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Radical Substitution in the Nickeladithiolene Ring in Bis(1-phenyl-1,2-ethenedithiolato)nickel(0)

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Substitution of the 1-cyano-1-methylethyl group for hydrogen in the nickeladithiolene ring occurs in the reaction of bis(1-phenyl-1,2-ethenedithiolato)nickel(0) with 2,2′-azobis(isobutyronitrile). A radical mechanism is evidenced by the inhibition of the substitution in the presence of the radical scavenger TEMPO. 2,2′-Azobis(methyl isobutyrate) and 1,1′-azobis(1-cyanocyclohexane) undergo similar substitution reactions. The reaction is accompanied by the exchange of dithiolato ligands. Phenylation of the nickeladithiolene ring occurs in the reaction of (phenylazo)triphenylmethane. The *cis*−*trans* isomerization and the exchange of dithiolato ligands are discussed in connection with the radical substitution.

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Introduction

A metalladithiolene is a unique conjugated metal chelate ring having six π electrons. A variety of interesting properties have been reported.[1] Its aromaticity has been mainly demonstrated in terms of ring current in NMR,[2] while chemical evidence has been reported only in a very short description by Schrauzer and Mayweg on the Friedel−Crafts alkylation in a molybdenadithiolene ring.[3] Very recently, we have reported electrophilic and radical substitution reactions in cobaltadithiolene rings in (η^5-cyclopentadienyl)(1,2-ethenedithiolato)cobalt(III) complexes.[4] This is the first example of a radical substitution in quasi-aromatic metallacycles and conjugated chelate complexes. Here we report a radical substitution in a nickeladithiolene ring in another type of (dithiolato)metal complex, bis(1-phenyl-1,2-ethenedithiolato)nickel(0) (**1**).

Results and Discussion

Structure of Bis(1-phenyl-1,2-ethenedithiolato)nickel(0). For the planar bis(1-substituted 1,2-ethenedithiolato)metal(0) complexes, a pair of geometrical isomers may exist. Mueller-Westerhoff *et al.* determined the crystal structure of bis[1-(octylphenyl)-1,2-ethenedithiolato]nickel(0) and showed that it exists as the *trans* isomer in crystals.[5] In solutions, an equilibrium between *cis* and *trans* forms has been suggested on the basis of NMR results.[6] The complex used in this study, bis(1-phenyl-1,2-ethenedithiolato)nickel(0) (**1**), was prepared by the reaction of nickel(II) chloride with 4-phenyl-1,3-dithiol-2-one. Only one product was isolated. The X-ray structure analysis shows that the complex has a *trans* configuration (**1a**) in the crystalline state (Figure 1). Selected bond lengths and angles are shown in Figure 1.

