The Oxidative Cycloaddition of Metal Dithiolenes to Olefins. Synthesis and Characterization of Norbornadiene–Bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel

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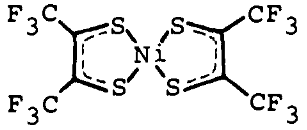
Abstract: Reaction of $Ni[S_2C_2(CF_3)_2]_2$ with norbornadiene and norbornene gives products which appear to be formed by the oxidative addition of the inorganic complex to the olefin. The structure of the norbornadiene adduct has been established by a single-crystal X-ray diffraction study. Briefly, the structure shows that two sulfur–carbon bonds have been formed between the reactants and that one of the norbornadiene carbon–carbon double bonds has been transformed into a single bond. The sulfur atoms are in the *exo* configuration, with one from each ligand being involved in the new bonds, which are about 0.1 Å longer than the sulfur–carbon bonds within the ligands. The structural, spectroscopic, and electrochemical properties of the adducts closely resemble those of the dianionic form of the nickel complex, suggesting that the reaction be considered an oxidative cycloaddition. The crystals studied were triclinic, $P\bar{1}$, with $a_0 = 11.76$ Å, $b_0 = 12.85$ Å, $c_0 = 8.15$ Å, $\alpha = 105.8°$, $\beta = 78.7°$, and $\gamma = 122.0°$, with the unit cell containing two formula units. The structure was solved using 1606 visually estimated unique reflections collected by a film method and refined to a final R factor of 10.7% based on F.

When previous studies of reactions of bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel (**1**) (nickel dithiete) revealed the formation of semiconducting donor–acceptor complexes,[1] we were immediately led to look at nickel dithiete as a catalyst system. Specifically we decided to look at the quadricyclene–norbornadiene valence isomerization, which is a forbidden thermal process for which metal ion catalysis has been demonstrated.[2] Our premise was that the interactions between nickel dithiete and organic substrates would be sufficiently strong to allow for metal-ion promotion of reactions. Further, a catalyst system of this sort would be simpler than those previously studied[2] and would permit theoretical prediction of reaction paths.



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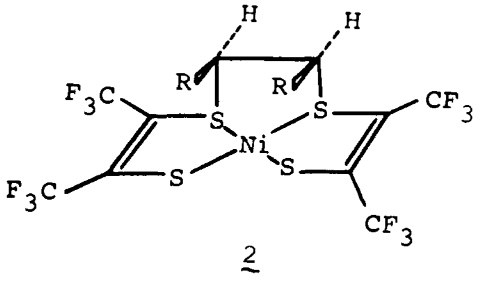
The reaction of nickel dithiete with various olefins (*e.g.*, norbornadiene) to form an addition product, **2**, is a facile reaction, however, and serves to poison the catalyst system. Since the reaction of metal 1,2 dithiolenes with olefins to give **3** had been previously suggested by Schrauzer,[3,4] *et al.*, as being slow (for the diphenyl substituted dithiolenes) we did not anticipate this problem.



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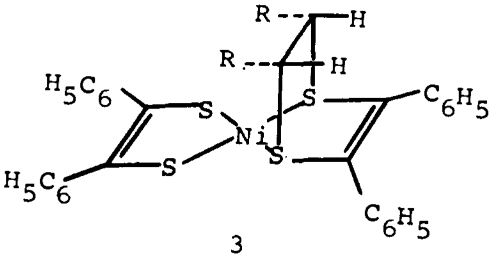

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The present report emphasizes the synthesis and structural chemistry of the nickel dithiete–olefin complexes.

Experimental Section

Preparation of Compounds. $Ni(S_2C_2(CF_3)_2)_2$ was prepared according to the method of Davison, *et al.*[5] Reagent grade solvents were dried (molecular sieves), then distilled. Reactions were carried out under nitrogen with magnetic stirring. Microanalyses were carried out by Galbraith Laboratories. The olefins, obtained commercially, were purified before use as described below.

