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Alkylation-Induced O-Atom Rearrangement in Nickel S-Oxygenates

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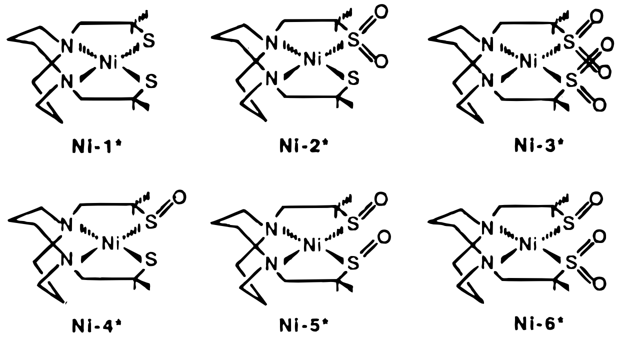
Reactions of organic halides MeI and $Br(CH_2)_3Br$ with square planar nickel complexes of tetradentate N_2SS' or $N_2S'_2$ ligands ($S' = RS(=O)$) have been explored for their potential to direct alkylation of metallosulfoxide sulfur and yield metal-bound organic sulfoxides. In fact, as established by spectroscopic and electrochemical signatures, isolated products were characterized as the result of O-atom rearrangements or transfers leading primarily to metallosulfones ($Ni-SO_2R$) and metallothiolates ($Ni-SR$) (which were subsequently alkylated to nickel-bound thioethers). Proposed intermediates in the reactions of the monosulfoxide, **Ni-4***, *N*-(2-mercapto-2-(methylpropyl))-*N′*-(2-sulfenato-2-(methylpropyl))-1,5-diazacyclooctanenickel(II) and the bis-sulfoxide, **Ni-5***, *N*,*N′*-bis(2-sulfenato-2-(methylpropyl))-1,5-diazacyclooctanenickel(II), with 1,3-dibromopropane include S-bound $R'S-OR$ moieties resulting from ring closure of the pendant alkyl bromide on the nucleophilic sulfoxide oxygen. X-ray crystal structures of *N*-(sulfinato-2-(methylpropyl))-*N′*-(2-thia-2-(methylpropyl))-1,5-diazacyclooctanenickel(II) iodide and a bimetallic composed of two units of *N*-(2-mercapto-2-(methylpropyl))-*N′*-(2-sulfinato-2-(methylpropyl))-1,5-diazacyclooctanenickel(II) linked by $(CH_2CH_2CH_2)$ are reported.

Chiral sulfoxides are important building blocks in organic synthesis as chiral auxiliaries and as important biological functionalities.[1] Since the first report of optically active sulfoxides in the late 1920s, much effort has been directed at the resolution of enantiomers as well as the direct asymmetric synthesis of optically pure sulfoxides. Transition metal complexes have typically been used to resolve enantiomers of sulfoxides, through selective binding at a chiral metal center.[2] An alternate approach uses the transition metal complex to introduce chirality into a molecule.

Schenk et al.[3] accessed sulfoxide chirality by selectively binding a prochiral sulfide, RSR′, in a stereospecific manner to ruthenium(II), which was further ligated by a cyclopentadienyl ring and a chiral diphosphine ligand. The single O-atom transfer reagent, dimethyldioxirane, oxygenated the coordinated thioether stereospecifically to yield the sulfoxide. On reflux with NaI, the sulfoxide was released in high enantiomeric excess without epimerization.

The *cis*-dithiolate, **Ni-1***, has served as a precursor to a variety of mixed thiolato, sulfenato, and sulfinato nickel complexes, Chart 1.[4] Interestingly, isotopic labeling studies on the oxygenation of **Ni-1*** to yield **Ni-5*** using $^1\Delta$ O_2 indicated that the labels were conserved across the thiolates, implying a role for *cis*-dithiolates in templating molecular oxygen addition.[5] Furthermore, the X-ray crystal structure of **Ni-5*** finds the oxygens on the same side of the N_2S_2 plane, as indicated in Chart 1, suggesting stereoselectivity in the oxygenation reaction. Since nickel *cis*-dithiolates are also well-known to template macrocyclization reactions,[6,7] we reasoned that a unique macrocyclic bis-sulfoxide ligand might be produced via one or both paths expressed in Scheme 1. As noted, the oxygenation of the coordinated dithioether sulfurs was unsuccessful. A reaction, however, was observed by the alternate route of alkylation of the *cis*-bis-sulfoxide **Ni-5***. The following report is of attempts to develop the reactivity of **Ni-5*** with 1,3-dibromopropane. While the target molecule was not

Chart 1



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[6] Thompson, M. C.; Busch, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 3651.

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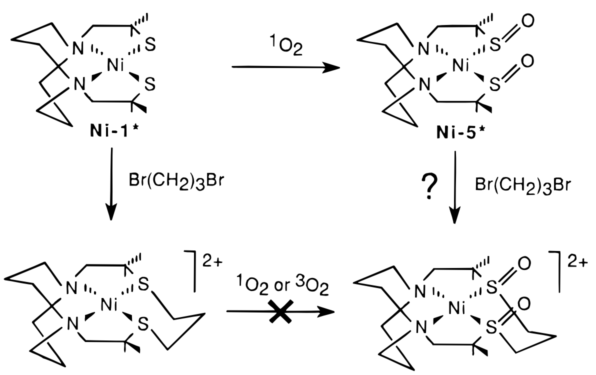
10.1021/om980587e CCC: $15.00

Scheme 1



obtained, observations made have resulted in a better understanding of the reactivity patterns of metal bound S-oxygenates in the presence of alkylating agents.

Experimental Section

Techniques and Sources. Reagent-grade solvents were dried using standard techniques and were freshly distilled before use. **Ni-1**, **Ni-1***, **Ni-2***, **Ni-3***, **Ni-4***, **Ni-5***, and **Ni-6*** were synthesized according to published procedures.[4,8-10] Methyl iodide (MeI), trimethyloxonium tetrafluoroborate (Me_3OBF_4), and ^{13}C-enriched MeI were purchased from Aldrich Chemical Co. and used without further purification. The 1,3-dibromopropane (Lancaster Chemical Co.) and acetonitrile-d_3 (Cambridge Isotope Laboratories, Inc.) were used as received. The reactions of **Ni-4***, **Ni-5***, and **Ni-6*** with a variety of electrophiles (MeI, Me_3OBF_4, 1,3-dibromopropane) were carried out under anaerobic conditions.

Chromatography. The alkylation products were isolated by separation on a neutral alumina column (20 cm × 1 cm) with acetonitrile or an acetonitrile/methanol mix as eluent. Products of methylation eluted in the following order using the indicated solvent(s): **[Ni-2*Me]**$^+$, acetonitrile; **[Ni-4*Me]**$^+$, 50:1 acetonitrile−methanol; **Ni-6***, methanol. For the 1,3-dibromopropane reactions the products eluted in the following order using the solvent systems indicated: **[Ni-1*-macrocycle]**$^+$, 50:1 acetonitrile:methanol; **[Ni-2*(CH$_2$)$_3$Br]**$^+$, 50:1 acetonitrile−methanol; **Ni-6***, methanol. Products were identified by comparing the UV/vis spectra with those of authentic samples. Isolated yields, based on nickel complex reactant, were determined by evaporation of solvent in a preweighed vial.