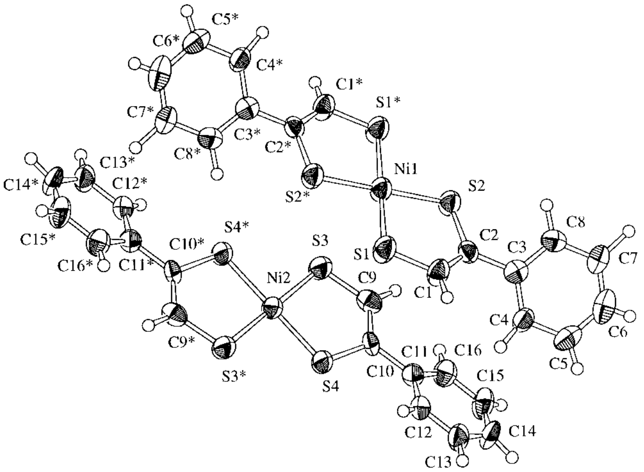

Figure 1. ORTEP drawing of **1** and selected bond lengths and angles. Bond lengths (Å): Ni(1)−S(1), 2.127(2); Ni(1)−S(2), 2.129(2); S(1)−C(1), 1.694(9); S(2)−C(2), 1.689(8); C(1)−C(2), 1.36(1); C(1)−H(1), 0.89(6); C(2)−C(3), 1.491(10); C(3)−C(4), 1.40(1); C(4)−C(5), 1.39(1); C(5)−C(6), 1.40(1); C(6)−C(7), 1.35(1); C(7)−C(8), 1.390(10); C(8)−C(3), 1.41(1). Bond angles (deg): S(1)−Ni(1)−S(2), 91.39(9); S(1)−Ni(1)−S(2)*, 88.61(9); Ni(1)−S(1)−C(1), 103.5(3); Ni(1)−S(2)−C(2), 105.2(3); S(1)−C(1)−C(2), 121.7(7); S(2)−C(2)−C(1), 118.2(6); S(2)−C(2)−C(3), 118.9(7); C(1)−C(2)−C(3), 122.9(8); S(1)−C(1)−H(1), 117(4); C(2)−C(1)−H(1), 121(4); S(1)−Ni(1)−S(1)*, 180.00.

In the unit cell, two independent molecules are paired and both have the *trans* configuration. The two dithiolene rings in the complex are coplanar. The bond lengths and bond angles are similar to those in bis(1,2-diphenyl-1,2-ethenedithiolato)nickel(0).[7] The C=C bond

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⊗ Abstract published in *Advance ACS Abstracts,* December 1, 1996.

(1) Reviews: (a) Schrauzer, G. N. *Acc. Chem. Res.* **1969**, *2*, 72−80. (b) McCleverty, J. A. *Prog. Inorg. Chem.* **1969**, *10*, 49−221. (c) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303−348. (d) Mueller-Westerhoff, U. T.; Vance, B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 2, pp 595−631. (e) Sugimori, A. *Yuki Gosei Kagaku Kyokai Shi* **1990**, *48*, 788−796.

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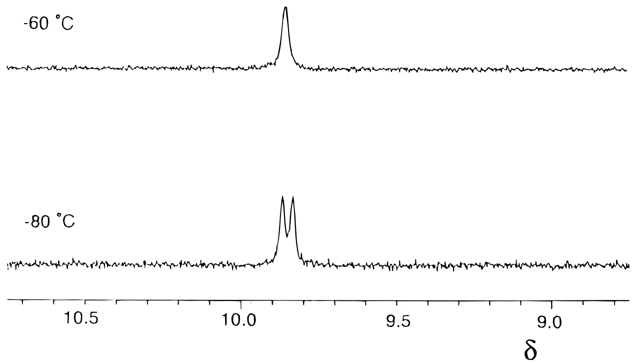
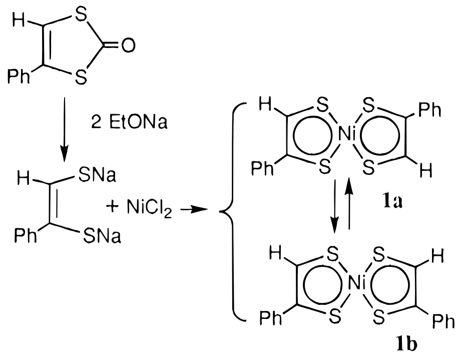


Figure 2. Temperature dependence of ^{1}H NMR signals assigned to the hydrogen attached to the nickeladithiolene ring in **1**.

length of 1.36(1) Å in the nickeladithiolene ring suggests the delocalization of π electrons.

In the ^{1}H NMR spectrum in dichloromethane-d_2 at −60 °C, we observe a single signal at δ 9.85 for the ring protons, but at −80 °C the signal is split into two peaks.[8] This suggests that the complex exists in two isomeric forms, **1a** and **1b**, and that they are interconverted easily at room temperature. In the following discussions we represent the complex in the *trans* form, **1a**.

The *cis*−*trans* isomerization may be explained by the ligand exchange. However, as will be discussed at the end of the article, the ligand exchange is a slow process. Thus, the *cis*−*trans* isomerization should be explained by another mechanism. The *cis*−*trans* isomerization would occur by the rotation of the ligand around the metal atom.



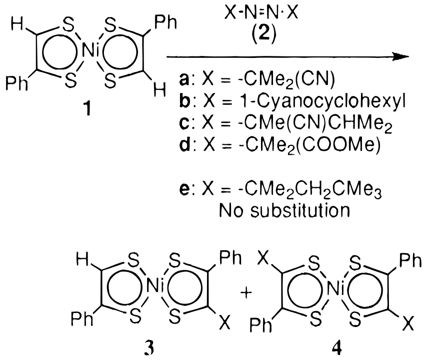
Radical Substitution. Refluxing a benzene solution of **1** and the azo compounds **2a**−**c** gives substitution products in which the hydrogen atom of the dithiolene ring is replaced by the substituted alkyl groups derived from the decomposition of the azo compounds. Both mono- and disubstitution products (**3** and **4**) were obtained. The yields are summarized in Table 1.