The Norbornadiene–Bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel Adduct. Freshly distilled norbornadiene (1.00 cc, 9.9 mmol) was added to a deep purple solution of $Ni(S_2C_2(CF_3)_2)_2$ (181.1 mg, 0.345 mmol) in hexane (20 ml) with stirring at room temperature. The solution immediately turned dark green and green crystals precipitated. After solvent and excess olefin were removed under vacuum, the residue was redissolved in dichloromethane (10 ml). Slow evaporation of most of the solvent under a nitrogen stream deposited green crystals (104.0 mg, 50%), mp 205–206°. Repeated recrystallization from dichloromethane in a similar way provided the analytical sample, mp 206.0–206.5°.

Anal. Calcd for $C_{15}H_8S_4F_{12}Ni$: C, 29.87; H, 1.34; Ni, 9.73. Found: C, 29.70; H, 1.27; Ni, 10.68.

The infrared spectrum (Figure 3) and crystal structure of this material are described in the text.

The Norbornene–Bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel Adduct. Freshly sublimed norbornene (394.9 mg, 4.20 mmol) in dichloromethane (10 ml) was added to $Ni(S_2C_2(CF_3)_2)_2$ (134.2 mg, 0.235 mmol) in dichloromethane (20 ml) at room temperature. The initially deep purple solution turned green after *ca.* 1 min. The reaction mixture was concentrated under vacuum,

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[1] R. D. Schmitt, R. M. Wing, and A. H. Maki, *J. Amer. Chem. Soc.*, 91, 4394 (1969).

[2] H. Hogeveen and H. C. Volger, *ibid.*, 89, 2489 (1967).

[3] G. N. Schrauzer and V. P. Mayweg, *ibid.*, 87, 1483 (1965).

[4] G. N. Schrauzer and H. N. Rabinowitz, *ibid.*, 90, 4297 (1968).

[5] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 2, 1227 (1963).