Physical Measurements. UV/vis spectra were obtained using a Hewlett-Packard HP8452A diode array spectrophotometer. An IBM IR/32 Fourier transform spectrophotometer was used to record infrared spectra (KBr pellets). ^1H NMR spectra were recorded using a Varian XL-200 FT NMR spectrometer. ^{13}C NMR spectra were recorded using a Varian Unity Plus 300 FT-NMR spectrometer. EPR data on frozen solutions were obtained at 77 K on a Bruker ESP 300 spectrometer equipped with an Oxford Instruments ER910A cryostat. Conductivity measurements were in aqueous solution or pure acetonitrile solution using an ORION conductivity meter, model 160. Elemental analyses were performed by Canadian Microanalytical Services, Ltd., Delta, British Columbia.

Mass spectra were determined at the Center for Chemical Characterization and Analysis, Texas A&M University. Positive ion fast atom mass spectra were recorded in a nitrobenzyl alcohol (NBA) matrix using a VG-70S spectrometer with a xenon source having particle energy of 10 keV. Data were collected by a VG11-250J data system.

Table 1. Summary of X-ray Crystal Structure Data for [Ni-2*Me]I and [(Ni-2*)$_2$(CH$_2$)$_3$][NiBr$_4$]

	[Ni-2*Me]I	**[(Ni-2*)$_2$(CH$_2$)$_3$][NiBr$_4$]**
chemical formula	$C_{15}H_{31}N_2O_2S_2NiI$	$C_{33}H_{72}Br_4N_4Ni_3O_7S_4$
fw	521.1	1260.96
space group	$Pna2_1$	$P2_1/c$
a (Å)	19.387(2)	15.658(3)
b (Å)	12.677(2)	19.522(4)
c (Å)	8.206(2)	17.510(4)
α (deg)	90	90
β (deg)	90	111.37(3)
γ (deg)	90	90
V (Å^{-3})	2016.8(6)	4984(2)
Z	4	4
ρ (calcd, g/cm^3)	1.716	1.680
temp (K)	293(2)	293(2)
radiation (λ)	Cu Kα	Cu Kα
abs coeff (mm^{-1})	15.526	6.998
R^a	0.043	0.0850
R_w	0.051	0.1741

[a] Residuals: $R = \Sigma|F_o - F_c|\Sigma F_o$; $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(F_o)^2]\}^{1/2}$.

Cyclic voltammograms were obtained using a Bio-Analytical Systems 100A electrochemical analyzer with a glassy carbon stationary electrode and a platinum wire auxiliary electrode. Samples were measured in acetonitrile with tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) (0.1 M) as the supporting electrolyte and a Ag/AgNO$_3$ reference electrode. Potentials were standardized with Cp_2Fe^+/Cp_2Fe and referenced to NHE.

X-ray Crystal Structure Analyses. The X-ray crystal structures were solved at the Crystal & Molecular Structure Laboratory Center for Chemical Characterization and Analysis at Texas A&M University. For **[Ni-2*Me]I** and **[(Ni-2*)$_2$(CH$_2$)$_3$][NiBr$_4$]** X-ray crystallographic data were obtained on a Rigaku AFC5R diffractometer, operating at 55 kV and 180 mA, Cu Kα (λ = 1.541 78 Å) radiation. Structures were solved[11] using SHELXT-PLUS. X-ray experimental conditions for **[Ni-2*Me]I** and **[(Ni-2*)$_2$(CH$_2$)$_3$][NiBr$_4$]** are given in Table 1.

Syntheses. **[Ni-2*(CH$_2$)$_3$Br]Br.** A yellow-orange solution of **Ni-2*** (180 mg, 0.49 mmol) in 40 mL of dry acetonitrile was heated to reflux with subsequent addition of 1,3-dibromopropane (0.50 mL, 4.5 mmol). The solution was refluxed for 4 h, after which the solvent was removed by vacuum. The resulting solid, dissolved in a minimum amount of acetonitrile, was separated by alumina column chromatography (1 cm × 20 cm) with acetonitrile as the eluent. A single orange band of **[Ni-2*(CH$_2$)$_3$Br]Br** was collected, 230 mg, 80% yield. Molar conductance at 23 °C in water: 166 Λ^{-1} M^{-1}. The spectral characteristics (IR and UV/vis) are listed in Table 2 as well as the parent ion peak from the mass spectrum.

[Ni-2*Me]I or **BF$_4^-$.** A solution of **Ni-2*** 47 mg (0.12 mmol) in 40 mL of dry acetonitrile (3.1 mM) was injected with 77 μL (1.2 mmol) of MeI. The yellow-orange solution slowly turned bright yellow. After stirring overnight at room temperature, the solvent was removed by vacuum, leaving a yellow solid. A single yellow band was collected after alumina column chromatography, eluting with acetonitrile: **[Ni-2*Me]I**, 63 mg, 98% yield. The spectral characteristics (IR and UV/vis) and the parent ion peak from the mass spectrum are listed in Table 2. ^{13}C NMR for CH$_3$: δ = 14.6 ppm (TMS). Crystals suitable

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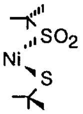
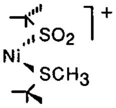
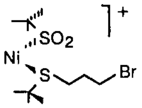
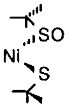
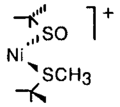
Table 2. Physical and Spectroscopic Properties of Compounds [Ni-4*Me]$^+$, [Ni-2*Me]$^+$, and [Ni-2*(CH$_2$)$_3$Br]$^+$

	 **Ni-2***[4]	 **[Ni-2*Me]$^+$**	 **[Ni-2*(CH$_2$)$_3$Br]$^+$**	 **Ni-4***[4]	 **[Ni-4*Me]$^+$**
Color	yellow	yellow	orange	orange	orange
IR ν(SO) (cm^{-1})^a					
Ni-SO				909	978
Ni-SO$_2$	1044, 1181	1060, 1201	1064, 1204		
UV (nm(ε))^{b,c}	302 (6727) 422 (51)	208 (19,800) 246 (26,600) 334 (11,700) 420 (881)	204 (25,300) 220 (21,800) 226 (9800) 244 (20,700) 336 (12,000) 424 (957)	374 (5,968) 474 (534)	210 (17,400) 248 (20,200) 330 (4,500) 416 (2180) 504 (998)
E$_{1/2}$ (mV)^d	-1630	-1020	-1028	-2030	-1360
Parent ion (m/z)^e	379	393	501	363	377

[a] KBr pellets. [b] Measured in methanol for **Ni-2*** and **Ni-4***; all others measured in acetonitrile solutions. [c] ϵ in M^{-1} cm^{-1}. [d] All potentials scaled to NHE referenced to a ferrocene standard ($E_{1/2}{}^{NHE} = -400$ mV) measured vs a Ag/AgNO$_3$ reference electrode. 0.1 M TBAHFP electrolyte. [e] FAB-MS, nitrobenzyl alcohol matrix.

for X-ray analysis were obtained by ether diffusion into a dichloromethane solution of **[Ni-2*Me]I**. Anal. Calcd (found) for **[Ni-2*Me]I** ($C_{15}H_{31}N_2S_2O_2NiI$): C, 34.5 (34.3); H, 5.99 (6.13); N, 5.37 (5.16). Molar conductance in acetonitrile at 23 °C: 167.9 ± 0.5 Λ^{-1} M^{-1}.