The presence of a radical scavenger, 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), completely inhibits the reaction, and the starting nickeladithiolene was recovered almost quantitatively. This indicates that the substitution occurs by a radical mechanism.

Table 1. Substitution Reactions of Nickeladithiolene 1 by Azo Compounds 2[a]

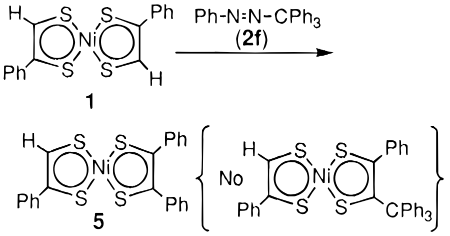
azo compd	additive	molar ratio **1**:**2**:additive	product yield, % **3**	product yield, % **4**	recovery of **1**, %
2a			18	30	trace
2a	TEMPO	1:1:10	trace	0	94
2b			35	7	33
2c			24	41	trace
2d			24	39	trace
2e			0	0	84

[a] Reaction conditions: solvent, benzene (100 cm^3); reaction temperature, 80 °C; reaction time, 22 h; amount of **1**, 0.3 mmol; amount of **2**, 0.3 mmol.



The mass balance in the presence of TEMPO is higher than that in its absence. This suggests that the radical species causes the decomposition of the nickeladithiolene in addition to the substitution reaction. TEMPO may inhibit the side reactions as well as the substitution reaction.

The radicals having electron-attracting substituents at the reaction center undergo substitution easily. However, an alkyl radical, 2,4-dimethylpent-2-yl, having no electron-attracting group at the radical center, affords no substitution products. When we used (phenylazo)triphenylmethane (**2f**) as a radical source, we obtained the phenylation product in 16% yield (recovery of **1** 32%). However, no substitution by the triphenylmethyl group occurred.



The substitution occurs only when the conjugated metalladithiolene system is present, as indicated by the failure of norbornene-5,6-diyl-bridged complexes to undergo a substitution reaction with 2,2′-azobis(isobutyronitrile).[9] In this case, 73% of the starting complex was recovered. This fact indicates that the conjugation (aromaticity) of the chelate ring is essential for the occurrence of the radical substitution.

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(8) The splitting of the signal of H in the nickeladithiolene ring at low temperature was not observed in the case of a trisubstituted nickeladithiolene, (1-phenyl-1,2-ethenedithiolato)(1,2-diphenyl-1,2-ethenedithiolato)nickel(0), for which no geometrical isomers are expected. Although the X-ray structure suggests an intermolecular interaction between Ni and S in the crystals, the NMR data for trisubstituted nickeladithiolene indicate that the complex exists in a single form. This excludes the monomer−dimer equilibrium in solution. The separation of the two signals in **1** is 9.8 Hz. This can not be explained by the coupling of protons.

(9) The configurations of the substituents in the nickeladithiolene rings have not been determined. The adduct would be a mixture of the isomers.

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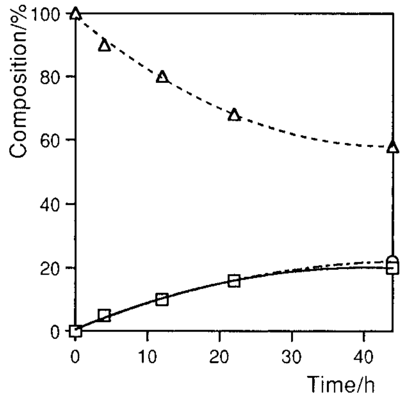


Figure 3. Equilibration among **3a**, **4a**, and **1**, with **3a** as starting material: (△) **3a**; (○) **4a**; (□) **1**.