Table I. Final Parameters in Norbornadiene–Nickel Dithiete

Atom	*x*[a]	*y*	*z*	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.3553 (2)	0.4163 (2)	0.1179 (2)	3.8 (1)	3.0 (1)	2.8 (1)	1.6 (1)	−0.6 (1)	1.0 (1)
S_{11}	0.2812 (4)	0.2479 (3)	−0.0758 (4)	4.9 (2)	3.8 (2)	3.7 (2)	1.8 (1)	−0.8 (1)	0.8 (1)
S_{12}	0.3530 (3)	0.3190 (3)	0.2978 (4)	4.3 (2)	3.7 (2)	3.5 (2)	2.3 (1)	−0.7 (1)	1.2 (1)
C_{11}	0.239 (1)	0.132 (1)	0.036 (1)	3.4 (3)					
C_{12}	0.259 (1)	0.158 (1)	0.203 (2)	3.3 (3)					
C_{13}	0.188 (2)	0.003 (1)	−0.071 (2)	4.8 (3)					
C_{14}	0.232 (2)	0.068 (2)	0.312 (2)	6.1 (4)					
F_{11}	0.162 (2)	−0.005 (1)	−0.223 (2)	22.4 (15)	3.7 (5)	10.2 (8)	4.1 (7)	−9.1 (9)	−2.4 (5)
F_{12}	0.079 (1)	−0.080 (1)	−0.005 (2)	9.7 (8)	5.4 (6)	13.5 (10)	0.2 (5)	4.3 (7)	1.3 (6)
F_{13}	0.271 (1)	−0.036 (1)	−0.097 (2)	11.2 (8)	9.1 (7)	14.6 (10)	7.6 (7)	−5.0 (7)	−3.9 (7)
F_{14}	0.265 (1)	0.128 (1)	0.472 (1)	15.5 (10)	6.3 (6)	6.5 (6)	5.6 (7)	−1.8 (6)	3.0 (5)
F_{15}	0.103 (2)	−0.013 (1)	0.330 (2)	12.3 (10)	8.9 (8)	15.8 (12)	1.3 (7)	−2.7 (9)	9.2 (9)
F_{16}	0.297 (2)	0.010 (1)	0.262 (2)	21.8 (15)	12.6 (10)	10.5 (8)	14.3 (11)	3.4 (9)	5.5 (8)
S_{21}	0.4112 (3)	0.5713 (3)	0.3303 (4)	3.7 (2)	3.4 (2)	2.8 (2)	1.4 (1)	−0.6 (1)	1.2 (1)
S_{22}	0.3311 (4)	0.5158 (3)	−0.0364 (4)	5.4 (2)	4.0 (2)	2.6 (2)	2.7 (1)	−0.6 (1)	1.1 (1)
C_{21}	0.374 (1)	0.673 (1)	0.269 (2)	3.3 (2)					
C_{22}	0.345 (1)	0.647 (1)	0.108 (1)	2.9 (2)					
C_{23}	0.392 (2)	0.785 (2)	0.407 (2)	5.0 (3)					
C_{24}	0.331 (2)	0.734 (1)	0.031 (2)	4.4 (3)					
F_{21}	0.406 (1)	0.773 (1)	0.556 (1)	15.6 (9)	5.2 (5)	3.5 (4)	4.6 (6)	−3.1 (5)	−0.6 (4)
F_{22}	0.297 (1)	0.811 (1)	0.424 (1)	7.9 (6)	7.9 (6)	10.2 (7)	5.6 (5)	−1.5 (5)	−1.7 (5)
F_{23}	0.507 (1)	0.890 (1)	0.378 (1)	9.1 (6)	3.5 (4)	7.5 (6)	0.7 (4)	−0.2 (5)	0.1 (4)
F_{24}	0.347 (2)	0.717 (2)	−0.129 (1)	37.9 (24)	15.5 (11)	4.9 (6)	21.4 (15)	1.5 (9)	3.1 (6)
F_{25}	0.217 (2)	0.721 (2)	0.066 (2)	12.5 (10)	20.5 (15)	20.8 (15)	11.7 (11)	3.9 (10)	14.9 (13)
F_{26}	0.411 (2)	0.851 (1)	0.080 (2)	16.4 (12)	7.5 (8)	19.7 (14)	3.9 (8)	−7.8 (11)	6.5 (9)
C_1	0.140 (1)	0.473 (1)	0.486 (2)	4.1 (3)					
C_2	0.065 (1)	0.430 (1)	0.648 (2)	5.1 (3)					
C_3	0.039 (2)	0.314 (2)	0.630 (2)	5.6 (3)					
C_4	0.093 (1)	0.276 (1)	0.461 (2)	4.4 (3)					
C_5	0.252 (2)	0.357 (1)	0.479 (2)	3.7 (3)					
C_6	0.281 (1)	0.496 (1)	0.498 (2)	3.5 (2)					
C_7	0.078 (2)	0.350 (2)	0.354 (2)	5.2 (3)					
H_1	0.16 (2)	0.55 (2)	0.49 (2)	5.0					
H_2	0.08 (2)	0.47 (2)	0.76 (2)	5.0					
H_3	0.00 (2)	0.27 (2)	0.77 (2)	5.0					
H_4	0.09 (2)	0.21 (2)	0.38 (2)	5.0					
H_5	0.25 (2)	0.38 (2)	0.56 (2)	5.0					
H_6	0.30 (2)	0.53 (1)	0.63 (2)	5.0					
H_7	0.01 (2)	0.31 (2)	0.34 (2)	5.0					
H_8	0.14 (2)	0.32 (2)	0.20 (2)	5.0					

[a] Estimated standard deviation of last significant figure given in parentheses. [b] All temperature factors are in units of Å,² with $B_{ij} = 4b_{ij}/a^*_i a^*_j$ and $T_r = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$.

and then the residue was dissolved in dichloromethane (10 ml). An insoluble blue material (unidentified) was removed by filtration, and the filtrate was slowly concentrated to *ca.* 1 ml under a nitrogen stream to afford dark green crystals (23.2 mg, 16%), mp 175.5–176.0°. The green solid was recrystallized twice from dichloromethane in a similar way to afford the analytical sample, mp 181.0–181.5°.

Anal. Calcd for $C_{15}H_{10}S_4F_{12}Ni$: C, 29.77; H, 1.66; Ni, 9.80. Found: C, 29.39; H, 1.41; Ni, 10.92.

A similar reaction carried out with hexane as a solvent afforded about 9% of the green adduct, mp 176–177°.

Infrared Spectra. Infrared spectra were taken on a Perkin-Elmer 621 grating spectrometer, and the samples were prepared by the KBr pellet method.

