aerobically than under anaerobic conditions, consistent with a homolytic process of C–S bond cleavage; **2** was previously[2] shown on aerobic photolysis to yield Ni(S₄C₄Ph₄) and products derived from benzyl radicals terminating either by H-abstraction reactions
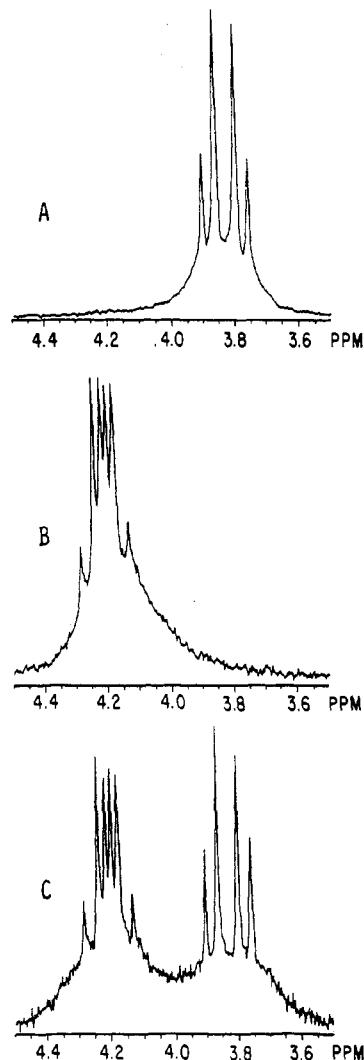
Figure 4. ¹H NMR spectra of isomers of **4**: (A) signals corresponding to the cis-anti isomers; (B) signals corresponding to the trans-anti and trans-syn isomers; (C) signals of unrecrystallized **4**, identifying it as a mixture of the trans-anti, trans-syn, and cis-anti isomers, in CDCl₃ at –50 °C.

or oxidation. In the series of nickel complexes **2** and **5–8**, the relative photolysis rates increase with increasing conjugation (complexes **7** and **8** vs **2**) or by electron-withdrawing substituents (NO₂ in **6**), while electron-donating substituents (CH₃O in **5**) reduce the photolysis rates. The comparative photolability of the platinum(II) dibenzyl dithiolene **4** indicates a labilization of the C–S(CH₂Ph) bonds, which in this case may be caused primarily by strong Pt–S bonding interactions. By selecting appropriate substituents, it should be possible to obtain highly photosensitive compounds for possible practical applications.