The BF$_4^-$ salt was obtained by reacting **Ni-2*** (43 mg 0.12 mmol) in 40 mL of dry acetonitrile (1.6 mM) with Me$_3$OBF$_4$ (170 mg, 1.2 mmol) dissolved in 5 mL of dry acetonitrile. The yellow-orange solution immediately turned yellow and was stirred overnight at room temperature. After removing the solvent by vacuum, the yellow solid was purified by alumina column chromatography, eluting with acetonitrile: **[Ni-2*Me]-BF$_4$**, 61 mg, 99.8% yield. The UV/vis spectrum was virtually identical to that of the iodide salt.

Methylation of Ni-4*. In a typical reaction, an orange solution of **Ni-4*** (52 mg, 0.14 mmol) in 40 mL of dry acetonitrile (3.5 mM) was heated to reflux, followed by addition of MeI (87 μL, 14 mmol). The solution was refluxed for 4 h, after which the solvent was removed by vacuum. The resulting orange-red solid was separated on an alumina column as previously described, with acetonitrile as eluent. Two bands were collected in the following order: yellow band, **[Ni-2*Me]-I**, 10 mg 13% yield; orange band, **[orange]I**, 53 mg, 73% yield. Spectral (IR and UV/vis) and mass spectral data are listed in Table 2. Highly hygroscopic crystals were obtained by ether diffusion into an acetonitrile solution of **[orange]I**. Anal. (see results for calculated values) for **[orange]I**: C, 34.9; H, 6.01; N, 5.49.

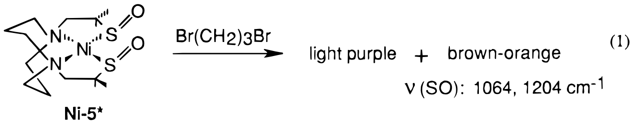
The BF$_4^-$ salt was obtained by reacting **Ni-4*** (76 mg, 0.28 mmol) in 40 mL of acetonitrile (6.9 mM) with Me$_3$OBF$_4$ (410 mg, 2.8 mmol) in 5 mL of dry acetonitrile. The orange solution immediately turned yellow and was stirred overnight at room temperature. After solvent removal by vacuum, the following products were obtained as described previously: yellow band, **[Ni-2*Me]BF$_4$**, 42 mg, 29% yield; orange band, **[orange]BF$_4$**, 8.5 mg, 6.0% yield. The UV/vis spectrum for **[orange]BF$_4$** was nearly identical to that of the iodide salt.

Reactions with Electrophiles. General procedures and conditions for the reactions of nickel sulfur-oxygenates with electrophiles are similar to those described above in the methylation of **Ni-4*** and are outlined as follows. Reactions of the nickel sulfur-oxygenates with electrophiles were carried out in acetonitrile on the millimolar scale with the electrophiles in a 10-fold excess. Using MeI or 1,3-dibromopropane as the electrophile required refluxing of these reactions for 4−5 h or until there were no longer changes in the UV/vis spectra. Reactions with Me$_3$OBF$_4$ were stirred overnight at room temperature to ensure complete reaction. Products were isolated and purified as described earlier.

^{13}C-Enriched MeI Alkylations of Ni-1*, Ni-2*, and Ni-4*. All ^{13}C-MeI alkylation reactions were carried out in NMR tubes. After addition of $^{13}CH_3I$ the tubes were capped and allowed to stand at room temperature for 48 h before the ^{13}C NMR spectra were obtained. ^{13}C NMR data were collected for ca. 50−200 transients. Samples were prepared as follows: (1) a purple solution of **Ni-1*** (11 mg, 0.032 mmol) in CD$_2$Cl$_2$ was treated with 4.0 μL of $^{13}CH_3I$ (0.064 mmol); (2) to a yellow solution of **Ni-2*** (7.2 mg, 0.019 mmol) was added 3.6 μL of $^{13}CH_3I$ (0.057 mmol); and (3) an orange solution of **Ni-4*** (8.6 mg, 0.024 mmol) in CD$_2$Cl$_2$ was reacted with 4.5 μL of $^{13}CH_3I$ (0.072 mmol).

Results and Discussion

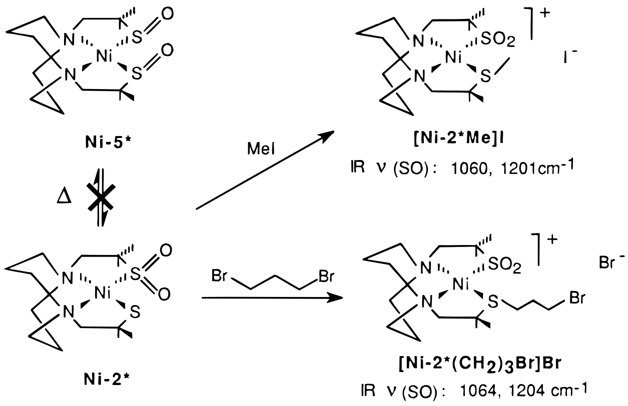
Reactivity. On addition of 1,3-dibromopropane in excess to a refluxing acetonitrile solution of the bis-sulfoxide, **Ni-5***, the color changed slowly from bright orange to a brown-orange, eq 1. Solvent removal resulted in a brown powder, which on column chromatography separated into two fractions: a light purple band and a brown-orange band. The former had no



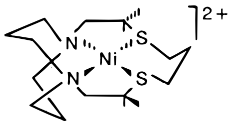
(1)

Ni-5*

Scheme 2



infrared stretches in the ν(SO) region and was identified as the previously synthesized **[Ni-1*macrocycle]Br$_2$**.[12]



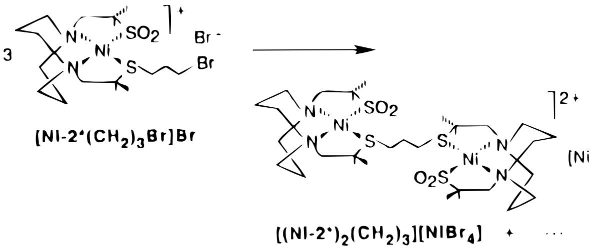
[Ni-1*macrocycle]$^{2+}$

The ν(SO) positions of the orange product are not in the range expected for metal-bound sulfoxides (O-bonded 915−950 cm^{-1}; S-bonded 1110−1160 cm^{-1})[13] and are in fact shifted slightly positively from the neutral monosulfone, **Ni-2***. This suggestion of oxygen rearrangement and sulfone production was confirmed by the control experiments expressed in Scheme 2. Under reflux conditions, **Ni-5*** does *not* isomerize to **Ni-2*** in the absence of alkylating agents. However, addition of 1,3-dibromopropane to the monosulfone, **Ni-2***, under the same conditions as for **Ni-5***, yielded a single brown-orange band upon column chromatography. Its IR and UV/vis spectra were identical to those for the orange band from the bis-sulfoxide reaction of eq 1. Addition of MeI to a refluxing solution of **Ni-2*** yielded only one yellow band after alumina column chromatography. The yellow compound had IR and UV/vis spectra identical to those collected from the yellow band from the **Ni-4*** and **Ni-5*** reactions with MeI, vide infra.

Oxygen rearrangements were also observed upon alkylation of the monosulfoxide **Ni-4*** and the sulfone/sulfoxide **Ni-6*** with dibromopropane, Table 3. Upon addition of excess 1,3-dibromopropane to **Ni-4***, **[Ni-1*macrocycle]Br$_2$** and **[Ni-2*(CH$_2$)$_3$Br]Br** were observed in nearly equimolar amounts, 35% and 24%, respectively. Alkylation of **Ni-6*** resulted in only 22% **[Ni-2*(CH$_2$)$_3$Br]Br**, while a majority of the starting material was recovered.