Electrochemistry. Controlled potential cyclic voltammetry was carried out using an instrument based on the design of DeFord[6] and modified by Goolsby and Sawyer.[7] The measurements were made in dichloromethane using *ca.* 0.1 *N* tetra(*n*-butyl) ammonium perchlorate as the supporting electrolyte. Potentials were measured at a platinum electrode *vs.* a saturated calomel electrode. The concentration of the metal complex was adjusted to *ca.* 10^{-3} *M* and the reference electrode was connected to this solution *via* a KCl–agar bridge.

X-Ray Diffraction. A prismatic dark green crystal (0.20 × 0.10 × 0.35 mm; *a*, *b*, *c*) was mounted in a borosilicate capillary (0.3-mm diam × 0.01-mm wall). Precession (Mo K$\bar{\alpha}$; λ 0.7107 Å) and Weissenberg (Cu K$\bar{\alpha}$; λ 1.5418 Å) photographs indicated that the crystal was triclinic, with a_0 = 11.76 (2) Å, b_0 = 12.85 (1) Å, c_0 = 8.15 (1) Å, α = 105.8 (2)°, β = 78.7 (2)°, and γ = 1.22.0 (2)°. An attempted Delaunay reduction failed to reveal any hidden symmetry. The density, 2.02 g/cc, measured by flotation in ethylene bromide-1,3-dibromopropane gave a calculated value of 1.98 molecules per unit cell.

Nickel-filtered copper radiation was used to collect a set of film intensities by the equiinclination Weissenberg method. Each film pack consisted of three films picked so that the relative intensities were about 100:10:1. Data were collected for the levels *hk*0 through *hk*7 and the intensities were estimated visually from the expanded side of the films by comparison with a set of timed exposures of a zero-level reflection of the same crystal. Of the 2023 unique reflections expected in the sphere $0.0 < \sin\theta \leq 0.77$, 1606 had finite intensities. These were corrected for Lorentz and polarization effects, but not for absorption ($\mu r = 0.5$). An empirical spot-shape correction was made to the severely elongated low-angle reflections on the upper levels.[8]

An IBM 360-50 computer was used in all calculations,[9] and the function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, with $w = (4.0 + F_o + F_o^2/90.0)^{-1}$.

Solution of the Structure

A three-dimensional map of the Patterson function was solved for the positions of the nickel and four sul-

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(6) D. D. DeFord, Abstracts, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958.

(7) A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, **39**, 411 (1967).

(8) A. K. Singh, *Z. Kristallogr.*, **124**, 378 (1967).

(9) The programs used were local modifications of Prewitt's DFSET and GAMP for data reduction; Zalkin's FORDAP for Patterson and electron density maps; Busing, Levy, and Martin's ORFLS for least-squares refinement; Johnson's ORTEP for drawings; and Wood's MGEOM for distances, angles, and planes.

fur atoms. After the coordinates of the five heavy atoms were improved by least-squares refinement, the residue, R_1,[10] was 0.52. An electron density map revealed the remaining atoms of the nickel dithiete moiety, but the positions of the norbornadiene atoms remained ambiguous. The positional and isotropic thermal parameters along with eight film scale factors were refined for three cycles improving R_1 to 0.33. The remaining seven carbon atoms were now located in a difference electron density map. Refinement of all positional, thermal, and film scale factors gave after four cycles a residual of 0.21. Four cycles of least-squares refinement with anisotropic thermal parameters for the Ni, S, and F atoms reduced R_1 to *0.12*.

Another difference Fourier had as its most prominent features ($\rho \sim 0.4$–0.6 e/Å^3), peaks in locations expected for the norbornadiene hydrogen atoms. These were now included in the refinement,[11] and two cycles reduced R_1 to 0.107.

The final weighted residue, R_2,[12] was 0.139 and the standard deviation of an observation of unit weight was 0.80. The observed and final calculated structure factors have been deposited with NAPS.[13]

Atom coordinates and thermal parameters are given in Table I, while derived parameters such as bond distances, angles, and some selected best planes are presented in Tables II, III, and IV.