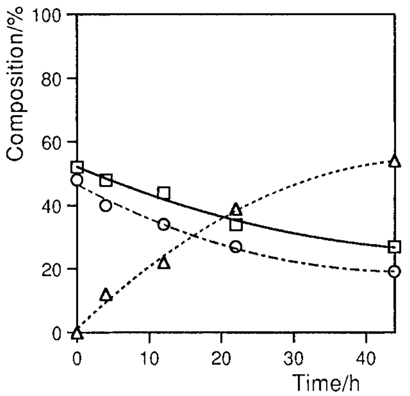
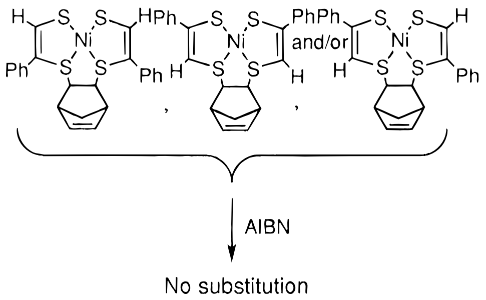
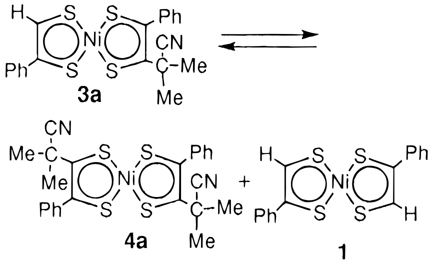


Figure 4. Equilibration among **3a**, **4a**, and **1**, with a mixture of **1** and **4a** (52:48) as starting material: (△) **3a**; (○) **4a**; (□) **1**.



Ligand Exchange. In some cases, the disubstituted products are formed even at low conversions. This is ascribable to the occurrence of ligand exchange reactions. The exchange of the dithiolato ligands has been reported for monoanionic nickeladithiolene complexes.[10] In our system, the ligand exchange is proved by refluxing of **3a** in a benzene solution.



The composition of the equilibrium mixture **1**:**3a**:**4a** is about 1:2:1 (Figure 3). When we start from a mixture of **1** and **4a** in the molar ratio of 52:48, we obtained an equilibrium mixture of similar composition (Figure 4).

Experimental Section

General Considerations. NMR spectra were recorded on a JEOL Model GX-270 instrument. Mass and UV−visible spectra were measured using a JEOL model SX 102A mass spectrometer and a Hitachi Model 228 UV−visible spectrometer, respectively.

Synthesis of Bis(1-phenyl-1,2-ethenedithiolato)nickel(0). 4-Phenyl-1,3-dithiol-2-one was prepared according to the literature.[11] The dianion of bis(1-phenyl-1,2-ethenedithiolato)nickel(0) (**1**) was prepared by the reaction of nickel chloride with 4-phenyl-1,3-dithiol-2-one at room temperature (for 10 min) in a modified method of the literature procedure,[12] using sodium methoxide instead of sodium hydroxide as a base in methanol. The neutral complex was obtained by oxidizing the dianion with I_2. The complex was purified by column chromatography using silica gel (Wako-gel C-300). The complex **1** was eluted with a mixed solvent of hexane and dichloromethane (ratio 5:1 by volume). Yield: 84%.

The crystals for the X-ray crystallographic analysis were prepared by the recrystallyzation from a mixed solvent of hexane and dichloromethane by slow evaporation of the solvent.

1: deep green crystals; mp 180−181 °C. UV (C_6H_6): 306 (ϵ 2200), 584 (1520), 820 nm (24 500). ^{1}H NMR ($CDCl_3$): δ 7.42−7.54 (m, 6H, Ph), 8.97−8.01 (m, 4H, Ph), 9.70 (s, 2H, H in the dithiolene ring). ^{13}C NMR ($CDCl_3$): δ 126, 129, 130, 138 (Ph), 166 (J_{CH} = 173.3 Hz, C of dithiolene ring attached to H), 183 (C of dithiolene ring). MS (70 eV): m/z 390 (M^+). Anal. Found: C, 49.22; H, 3.02. Calcd for $C_{16}H_{12}NiS_4$: C, 49.12; H, 3.09.

X-ray Crystallographic Determination and Refinement of 1. All measurements were made on a Rigaku AFC5S diffractometer with graphite-monochromated Mo Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the $20.08 < 2\theta < 24.55°$ range, corresponded to a primitive monoclinic cell with the dimensions in Table 2.