Further characterization of the sulfone alkylates, **[Ni-2*Me]$^+$** and **[Ni-2*(CH$_2$)$_3$Br]$^+$**, include the nearly identical vis/UV spectra, Figure 1 and the electrochemical data given in Table 2. Redox potential data for **[Ni-2*Me]$^+$** and **[Ni-2*(CH$_2$)$_3$Br]$^+$** and the X-ray crystal structure for **[Ni-2*Me]I** are discussed below. The electrochemical and spectroscopic properties of the brown-orange product in eq 1 are identical to **[Ni-2*(CH$_2$)$_3$Br]$^+$**.

X-ray Crystal Structure Analyses. Crystals suitable for X-ray diffraction analysis of the **[Ni-2*Me]I** salt were obtained by ether diffusion into a dichloromethane solution of the nickel complex. In attempts (requiring over a week) to crystallize the **[Ni-2*(CH$_2$)$_3$Br]Br** salt a further reaction occurred, producing a propylene-linked binuclear complex cation as its NiBr$_4^{2-}$ salt, eq 2.



(2)

The molecular structure of the **[Ni-2*Me]$^+$** cation is shown in Figure 2, and that of **[(Ni-2*)$_2$(CH$_2$)$_3$]$^{2+}$** is in Figure 3. Selected bond lengths and angles for these new complex cations as well as **Ni-2***, **[Ni-2*Me]$^+$**, **[Ni-1*Me]$^+$**, and **[(Ni-2*)$_2$(CH$_2$)$_3$]$^{2+}$** are compared in Table 4. Full crystallographic reports are available as Supporting Information.

In both **[Ni-2*Me]$^+$** and the binuclear complex, **[(Ni-2*)$_2$(CH$_2$)$_3$]$^{2+}$**, the coordination about nickel is substantially square planar. The average deviation from the best Ni−N$_2$S$_2$ square plane for **[Ni-2*Me]$^+$** is 0.0595 Å; for **[(Ni-2*)$_2$(CH$_2$)$_3$]$^{2+}$**, 0.1082 and 0.1331 Å. The Ni−N distances are statistically indistinguishable for the two structures reported here. This consistency in Ni−N distances is observed throughout the Ni^{II} derivatives based on diazacyclooctane and reflects the strong chelate bonding ability of this ligand.[4,8−10]

The Ni−S$_{thioether}$ distance is approximately 0.04 Å longer than the Ni−S$_{SO_2}$ in both **[Ni-2*Me]$^+$** and **[(Ni-2*)$_2$(CH$_2$)$_3$]$^{2+}$**. The smaller Ni−S$_{SO_2}$ distance compared to Ni−S$_{thioether}$ or Ni−S$_{thiolate}$ has been attributed to the decrease in the sulfur radius in its oxidized, S^{2+}, state.[12] As expected, in **[Ni-1*Me]$^+$** there is less discrepancy between the Ni−S$_{thiolate}$ and Ni−S$_{thioether}$ distances with the latter, due to the poor donor ability of thioethers, being slightly longer. That is, the overall order of Ni−S distances is Ni−S$_{thioether}$ > Ni−S$_{thiolate}$ > Ni−S$_{SO_2}$. Nevertheless the coordination sphere of the Ni is substantially the same throughout the series. A comparison of the parent, thiolate/sulfinate **Ni-2*** complex with the alkylates finds the sulfur−oxygen distances remain relatively unchanged upon alkylation of the adjacent thiolate. The short S−O distances of 1.44−1.47 Å are typical of S-coordinated metallosulfones.[4] There are no other significant differences in metric data within the structures listed in Table 4. Neither are there any intermolecular or ionic contacts that might influence the coordination sphere of nickel in the two salts.

While the nickel coordination spheres in the binucleated complex are the same as the monomer, **[Ni-2*Me]$^+$**, the overall structure of **[Ni-2*(CH$_2$)$_3$]$^{2+}$** shows two distinguishing features: the Ni−Ni distance is 7.628 Å and the two N$_2$S$_2$ planes bisect each other at an angle of 108.7°.

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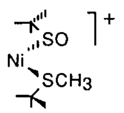
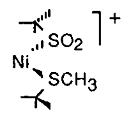
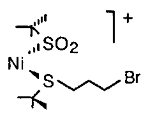
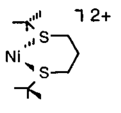
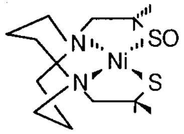
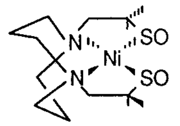
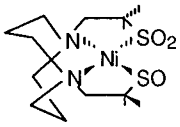
(13) Cotton, F. A.; Francis, R.; Horrocks, W. D. *J. Phys. Chem.* **1960**, *64*, 1534.

Table 3. Product Distributions[a] from Alkylation of Nickel-Oxygenates (Products Represented by the Sulfur Site Composition without the Remainder of the Complex Shown)

Complex	alkylating agent[b]				
 **Ni-4***	MeI	73	13		
	Me_3OBF_4	7	32		
	$Br(CH_2)_3Br$			24	35
 **Ni-5***	MeI	36	3.2		
	Me_3OBF_4	4	14		
	$Br(CH_2)_3Br$			52	10
 **Ni-6***	MeI[c]		11		
	Me_3OBF_4		55		
	$Br(CH_2)_3Br$			22	

[a] Percent yields based on starting complex. [b] Conditions: MeI, reflux, acetonitrile solution, 4 h; Me_3OBF_4, 22 °C, acetonitrile solution, 12 h; 1,3-dibromopropane, reflux, acetonitrile solution, 4 h. [c] 13% of **Ni-2*** and 35% of **Ni-6*** recovered.

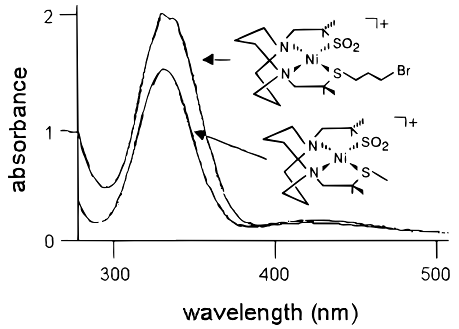


Figure 1. UV/vis spectra of **[Ni-2*(CH$_2$)$_3$Br]Br** and **[Ni-2*Me]I** in acetonitrile (0.25 mM).

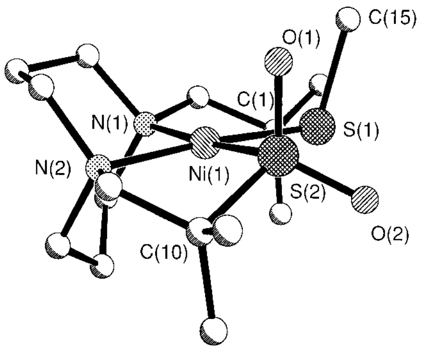


Figure 2. Molecular stucture of **[Ni-2*Me]I**. Selected bond lengths (Å): Ni(1)–S(1) 2.170(3); Ni(1)–S(2) 2.125(4); Ni(1)–N(1) 1.979(9); Ni(1)–N(2) 1.965(9); S(2)–O(1) 1.45(1); S(2)–O(2) 1.43(1); S(1)–C(15) 1.81(1). Selected bond angles (deg): S(1)–Ni(1)–S(2) 89.3(1); N(1)–Ni(1)–N(2) 91.9(4); Ni(1)–S(2)–O(1) 106.0(5); Ni–(1)–S(2)–O(2) 118.0(4); Ni(1)–S(1)–C(15) 106.3(4); N(1)–Ni(1)–S(1) 91.2(3); N(2)–Ni(1)–S(2) 87.9(3).