Table II. Bond Lengths in Norbornadiene–Nickel Dithiete[a]

$\mathrm{Ni-S_{11}}$	2.149 (4)	$\mathrm{C_{13}-F_{11}}$	1.30 (2)
$\mathrm{Ni-S_{12}}$	2.159 (4)	$\mathrm{C_{13}-F_{12}}$	1.29 (2)
$\mathrm{Ni-S_{21}}$	2.139 (4)	$\mathrm{C_{13}-F_{13}}$	1.28 (2)
$\mathrm{Ni-S_{22}}$	2.168 (4)	$\mathrm{C_{14}-F_{14}}$	1.33 (2)
		$\mathrm{C_{14}-F_{15}}$	1.31 (2)
$\mathrm{S_{11}-C_{11}}$	1.75 (1)	$\mathrm{C_{14}-F_{16}}$	1.28 (3)
$\mathrm{S_{22}-C_{22}}$	1.72 (1)	$\mathrm{C_{23}-F_{21}}$	1.31 (2)
$\mathrm{S_{12}-C_{12}}$	1.77 (1)	$\mathrm{C_{23}-F_{22}}$	1.30 (2)
$\mathrm{S_{21}-C_{21}}$	1.79 (1)	$\mathrm{C_{23}-F_{23}}$	1.35 (2)
$\mathrm{S_{12}-C_5}$	1.84 (1)	$\mathrm{C_{24}-F_{24}}$	1.26 (2)
$\mathrm{S_{21}-C_6}$	1.87 (1)	$\mathrm{C_{24}-F_{25}}$	1.24 (2)
		$\mathrm{C_{24}-F_{26}}$	1.27 (2)
$\mathrm{C_{11}-C_{12}}$	1.35 (2)	⟨C–F⟩	1.29 (3)
$\mathrm{C_{21}-C_{22}}$	1.32 (2)		
$\mathrm{C_{11}-C_{13}}$	1.49 (2)	$\mathrm{C_2-C_3}$	1.32 (2)
$\mathrm{C_{12}-C_{14}}$	1.51 (2)	$\mathrm{C_1-C_2}$	1.49 (2)
$\mathrm{C_{21}-C_{23}}$	1.50 (2)	$\mathrm{C_3-C_4}$	1.47 (2)
$\mathrm{C_{22}-C_{24}}$	1.51 (2)	$\mathrm{C_4-C_5}$	1.60 (2)
⟨C–C⟩	1.50 (1)	$\mathrm{C_5-C_6}$	1.59 (2)
		$\mathrm{C_6-C_1}$	1.54 (2)
		$\mathrm{C_1-C_7}$	1.53 (2)
		$\mathrm{C_7-C_4}$	1.54 (2)
		⟨C–C⟩	1.54 (5)

[a] Estimated standard deviation of last significant figures in parentheses.

Table III. Selected Bond Angles in Norbornadiene–Nickel Dithiete

Angle	Degrees[a]	Angle	Degrees
$\mathrm{S_{11}-Ni-S_{12}}$	91.3	$\mathrm{S_{22}-C_{22}-C_{21}}$	123
$\mathrm{S_{12}-Ni-S_{21}}$	84.2	$\mathrm{C_{21}-C_{22}-C_{24}}$	123
$\mathrm{S_{21}-Ni-S_{22}}$	91.7		
$\mathrm{S_{22}-Ni-S_{11}}$	92.0	$\mathrm{C_2-C_1-C_6}$	104
		$\mathrm{C_2-C_1-C_7}$	102
$\mathrm{Ni-S_{11}-C_{11}}$	103.0 (4)	$\mathrm{C_6-C_1-C_7}$	102
$\mathrm{Ni-S_{22}-C_{22}}$	102.8 (4)	$\mathrm{C_1-C_2-C_3}$	107
$\mathrm{Ni-S_{12}-C_{12}}$	104.7 (4)	$\mathrm{C_2-C_3-C_4}$	109
$\mathrm{Ni-S_{12}-C_5}$	101.0 (5)	$\mathrm{C_3-C_4-C_5}$	103
$\mathrm{C_{12}-S_{12}-C_5}$	109.2 (6)	$\mathrm{C_3-C_4-C_7}$	102
$\mathrm{Ni-S_{21}-C_{21}}$	103.5 (4)	$\mathrm{C_5-C_4-C_7}$	100
$\mathrm{Ni-S_{21}-C_6}$	100.9 (4)	$\mathrm{C_4-C_5-C_6}$	102
$\mathrm{C_{21}-S_{21}-C_6}$	108.2 (6)	$\mathrm{C_4-C_5-S_{12}}$	115
		$\mathrm{C_6-C_5-S_{12}}$	111
$\mathrm{S_{11}-C_{11}-C_{13}}$	115	$\mathrm{C_5-C_6-C_1}$	102
$\mathrm{S_{11}-C_{11}-C_{12}}$	123	$\mathrm{C_1-C_6-S_{21}}$	116
$\mathrm{C_{12}-C_{11}-C_{13}}$	122	$\mathrm{C_5-C_6-S_{21}}$	110
$\mathrm{S_{12}-C_{12}-C_{14}}$	115	$\mathrm{C_1-C_7-C_4}$	94
$\mathrm{S_{12}-C_{12}-C_{11}}$	116		
$\mathrm{C_{11}-C_{12}-C_{14}}$	128		
$\mathrm{S_{21}-C_{21}-C_{23}}$	114		
$\mathrm{S_{21}-C_{21}-C_{22}}$	117		
$\mathrm{C_{22}-C_{21}-C_{23}}$	129		
$\mathrm{S_{22}-C_{22}-C_{24}}$	113		