The data were collected at a temperature of 23 ± 1 °C using the ω−2θ scan technique to a maximum 2θ value of 55.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.15° with a takeoff angle of 6.0°. Scans of $(0.84 + 0.30 \tan \theta)°$ were made at a speed of 6.0 °/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of three scans), and the counts were accumulated to assure good counting statistics.

Of the 3280 reflections which were collected, 3054 were unique (R_{int} = 0.061). The intensities of 3 representative reflections were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ, for Mo Kα radiation is 17.4 cm^{-1}. An empirical absorption correction using the program DIFABS was applied which resulted in transmission factors ranging from 0.90 to 1.03. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SAPI91 of Rigaku Corp.) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1043 observed reflections ($I > 3.00\sigma(I)$) and 241 variable parameters

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Table 2. Crystal Data for 1

empirical formula	$C_{16}H_{12}S_4Ni$
fw	391.21
temp	23(1) °C
wavelength	0.710 69 Å
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell dimens	$a = 9.420(3)$ Å
	$b = 9.579(3)$ Å
	$c = 17.844(2)$ Å
	$\beta = 106.70(2)°$
	$\gamma = 91.61(2)°$
V, Z	1609.5(7) Å^3, 4
D(calcd)	1.61 g/cm^3
abs coeff, μ(Mo Kα)	17.12 cm^{-1}
F(000)	800.00
cryst size	0.10 × 0.13 × 0.50 mm
radiation	Mo Kα ($\lambda = 0.710$ 69 Å)
scan type	$\omega-2\theta$
$2\theta_{max}$ for data collection	55.0°
no. of rflns collected	3280
no. of indep rflns	3054
refinement method	full-matrix least squares
no. of data/params	1043/241
goodness of fit on F	1.19
final R indices ($I > 3\sigma(I)$)	$R = 0.039$, $R_w = 0.026$
largest diff peak and hole	0.32 and -0.31 e^-/Å^3

and converged (largest parameter was 0.16 times its esd) with unweighted and weighed agreement factors of

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.039$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.026$$

All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corp. Crystal data and details of the X-ray experiments are given in Table 2.

Reaction of Nickeladithiolene 1 with Azo Compounds. The complex **1** (*ca*. 0.3 mmol) and azo compound **2** (*ca* 0.3 mmol) were reacted in benzene (100 cm^3) under reflux for 22 h under an Ar atmosphere.

The products were separated by column chromatography using silica gel (Wako-gel C-300). The eluent was a mixture of hexane and dichloromethane. Chromatography afforded satisfactorily pure product.

Identification of (1-phenyl-1,2-ethenedithiolato)[1-phenyl-2-(1-cyano-1-methylethyl)-1,2-ethenedithiolato]nickel(0) (**3a**): deep blue crystals; mp 135 °C. UV−vis (benzene): 318 (ϵ 44 000), 576 (1900), 796 nm (28 000). ^{1}H NMR ($CDCl_3$): δ 1.91 (s, 6H, Me), 7.44−7.66 (m, 8H, H in Ph at the *m*- and *p*-positions), 8.02 (m, 2H, H at the *o*-position of Ph adjacent to H), and 10.05 (s, 1H, H in the nickeladithiolene ring). ^{13}C NMR ($CDCl_3$): δ 30.5 (Me), 40.0 (*C*Me_2), 121.7 (CN), 126.84, 126.89, 128.23, 128.95, 129.23, 129.41, 129.68, 130.49, 138.47, 139.98 (Ph), 170.98 (J_{CH} = 173.4 Hz, *C*H in the nickel dithiolene ring), 175.70, 179.42, 189.40 (C in the nickeladithiolene ring). Mass (70 eV): *m*/*z* 457 (M^+, 29.3), 390 ($M^+ - C_4H_6N+H$, 11.5), 288 ($[Ni(S_2C_2Ph(H))S_2]^+$, 31.5), 233 ($[S_2C_2Ph(C_4H_6)]^+$, 41.4), 224 ($[Ni(S_2C_2Ph(H)]^+$, 21.1), 218 ($[S_2C_2(Ph)(C_3H_3N)]^+$, 30.2). Anal. Found: C, 52.93; H, 3.78; N, 3.23. Calcd for $C_{20}H_{17}NNiS_4$: C, 52.41; H, 3.74; N, 3.06.