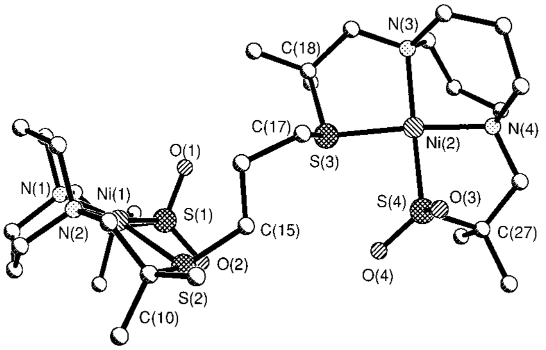
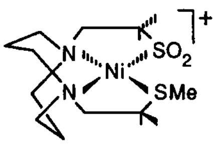
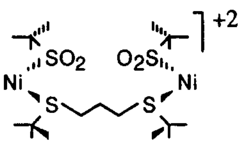
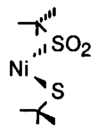
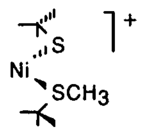


Figure 3. Molecular structure of **[(Ni-2*)$_2$(CH$_2$)$_3$][NiBr$_4$]**. Selected bond lengths (Å): Ni(1)–S(1) 2.129(6); Ni(1)–S(2) 2.174(6); Ni(1)–N(1) 1.97(2); Ni(1)–N(2) 1.99(2); S(1)–O(1) 1.473(14); S(1)–O(2) 1.457(14); S(2)–C(15) 1.82(2); S(3)–C(17) 1.78(2); S(1)–C(1) 1.82(2); S(2)–C(10) 1.83(2); Ni(1)–Ni(2) 7.628. Selected bond angles (deg): S(1)–Ni(1)–S(2) 90.1(2); S(1)–Ni(1)–N(2) 172.3(5); S(2)–Ni(1)–N(1) 172.2(5); N(1)–Ni(1)–N(2) 91.9(7); Ni(1)–S(1)–O(1) 105.8(6); Ni(1)–S(1)–O(2) 120.2(6); Ni(1)–S(2)–C(15) 105.9(8); O(1)–S(1)–C(1) 108.1(9); O(2)–S(1)–C(1) 109.2(9); C(15)–S(2)–C(10) 105.8(10).

Mechanistic Implications. Two possible pathways that can account for the observed products from the reaction of **Ni-4*** with dibromopropane are presented in Schemes 3 and 4. Scheme 3 invokes a seven-membered metalloheterocycle formed by ring closure on the oxygen by the pendant alkyl bromide. O-atom transfer from this persulfoxy species to the parent monosulfoxide, **Ni-4***, produces **Ni-2*** and one of the observed products, **[Ni-1*macrocycle]$^{2+}$**. The **Ni-2*** reacts with excess dibromopropane to give the other observed product, **[Ni-2*(CH$_2$)$_3$Br]$^+$**.

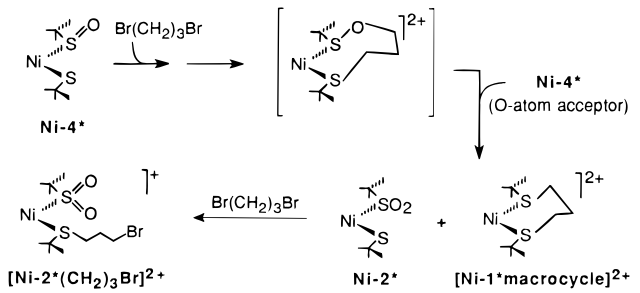
Despite the stability of RSSR and ROOR species, the proposed S-bound intermediate R–S–O–R′ is an uncommon moiety in organic chemistry.[15] Nevertheless the polarization of electron density toward the sulfoxide oxygen creates a reasonably nucleophilic oxygen. In fact, it has been proposed for electron-rich metals that the reactivity of the nucleophilic sulfoxide oxygen with electrophiles, such as O-atom source reagents, is re-

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds [Ni-2*Me]I, [(Ni-2*)$_2$(CH$_2$)$_3$][NiBr$_4$], Ni-2*, and [Ni-1*Me]I

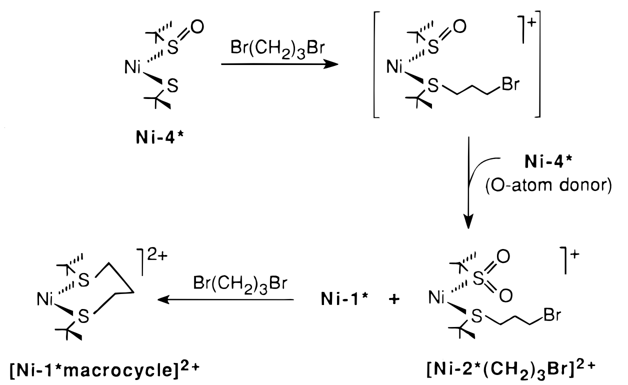
	 [Ni-2*Me]$^+$	 [(Ni-2*)$_2$(CH$_2$)$_3$]$^{+2}$ [a]	 Ni-2*[4]	 [Ni-1*Me]$^{+1}$ [4]
Ni-S$_{thiolate}$			2.132 (4)	2.156 (2)
Ni-S$_{SO2}$	2.125 (4)	2.131 (7)	2.109 (4)	
Ni-S$_{thioether}$	2.170 (3)	2.180 (7)		2.173 (2)
Ni-N (avg.)	1.971 (9)	1.98 (2)	2.00 (1)	1.970 (5)
S-C$_{thioether}$	1.81 (1)	1.80 (2)		1.798 (7)
S-O (avg.)	1.44 (1)	1.460 (14)	1.47 (1)	
S-Ni-S (avg.)	89.3 (1)	90.8 (2)	91.2 (1)	86.3 (1)
N-Ni-N (avg.)	91.9 (4)	92.1 (7)	91.1 (4)	91.6 (2)

[a] For the bridged complex values are averaged for all the appropriate lengths and angles.

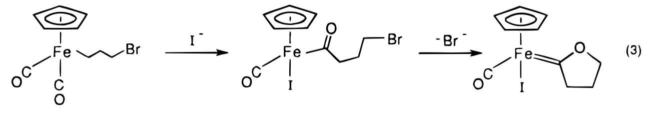
Scheme 3



Scheme 4



sponsible for the observation of sulfone but not sulfoxide products.[16] A Mulliken charge analysis of **Ni-4*** modeled using nonlocal density functional calculations revealed that the sulfenato oxygen is indeed the most negative site, −0.6525, while the sulfenato sulfur is the more positive, 0.7967.[17] For comparison, the thiolate sulfur has a charge of 0.0215 by this calculation.[17] An analogous ring-closing reaction is observed in the formation of oxycarbenes via intramolecular attack of an acyl oxygen on a bromocarbon site, eq 3.