[a] Standard deviations in last place are 1 unless otherwise indicated.

Table IV. Some Best Least-Squares Planes[a] in Norbornadiene–Nickel Dithiete

Atom	Wt	Distance from plane, Å
	Plane 1	
$\mathrm{S_{11}}$	32	−0.034
$\mathrm{S_{12}}$	32	0.033
$\mathrm{S_{21}}$	32	−0.029
$\mathrm{S_{22}}$	32	0.031
Ni	0	−0.128
$-0.9339X + 0.1474Y + 0.3256Z = -2.5590$		
	Plane 2	
$\mathrm{S_{11}}$	32	0.002
$\mathrm{S_{12}}$	32	−0.001
$\mathrm{C_{11}}$	12	−0.052
$\mathrm{C_{12}}$	12	0.050
$\mathrm{C_{13}}$	0	−0.307
$\mathrm{C_{14}}$	0	−0.025
Ni	0	0.317
$-0.8469X + 0.4298Y + 0.3131Z = -1.8437$		
	Plane 3	
$\mathrm{S_{21}}$	32	−0.001
$\mathrm{S_{22}}$	32	0.001
$\mathrm{C_{21}}$	12	0.023
$\mathrm{C_{22}}$	12	−0.024
$\mathrm{C_{23}}$	0	−0.015
$\mathrm{C_{24}}$	0	−0.207
Ni	0	0.281
$-0.9467X - 0.1255Y + 0.2968Z = -3.7772$		

[a] Orthogonal coordinate system with $X \parallel b$, and $Z \parallel c^*$.

Discussion

Description of the Structure. A third five-atom chelate ring has been created by the addition of a pair of nickel dithiete sulfur atoms (one from each ligand) across one of the carbon–carbon double bonds of norbornadiene. The resulting complex seems to be strained (Figure 1), with the two attacking sulfurs ($\mathrm{S_{12}}$ and $\mathrm{S_{21}}$) achieving tetrahedral rather than trigonal configuration. Although the sulfurs are in the expected *exo* configuration with respect to norbornadiene, the norbornadiene is in an *endo* configuration with respect to the inorganic moiety, placing the bridge carbon ($\mathrm{C_7}$) directly over and 3.28 Å away from the nickel atom. The new S–C bonds, although *ca.* 0.1 Å longer than the

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(10) $R_1 = \Sigma||F_o| - |F_c||/|F_o|$.

(11) The hydrogen atoms were refined as a check on their presence and not for any anticipated improvement in their positions or the residue.

(12) $R_2 = (\Sigma w(|F_o| - |F_c|)^2/wF_o^2)^{1/2}$.