Identification of bis[1-phenyl-2-(1-cyano-1-methylethyl)-1,2-ethenedithiolato]nickel(0) (4a): deep purple crystals; mp 237.8−239.5 °C. UV−vis (benzene): 321 (ϵ 49 000), 579 (2400), 776 nm (27 000). ^{1}H NMR ($CDCl_3$): δ 1.91 (s, 12H, Me), 7.37−7.62 (m, 10H, H in Ph). ^{13}C NMR ($CDCl_3$): δ 30.51 (Me), 40.52 (*C*Me_2), 121.29 (CN), 128.28, 128.95, 129.90, 140.05 (Ph), 180.23, 183.93 (C in the nickeladithiolene ring). Mass (70 eV): *m*/*z* 524 (M^+, 95.9), 457 ($M^+ - C_4H_6N+H$, 15.2), 355 ($M^+ - C_4H_6C_2Ph$, 12.9), 291 ($M^+ - S_2C_2Ph(H)$, 45.2), 233 ($[S_2C_2Ph(C_4H_6N)]^+$, 44.6), 223 ($[NiS_2C_2Ph]^+$, 28.8), 207 ($[S_2C_2Ph(C_3H_6)]^+$, 42.6), 206 ($[S_2C_2PhC_3H_5]^+$, 13.8). Anal. Found: C, 54.43; H, 4.36; N, 5.10. Calcd for $C_{24}H_{22}N_2NiS_4$: C, 54.86; H, 4.22; N, 5.33.

Identification of (1-phenyl-1,2-ethenedithiolato)[1-phenyl-2-(1-cyanocyclohexyl)-1,2-ethenedithiolato]nickel(0) (3b): deep blue crystals; mp 128−129.2 °C. ^{1}H NMR ($CDCl_3$): δ 1.59−1.88, 2.11−2.39 (m, 10H, C_6H_{10}), 7.42−7.59 (m, 8H and 5H H in Ph adjacent to the substituent and H of *m*- and *p*-positions of Ph adjacent to H), 8.00 (d, $J = 7.33$ Hz, 2H, H *o*-position of Ph adjacent to H), 10.3 (s, 1H, H in the nickeladithiolene ring). ^{13}C NMR ($CDCl_3$): δ 23.07, 24.65, 38.35, 46.65 (C_6H_{10}), 119.30 (CN), 126.83, 126.90, 128.16, 129.27, 129.38, 129.59, 130.40, 139.96 (Ph), 166.77, 170.55 (J_{CH} = 169.7 Hz, *C*H in the nickeladithiolene ring), 176.51, 180.09 (C in the nickeladithiolene ring). Mass (70 eV): *m*/*z* 497 (M^+, 3.4), 390 ($M^+ - C_6H_{10}CN + H$, 100), 290 ($[NiS_2C_2Ph(H)S_2H_2]^+$, 21), 273 ($[S_2C_2Ph(H)(C_6H_{10}CN)]^+$, 34.4), 236 ($[Ni(S_2C_2H)_2]^+$, 75.3), 224 ($[Ni(S_2CPh(H)]^+$, 32.9). Anal. Found: C, 55.87; H, 5.03; N, 3.06. Calcd for $C_{23}H_{21}NNiS_4$: C, 55.43; H, 4.25; N, 2.81.

Identification of bis[1-phenyl-2-(1-cyanocyclohexyl)-1,2-ethenedithiolato]nickel(0) (4b): deep purple crystals; mp 270.8−271.0 °C. ^{1}H NMR ($CDCl_3$): δ 1.57−1.86, 2.11−2.86 (m, 20H, C_6H_{10}), 7.42−7.56 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): δ 23.04, 24.60, 38.33, 47.13 (C_6H_{10}), 118.96 (CN), 128.16, 128.98, 129.76, 140.12 (Ph), 180.54, 184.11 (C in the nickeladithiolene ring). Mass (70 eV): *m*/*z* 604 (M^+, 0.63), 395 ($M^+ - C_2(Ph)(C_6H_{10}CN)$, 0.18), 331 ($[NiS_2C_2Ph(C_6H_{10}CN)]^+$, 0.57), 273 ($[SC(Ph)C(C_6H_{10}CN)]^+$, 65.9), 246 ($[SC(Ph)C(C_6H_9)]^+$, 11). Anal. Found: C, 59.02; H, 5.43; N, 4.57. Calcd for $C_{30}H_{30}N_2NiS_4$: C, 59.51; H, 4.99; N, 4.63.