Scheme 4 illustrates an alternative possibility. Alkylation of the thiolate sulfur would produce a monocationic thioether−sulfenato intermediate, which becomes an O-atom acceptor from another **Ni-4*** to produce **Ni-1*** and the observed **[Ni-2*(CH$_2$)$_3$Br]**$^+$. The dithiolate **Ni-1*** reacts further with dibromopropane to give the other observed product, **[Ni-1*macrocycle]**$^{2+}$. The speculation in Scheme 4 parallels chemistry observed in the redox-promoted O-atom transfer reaction reported previously for **Ni-4**.[19] Oxidation of **Ni-4** induces a disproportionation producing **Ni-2** and **Ni-1**, i.e., products of O-atom transfer. In analogy, alkylation of **Ni-4*** reduces the electron density on the nickel, potentially making the cationic **[Ni-4*(CH$_2$)$_3$Br]**$^+$ an O-atom acceptor from the nucleophilic **Ni-4***. However, as described below, when MeI is employed as the alkylating agent, the product is a single oxy species, **[Ni-4*Me]**$^+$. That is, if alkylation of the sulfoxide/thiolate to a sulfoxide/thioether alone were sufficient to induce O-atom transfer, such reactivity should be observed regardless of whether MeI or dibromopropane is employed. That such rearrangement occurs only with dibromopropane suggests that the presence of the tethered alkyl halide is responsible for the observed reactivity.

Note that the most likely mechanism for the bissulfoxide, **Ni-5***, involves sulfenato O-alkylation. O-transfer may occur either intramolecularly to directly yield **[Ni-2*(CH$_2$)$_3$Br]Br** or intermolecularly to yield the less reactive **Ni-6*** species and the metalloheterocycle shown

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(14) Grapperhaus, C. A.; Bellefeuille, J. A.; Font, I.; Goodman, D. C.; Buonomo, R. M.; Reibenspies, J. H.; Derecskei-Kovacs, A.; Darensbourg, M. Y. In preparation.

(15) (a) Gregory, D. D.; Jenks, W. S. *J. Org. Chem.* **1998**, *63*, 3859. (b) Guo, T. Jenks, W. S. *J. Org. Chem.* **1995**, *60*, 5480. (c) Guo, T. Jenks, W. S. *J. Org. Chem.* **1997**, *62*, 857.

(16) Schenk, W.; Frisch, J.; Adam, W.; Prechtl, F. *Inorg. Chem.* **1992**, *31*, 3329.

(17) Grapperhaus, C. A. Ph.D. Dissertation, Texas A&M University, College Station, TX, 1998.

(18) Adams, H.; Bailey, N. A.; Grayson, M.; Ridgway, C.; Smith, A. J.; Taylor, P.; Winter, M. J.; Housecroft, C. E. *Organometallics* **1990**, *9*, 2621.

(19) Farmer, P. J.; Verpeaux, J. N.; Amatore, C.; Darensbourg, M. Y.; Musie, G. *J. Am. Chem. Soc.* **1994**, *116*, 9355.

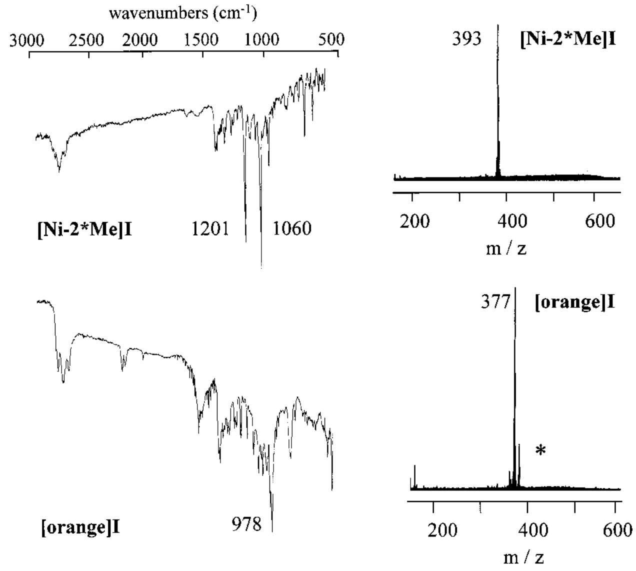
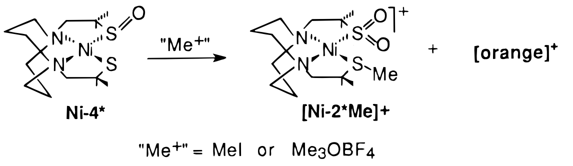


Figure 4. Infrared (KBr) and electrospray ionization mass spectra of **[Ni-2*Me]I** and **[orange]I**. (*) Peak attributed to **[Ni-2*Me]I**.

in Scheme 3. The latter would ultimately lead to the observed sulfone/thioether product.

Reactivity of Ni-4* with MeI and Me$_3$OBF$_4$. Since the reactivity of 1,3-dibromopropane with nickel S-oxygenates is complicated by the presence of two reactive sites on the alkylating agent, alternative alkylating agents were examined for their reactivity with the nickel sulfur-oxygenates. Thus, MeI and Me$_3$OBF$_4$ were reacted with **Ni-4*** with results expressed by eq 4.

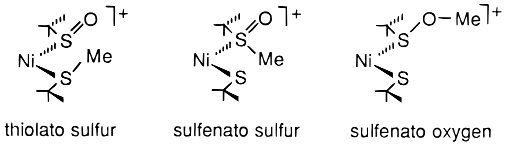


(4)

The product mixture from the methylation of **Ni-4*** was separated by column chromatography, with a yellow band eluting first, followed by an orange component. The former band was assigned as **[Ni-2*Me]**$^+$ on the basis of comparison of spectral data to that of the known complex cation, vide supra. Ether diffusion into a dichloromethane solution of the orange component, herein referred to as **[orange]I**, yielded highly hygroscopic crystals which were unsuitable for X-ray diffraction analysis despite attempts utilizing various counterions and solvent systems. Although there were other unidentified products when Me$_3$OBF$_4$ was used as the alkylating agent, there was no evidence for the well-known dimethylated **[Ni-1*Me$_2$]**$^{2+}$ species,[14,20] which would be analogous to the light purple product, **[Ni-1*macrocycle]**$^{2+}$, in the dibromopropane reactions.

The elemental analysis of **[orange]I** was not definitive as to the formulation; that is, the C,H,N analysis (C, 34.9; H, 6.01; N, 5.49) is equally consistent with **[Ni-4*Me]I**, its hydrate, and **[Ni-2*Me]I.** A better tool is electrospray ionization mass spectrometry, which is interpreted as a single oxy, monomethylated species. As shown in Figure 4, the mass spectrum for **[Ni-2*Me]I** shows a parent ion peak with a $m/z = 393$ corresponding to the mass of the complex cation, with no signal 16 units lower. In contrast, the parent ion peak for **[orange]I** is precisely 16 units lower with $m/z = 377$. Adding the mass of a methyl group to that of **Ni-4*** gives a combined mass of 378, suggesting that **[orange]I** be formulated as the single oxy species **[Ni-4*Me]I**.

Chart 2. Possible Sites of Methylation



Since the thiolato sulfur, sulfenato sulfur, and sulfenato oxygen are possible sites for methylation, Chart 2, attempts to identify the reactive site used infrared spectroscopy in the ν(SO) region, ^{13}C NMR and cyclic voltammetry data as presented below.