(13) A table of the structure amplitudes of norbornadiene-bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel has been deposited as Document No. NAPS-00853 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $3.00 for photoprints or $1.00 for microfiche. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

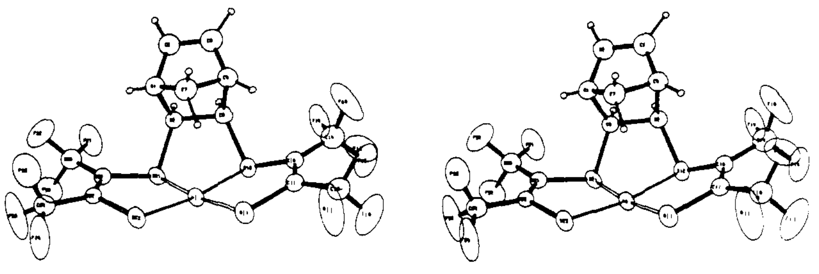


Figure 1. The norbornadiene–nickel dithiete adduct. This drawing constitutes a stereopair and is best seen with the aid of a hand viewer.

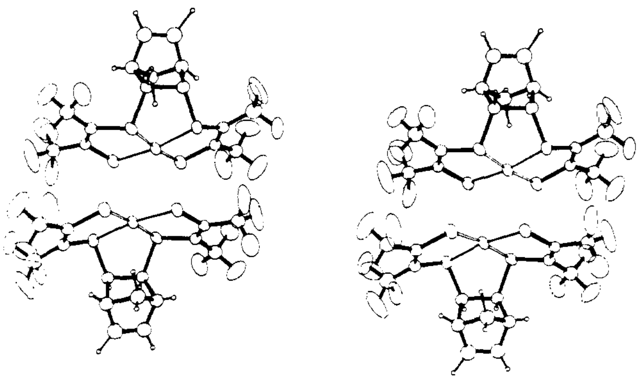


Figure 2. A stereopair showing the back-to-back packing of the norbornadiene–nickel dithiete adduct.

mean of the S–C bonds internal to the thiete ligands (1.76 (3) Å), are still within reasonable limits for single bonds. Beyond the increase of the C_5–C_6 distance to 1.59 (2) Å from the 1.33 Å expected for a double bond, and the imposition of tetrahedral stereochemistry on those same carbon atoms, the norbornadiene is essentially unchanged from the free molecule.[14]

The nickel dithiete moiety is nonplanar, with the nickel atom lying 0.13 Å below the plane described by the four coordinated sulfur atoms, and *ca.* 0.3 Å above the best planes of the thiete ligands which are themselves also nonplanar (Table IV). The inorganic moiety is thus continuously curved so that it is bowl-shaped in appearance. The direction of displacement of the nickel is away from the norbornadiene bridge carbon, with the cause clearly being the new five-membered chelate ring and the tetrahedral stereochemistry of S_{12} and S_{21} (*vide supra*). Within experimental accuracy the complex possesses a mirror plane containing the nickel and C_7 atoms and bisecting the S_{12}–Ni–S_{21} angle. This being the only symmetry element, the complex belongs to the C_s point group.

The closest intermolecular contacts are involved in the back-to-back packing of complex pairs as illustrated in Figure 2. These pairs are related to one another by a center of symmetry and the shortest distance, 3.28 Å, is between nickel and S_{22}. The only other close contacts are between fluorine atoms and are well above the sum of van der Waals radii (2.8 Å) with only two as small as 3.1 Å, three at 3.2 Å, and the rest above 3.3 Å.

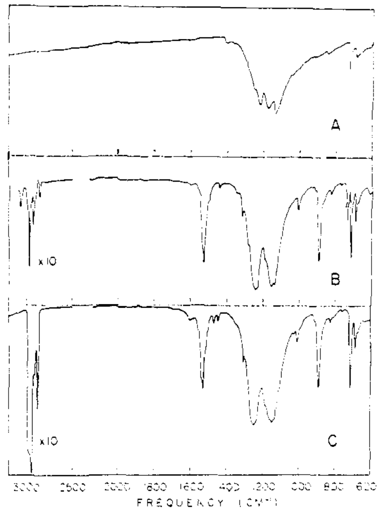
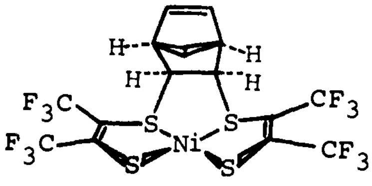


Figure 3. The infrared spectra of (A) nickel dithiete, (B) norbornadiene–nickel dithiete, and (C) norbornene–nickel dithiete. The intensities in the 3000-cm⁻¹ region have been expanded by a factor of 10.