Identification of (1-phenyl-1,2-ethenedithiolato)[1-phenyl-2-(1-cyano-1,3-dimethylbutyl)-1,2-ethenedithiolato]nickel(0) (3c): deep blue crystals; mp 50.5−52 °C. ^{1}H NMR ($CDCl_3$): δ 1.93 (s, 3H, CH_3CCN), 1.90 (dd, $J = 14.04$, 5.5 Hz, 1H, *H*CH), 2.25 (dd, $J = 14.04$, 5.5 Hz, 1H, HC*H*), 1.69−1.87 (m, 1H, Me_2C*H*), 0.97 (d, $J = 6.71$ Hz, 3H, CH_3CH(CH_3)), 0.83 (d, $J = 6.10$ Hz, 3H, CH_3CH(CH_3)). ^{13}C NMR ($CDCl_3$): δ 23.43, 23.64, 26.06 (Me), 30.80, 45.16, 50.89 (C in side chain), 121.26 (CN), 126.80, 128.07, 129.22, 129.38, 129.65, 130.44, 138.49, 139.96 (Ph), 170.90 (J_{CH}, 172.1 Hz, C having H in the nickeladithiolene ring), 175.50 (C in the nickeladithiolene ring), 178.63, 189.29 (C in the nickeladithiolene ring). Anal. Found: C, 55.50; H, 5.48; N, 2.76. Calcd for $C_{23}H_{23}NNiS_4$: C, 55.21; H, 4.63; N, 2.80.

Identification of bis[1-phenyl-2-(1-cyano-1,3-dimethylbutyl)-1,2-ethenedithiolato]nickel(0) (4c): deep blue crystals; mp 153.5−154.6 °C. ^{1}H NMR ($CDCl_3$): δ 1.94 (s, 3H, CH_3CCN), 1.90 (dd, $J = 14.04$, 6.71 Hz, 1H, *H*CH), 2.25 (dd, $J = 14.04$, 5.5 Hz, 1H, HC*H*), 1.67−1.86 (m, 1H, Me_2C*H*), 0.97 (d, $J = 6.71$ Hz, 3H, CH_3CH(CH_3)), 0.83 (d, $J = 6.71$ Hz, 3H, CH_3CH(CH_3)). ^{13}C NMR ($CDCl_3$): δ 23.43, 23.64, 26.06 (Me), 30.80, 45.16, 50.89 (C in side chain), 121.26 (CN), 126.80, 128.07, 129.22, 129.38, 129.65, 130.44, 138.49, 139.96 (Ph), 170.90 (J_{CH}, 172.1 Hz, C having H in the nickeladithiolene ring), 175.50 (C in the nickeladithiolene ring), 178.63, 189.29 (C in the nickeladithiolene ring). Anal. Found: C, 58.59; H, 5.50; N, 4.66. Calcd for $C_{30}H_{34}N_2NiS_4$: C, 59.11; H, 5.62; N, 4.60.