The IR spectra for **[Ni-2*Me]I** and **[orange]I**, Figure 4, indicate that the level of oxygenation is different for the two complexes. While **[Ni-2*Me]I** shows two absorptions characteristic of sulfones at 1201 and 1060 cm^{-1}, the **[orange]I** salt has a band at 978 cm^{-1}. The **[Ni-2*Me]I** product is shifted ~+20 cm^{-1} from **Ni-2***, whereas **[orange]I** is shifted +69 cm^{-1} from **Ni-4***. Solution infrared data for transition metal complexes of dimethyl sulfoxide, DMSO, exhibit ν(SO) frequencies in the range 915−960 cm^{-1} for O-bound DMSO.[13] The S-bound PdCl$_2$·2DMSO complex shows a ν(SO) stretch at 1116 cm^{-1}.[13] For **[orange]I**, the ν(SO) stretch is inconclusive as to the site of alkylation, but is consistent with S=O double-bond character.

Products of alkylation of **Ni-4*** with ^{13}C-enriched MeI were studied by ^{13}C NMR. Noncomplexed thioethers have α-carbon resonances further upfield than sulfoxides; that is, for *Me*−S−Me, $\delta = 19.3$ ppm, and for *Me*−S(O)−Me, $\delta = 39.1$ ppm, referenced to TMS.[21] Oxygen-bound methyl groups would be found even further downfield; that is, *Me*OH, $\delta = 49.2$ ppm.[21] The following "NMR tube" experiments (see Experimental Section) were carried out in CH$_2$Cl$_2$ on the primary reaction mixture. Alkylation of **Ni-4*** with ^{13}CH$_3$I results in two resonances at 14.6 and 13.3 ppm. Alkylation of **Ni-2*** with ^{13}CH$_3$I produces a resonance at 14.6 ppm which is assigned to **[Ni-2*Me]**$^+$. Consequently, the 13.3 ppm resonance is assigned to the methyl group of **[orange]**$^+$. For comparison, alkylation of the dithiolate **Ni-1*** yields the bismethylated dithioether complex **[Ni-1*Me$_2$]**$^{2+}$, which displays a singlet resonance at 15.3 ppm. All of the observed resonances of methylated **Ni-4*** are a maximum of 6 ppm removed from the free Me$_2$S value of 19 ppm. Had alkylation occurred at the sulfenato sulfur or oxygen, the frequency of the methyl would be expected much further downfield. Thus we conclude CH$_3$$^+$ binding at the thiolato sulfur in **[orange]I** most reasonably accounts for the similarity of CH$_3$ resonances of the three complexes, a range of only 2.0 ppm. Both IR and NMR results indicate **[orange]I** is a single-oxygen species to which we refer as **[Ni-4*Me]I** from here forward.

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(20) Font, I. Ph.D. Dissertation, Texas A&M University, College Station, TX, 1994.

(21) *Spectrometric Identification of Organic Compounds*, 5th ed.; Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. John Wiley & Sons: New York, 1991.

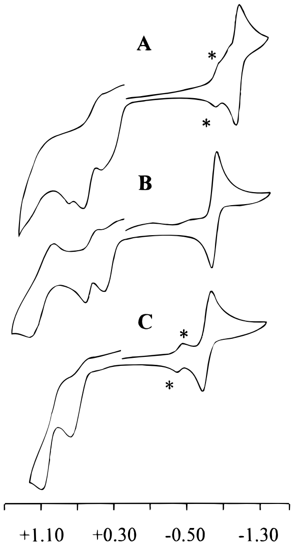


Figure 5. Cyclic voltammograms for **[Ni-4*Me]I**: (A) **[Ni-2*Me]I**, (B) **[Ni-2*PrBr]Br**, (C) samples measured in 0.1 M TBAHFP in acetonitrile using a glassy carbon electrode. Potentials referenced to NHE with $Cp_2{-}Fe^+/Cp_2{-}Fe$.

Table 5. Electrochemical Data from Cyclic Voltammetry in Acetonitrile[a]

complex	$E_{1/2}$, $Ni^{II/I}$ (mV)	E_c (mV)	calcd[b]
[Ni-2*Me]I	−1020	1348 quasi	−1150
[Ni-2*(CH$_2$)$_3$Br]Br	−1028	1348 irr	−1150
[Ni-4*Me]I	−1360	1078 irr	−1350
Ni-2*	−1630		
Ni-4*	−2030		
Ni-1*	−2120		

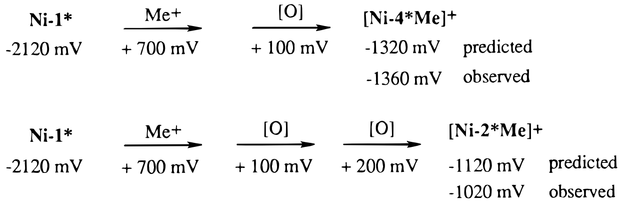
[a] All potentials scaled to NHE referenced to a ferrocene standard ($E_{1/2}^{NHE} = -400$ mV) measured vs a $Ag/AgNO_3$ reference electrode. 0.1 M TBAHFP electrolyte. [b] See main text.

Comparative Electrochemical Studies. Cyclic Voltammetry. Cyclic voltammograms for **[Ni-2*Me]I**, **[Ni-4*Me]I**, and **[Ni-2*(CH$_2$)$_3$Br]Br** are stacked in Figure 5. The electrochemical data are summarized in Table 5 with additional electrochemical data for other Ni-oxygenates and Ni-thiolate and thioether complexes reported for comparison. Cyclic voltammograms of **[Ni-4*Me]I** and **[Ni-2*(CH$_2$)$_3$Br]Br** show small peaks before the reduction event attributable to contamination by **[Ni-2*Me]**$^+$ and **[Ni-1*macrocycle]**$^{2+}$, respectively.

Each of the complexes **[Ni-2*Me]**$^+$, **[Ni-4*Me]**$^+$, and **[Ni-2*(CH$_2$)$_3$Br]Br** show a reversible $Ni^{II/I}$ redox couple and an irreversible or quasireversible cathodic event assigned to the $Ni^{III/II}$ couple in accordance with earlier studies.[12] The Ni^I and Ni^{III} oxidation states are separated by ca. 2.30−2.41 V, which is in agreement with other $Ni{-}N_2S_2$ complexes.[12]

Previous work has shown that, as a result of the relief of the four-electron $Ni_{d\pi}{-}S_{p\pi}$ antibonding interaction, a single O-atom addition to a nickel thiolate sulfur results in a 100 mV increase in accessibility of the $Ni^{II/I}$ couple relative to the dithiolates **Ni-1** and **Ni-1***.[12] Further oxygenation to the sulfone produces an additional 200 mV gain in accessibility.[12] Upon alkylation of a thiolate, resulting in a monocationic thioether complex, a 700 mV positive shift in the $Ni^{II/I}$ couple is noted.[12] These observed shifts in redox potentials can be used in an additive manner to predict the reduction potentials for oxygenated and alkylated analogues of the parent nickel dithiolate complexes. Scheme 5 illustrates a typical calculation.