Electronic Structure. First we consider the infrared spectra, Figure 3, of nickel dithiete, **1**, norbornadiene–nickel dithiete, **4**, and norbornene–nickel dithiete, **5**. The two olefin adducts, **4** and **5**, have strikingly similar spectra[15] with a prominent new band at 1535 cm⁻¹, which, because of its presence in both **4** and **5**, clearly cannot be assigned to the vibration of a free double bond of the olefin. Nickel dithiete dianion, $\mathbf{1}^{2-}$, does, however, show a very weak absorption due to a C=C stretching vibration in this region.[16] The distortion extant in these complexes **4** and **5** should be sufficient to account for the increase in intensity, with the major contribution to the increase probably being due to the dipole gradient within the mirror plane. The elevated vibrational frequency is consistent with the reduction of the C=C bond length from 1.38 Å[1] in the neutral complex **1** to 1.33 Å in the olefin adduct **4**. Taken together they strongly imply that the nickel dithiete moiety has been reduced by two electrons.[4,17]



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[14] C. F. Wilcox, Jr., S. Winstein, and W. H. McMillon, *J. Amer. Chem. Soc.*, 82, 5450 (1960), refer to a private communication from V. Schomaker. See also N. C. Baenzinger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, 3, 1535 (1964).

[15] The two noticeable differences between the adducts **4** and **5** are (1) the presence of an absorption at 3070 cm⁻¹ characteristic of an olefinic C–H stretch in the former, and (2) the addition of a weak band at 1470 cm⁻¹ in the latter, which may be due to a CH_2 scissoring vibration.

[16] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 3, 814 (1964).

[17] The visible spectrum of the complex **4** is much like that expected for $\mathbf{1}^{2-}$. This will be reported later along with a study of the photoreversible decomposition of **4**: R. M. Wing and J. Baker, in preparation.

This implication is strengthened when one contrasts the electrochemical behavior of **1** and **4**. **4** mimics the electrochemical behavior of **1**$^-$, indicating an increase of electron density on the inorganic moiety. This behavior is to be compared with that of **1**,[18] which will only undergo reduction.

$$\mathbf{4}^+ \xrightleftharpoons{0.83} \mathbf{4} \xrightleftharpoons{-0.14\ \mathrm{V_{sce}}} \mathbf{4}^-$$

$$\mathbf{1} \xrightleftharpoons{0.80} \mathbf{1}^- \xrightleftharpoons{-0.19} \mathbf{1}^{2-}$$

It is also interesting to note that in spite of the extreme nonplanarity of **4**, it is diamagnetic. Thus while it seems that adduct formation has resulted in a formal two-electron reduction of nickel dithiete, it is certain (that being the case) that the transferred electrons reside in the thiete ligand π system. This is consistent with the current understanding of the nickel dithiolene electronic structure.[4,19]

Summary and Conclusions

We find that norbornadiene and norbornene react with nickel dithiete to give a cycloaddition product. The properties of the adduct suggest that the olefin suffers a two-electron oxidation.

Experiments with quadricyclene[20] have led to the rapid production of norbornadiene, but a product identical in every respect to that obtained in the norbornadiene reaction has been isolated from this reaction. A lesser oxidizing metal dithiolene could possibly be incorporated with advantage into this reaction.

The olefin adducts reported by Schrauzer,[3,4] *et al.*, have properties remarkably similar to those discussed here. In view of the reported similarity for the ground states of all known dithiolenes,[4,19] we would expect the olefin adducts to be the same, so long as they were all formed by the oxidative cycloaddition process proposed here. It is possible, however, that a different reaction path is extant for the weak oxidizing agent $Ni(S_2C_2Ph_2)_2$, and we are investigating that possibility. In fact, 1,4 addition to give **3** represents the orbitally allowed pathway for reaction of **1** with monoolefins.

Finally we feel that macrocycle synthesis is a real possibility in this system.

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(18) Voltammetric data for nickel dithiete in H_2CCl_2: R. D. Schmitt, private communication.

(19) R. D. Schmitt and A. H. Maki, *J. Amer. Chem. Soc.*, **90**, 2288 (1968).

(20) L. Wolinsky, G. C. Tustin, W. H. Okamura, and R. M. Wing, unpublished results.