Identification of (1-phenyl-1,2-ethenedithiolato){1-phenyl-2-[1-(methoxycarbonyl)ethyl]-1,2-ethenedithiolato}nickel(0) (3d): deep blue crystals; mp 135 °C. ^{1}H NMR ($CDCl_3$): δ 1.76 (s, 6H, Me), 3.35 (s, 3H, OMe), 7.32 (dd, $J =$ 6.10, 1.83 Hz, 2H, H at *o*-position of Ph adjacent to the substituent), 7.38−7.55 (m, 6H, H in Ph at the *m*- and *p*-positions), 8.00 (dd, $J = 6.72$, 1.83 Hz, 2H, H at *o*-position of Ph adjacent to H), 9.82 (s, 1H, H in the nickeladithiolene ring). ^{13}C NMR ($CDCl_3$): δ 28.93 (Me), 52.09 (OMe), 126.84, 127.85, 128.88, 129.16, 129.22, 129.97, 138.61,140.25 (Ph), 167.80, 174.34 (C in the nickeladithiolene ring), 181.04 (COO), 186.05, 186.32 (C in the nickeladithiolene ring). Mass (70 eV): *m*/*z* 490 (M^+, 7.7), 390 ($M^+ - (C(CH_3)_2CO_2CH_3) + H$, 16.5), 290 ($[NiS_2C_2Ph(H)(S_2H_2)]^+$, 16.5), 288 ($[NiS_2C_2Ph(H)]^+$, 12.7), 266 ($[S_2C_2Ph(C_3H_6CO_2CH_3)]^+$, 23.0), 260 ($[Ni(PhC_2C_3H_6CO_2CH_3)]^+$, 5.4). Anal. Found: C, 51.57; H, 4.98. Calcd for $C_{21}H_{20}O_2NiS_4$: C, 51.34; H, 4.10.

Identification of bis{1-phenyl-2-[1-(methoxycarbonyl)-ethyl]-1,2-ethenedithiolato}nickel(0) (4d): deep blue crystals; mp 186.5−187.4 °C. ^1H NMR ($CDCl_3$): δ 1.75 (s, 12H, Me), 3.34 (s, 6H, OMe), 7.31 (dd, $J = 7.49$, $J = 1.83$ Hz, 2H, H at *o*-position of Ph), 7.35−7.49 (m, 8H, H in Ph at *m*- and *p*-positions). ^{13}C NMR ($CDCl_3$): δ 25.93 (CMe_2), 28.95 (Me), 52.06 (OMe), 127.80, 128.79, 129.07, 140.55 (Ph), 174.34 (C in the nickeladithiolene ring), 182.05 (COO), 186.99 (C in the nickeladithiolene ring). Mass (70 eV): *m*/*z* 590 (M^+, 79.7), 388 ($[NiS_4C_2(Ph)(C_5H_9O_2)]^+$, 12.4), 324 ($[NiS_2C_2(Ph)(C_5H_9O_2)]^+$, 100.0), 266 ($[S_2C_2(Ph)(C_5H_9O_2)]^+$, 29.0), 260 ($[NiC_2(Ph)(C_5H_9O_2)]^+$, 38.4), 207 ($[S_2C_2(Ph)(C_3H_6)]^+$, 39.0). Anal. Found: C, 53.19; H, 5.44. Calcd for $C_{26}H_{28}O_4NiS_4$: C, 52.80; H, 4.77.

Identification of (1-phenyl-1,2-ethenedithiolato)(1,2-diphenyl-1,2-ethenedithiolato)nickel(0) (3f): deep green crystals; mp 157 °C. ^1H NMR ($CDCl_3$): δ 7.27−8.02 (m, 15H, Ph), 9.76 (s, 1H, H in the nickeladithiolene ring). ^{13}C NMR ($CDCl_3$): δ 126.86, 128.41, 128.91, 129.02, 129.18, 129.90, 138.54, 140.93 (Ph), 166.95 ($J_{CH} = 172$ Hz, *C*H in the nickeladithiolene ring), 181.54 (C in the nickeladithiolene ring). Anal. Found: C, 56.35; H, 3.43. Calcd for $C_{22}H_{16}NiS_4$: C, 56.54; H, 3.45.

Ligand Exchange. The preparative experiment was carried out as follows. An equimolar mixture (each *ca.* 0.1 mmol) of **3a** and **3b** in benzene (100 cm^3) was refluxed under an atmosphere of Ar for 22 h. The products were separated by column chromatography as described above.

The process of the ligand exchange was followed by ^1H NMR. A $CDCl_3$ (0.5 cm^3) solution of **3a**,**b** (each 3.2 μmol) and ferrocene (as an internal standard) was warmed to 50 °C; ^1H NMR was followed at regular intervals.

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Supporting Information Available: Text giving details of the X-ray structure determination and tables of atomic coordinates, thermal parameters, all bond lengths and angles, torsion angles, and nonbonded contacts for **1** and figures giving ^1H NMR spectra at +25 and −80 °C for **1** and **5** (19 pages). Ordering information is given on any current masthead page.

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