Scheme 5



The $Ni^{II/I}$ reduction for **[Ni-4*Me]**$^+$ occurs at −1360 mV, with an irreversible oxidation taking place at +1078 mV. The expected potential for the reduction event is calculated to be −1320 mV, which is in close agreement with the empirical data. The parent **Ni-4*** complex is reduced at a potential of −2030 mV; that is, the $Ni^{II/I}$ couple of the neutral complex is ca. 700 mV destabilized relative to **[Ni-4*Me]**$^+$. This consistency in trend suggests that the Ni coordination sphere remains N_2S_2.

The **[Ni-2*(CH$_2$)$_3$Br]Br** complex shows a reversible reduction at −1028 mV, in close agreement with that measured for **[Ni-2*Me]**$^+$. This value is reasonably well predicted by previous studies, −1120 mV.[12] An irreversible oxidation event at +1348 mV is nearly identical to that observed for **[Ni-2*Me]**$^+$.

EPR Studies. Bulk chemical reductions of **[Ni-2*Me]**$^+$ and **[Ni-4*Me]**$^+$ were carried out at room temperature in acetonitrile using cobaltocene as the reducing agent. The samples were immediately frozen upon reduction. Both samples displayed an axial signal with $g_{\|} > g_{\perp}$, as seen in other pseudo-square planar d^9 systems with one unpaired electron. The g values of 2.20, 2.08 for **[N-2*Me]**$^+$ and 2.20, 2.05, 2.00 for **[Ni-4*Me]**$^+$ are typical of those observed previously in square planar NiN_2S_2 complexes.[12] The **[Ni-2*(CH$_2$)$_3$Br]Br** complex was reduced with K-Selectride. Upon reduction, an axial EPR signal with $g_{\|} = 2.19$ and $g_{\perp} = 2.05$ was observed. These results lend confidence to the $Ni^{II/I}$ electrochemical assignments above.

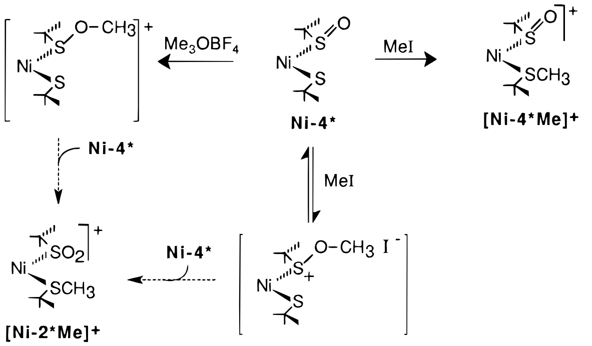
Further Studies of Ni S-Oxygenate Reactivity with Electrophiles. Product distributions for the reaction expressed by eq 4 as well as similar data for **Ni-5*** and **Ni-6*** as precursors are given in Table 3. Also given are reaction products from 1,3-dibromopropane as alkylating agent.

For MeI as alkylating agent of **Ni-4***, little O-atom rearrangement is observed; the major product is the **[Ni-4*Me]I**. With Me_3OBF_4, lower overall yields are obtained and there is a switch in product selectivity with the rearranged O-atom product, the sulfone−thioether in excess. The dihaloalkane gives the greatest O-atom lability; in fact, a complete loss of oxygen is observed in the form of the bicyclic thioether complex (light purple, **[Ni-1*macrocycle]Br$_2$**, above).

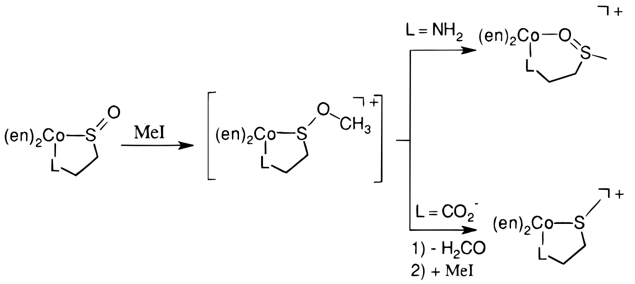
The **Ni-5*** complex shows similar trends in distribution for the methylating agents; however, the overall yields are less than with the **Ni-4***. For the dibromopropane reagent an increase in yield of the sulfone−thioether product is observed at the expense of the macrocycle; the overall yield of the reaction is similar to that of **Ni-4***.

A final study used the three oxy species, **Ni-6***. Low yields of products were observed for the dibromopro-

Scheme 6



Scheme 7



pane, while the methylating agents gave **[Ni-2*Me]**$^+$ in moderate yield for Me_3OBF_4 and low yield for MeI. For the latter, 35% of the starting material **Ni-6*** was recovered, and an additional 13% of the nonalkylated thiolate, **Ni-2***, was isolated.

The mechanism of **Ni-4*** methylation has yet to be fully elucidated. Clearly, the reaction is electrophile specific, with the major product shifting from the **[Ni-4*Me]**$^+$, 73%, with MeI to **[Ni-2*Me]**$^+$, 32%, with Me_3OBF_4. As expressed in Scheme 6, a possible explanation for the observed dependency is a competition between O- and S-alkylation. With MeI, the O-alkylation that occurs may be reversible, while S-alkylation leads to the observed product. With Me_3OBF_4, however, once alkylated, the methyl group cannot reassociate with the counterion and ultimately leads to **[Ni-2*Me]**$^+$.

An equally interesting issue is the observation of **[Ni-4*Me]**$^+$ as the major product when **Ni-5*** is reacted with MeI. Such an "oxygen loss" reaction has previously been reported by Deutsch and Lydon in the methylation of Co-sulfoxides.[22] The products are ligand dependent, as shown in Scheme 7. For L = NH_2 the alkylated sulfoxide isomerizes to the O-bound product, while for L = COO^-, "oxygen loss" (presumably via production of formaldehyde) occurs yielding a metallothiolate, which is subsequently alkylated.[22] This mechanism is based on the well-studied DMSO-promoted oxidation reactions.[23] A similar mechanism is proposed for the methylation of **Ni-5*** and **Ni-6***.

Conclusion

Despite the complexities and lack of definite mechanistic details in the nickel-sulfoxide alkylation reactions, it is quite evident that alkylation of the sulfenato ligand (whether at O or S) results in O-transfer. Methylation of the monosulfoxide, **Ni-4***, was indicated by ^{13}C NMR analysis to occur at the thiolato sulfur to yield the isolable **[Ni-4*Me]I**. Alkylation of **Ni-4*** with the bifunctional 1,3-dibromopropane induced O-transfer, suggesting that sulfenato alkylation was responsible for the observed transfer. O-loss, presumably via formaldehyde production, was observed upon methylation of the bis-sulfoxide, **Ni-5***, consistent with the previous efforts of Deutsch and Lydon.[22] However, that isomerization to an O-bound organic sulfoxide, also reported by Deutsch and Lydon, was not observed in tetradentate bme*−daco complexes is most likely due to the ligand's rigidity. This work demonstrates an undesirable possibility in the alkylation of metallosulfoxides route for chiral sulfoxide synthesis. Less restrictive sulfenato ligands that can isomerize to O-bound or even dissociate upon alkylation may be required for success in such an approach. Alternatively, the enhanced stability of platinum sulfenates might permit further S-modifications without O-transfer.[24]

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Note Added in Proof: It was recently reported (W. Weigand, R. Wünsch, N. Drescher, Abstracts, XIII International Conference on Coordination Chemistry, Florence, 1998; p 137) that platinum thiolate-sulfenates may be S-alkylated to produce uncoordinated organosulfoxides; however, Pt-complexes of the alkylated ligands were not isolated.

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