

Ruthenium Derivatives of NiS₂N₂ Complexes as Analogues of Bioorganometallic Reaction Centers

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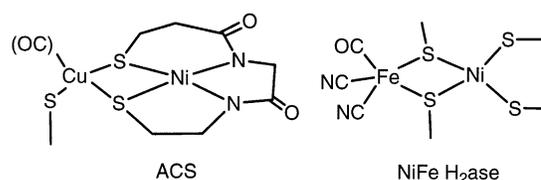
Recent results from structural biology demonstrate the catalytic significance of Ni(SR)₂L₂ centers attached to a second metal that binds CO, in particular the NiFe hydrogenases and acetyl CoA synthase. In experiments aimed at developing bimetallic derivatives exhibiting an affinity for CO, we have studied Ru(II) derivatives of nickel diaminodithiolates and the reactivity of these complexes toward CO and other small molecules. The reaction of [Cp*Ru(NCMe)₃OTf and NiS₂N₂ (S₂N₂ = *N,N*-bis(2-mercaptoethyl)-*N,N*-dimethyl-1,3-diaminoethane) gives [Cp*Ru(NiS₂N₂)₂(OTf)₂] ([1]₂(OTf)₂), which exists as a monomer–dimer equilibrium in MeCN solution. Crystallographic analysis of [1]₂(OTf)₂ reveals a centrosymmetric dication with the Ru being quasi-octahedral and the NiS₂N₂ coordination sphere being relatively planar, the metal centers being linked via pairs of μ₂-SR and μ₃-SR units. Complex [1]₂²⁺ oxygenates and sulfidizes with O₂ and S₈, respectively, to give [Cp*Ru(NiS₂N₂)(η²-E₂)]⁺ (E = O, S), which were characterized spectroscopically and crystallographically. Solutions of [1]₂(OTf)₂ also react with CO and MeNC to give the corresponding adducts [Cp*Ru(NiS₂N₂)L]OTf, where L = CO and MeNC. The ν_{CO} = 1901 cm⁻¹ for the CO adduct indicates the excellent donating power of the NiS₂N₂ ligand. The Cp*Ru⁺ derivative of the bulkier version of the NiS₂N₂ species, Ni(bme*-daco) (bme*-daco = [1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane]), is the monomeric analogue of 1⁺, [Cp*Ru(NCMe)(Ni(bme*-daco))]⁺, whose structure was confirmed spectroscopically and crystallographically. In this species the thiolato ligands are doubly bridging and the Cp*Ru subunit adopts the usual piano-stool geometry with a terminal MeCN ligand. The MeCN is readily displaced by CO and O₂ to give the corresponding adducts. The reaction of CpRu(PPh₃)₂Cl and NiS₂N₂ produced the PPh₃ adduct [CpRu(NiS₂N₂)(PPh₃)]Cl, wherein the PPh₃ ligand is nonlabile. The corresponding reaction of NiS₂N₂ with sources of (arene)RuCl⁺ gave the expected adducts [(arene)Ru(Cl)(NiS₂N₂)]⁺, isolated as their OTf⁻ salts.

Introduction

Nature employs hydrogenase enzymes for the sensing and conversions of dihydrogen. These enzymes can be classified according to the metal content at their active sites: Fe-only, NiFe, and metal free.¹ The active sites of all three enzyme classes exhibit remarkably novel structures, especially in the organometallic context. A mechanistic understanding of these enzymes would be significant for both basic organometallic chemistry as well as the commercial utilization of dihydrogen. In the case of the Fe-only hydrogenases, low molecular weight models have achieved at least a rudimentary level of success with respect to structure^{2,3} and function.⁴

Despite the fact that high-resolution crystal structures of the enzyme have been available for several years,^{5–7} little progress has been achieved in the characterization of Ni-Fe complexes with suitable re-

Chart 1. Active Site Structures for Acetyl CoA Synthase (ACS) and NiFe Hydrogenase



activity. The active sites of the NiFe enzymes consist of a dithiolate-linked Ni-Fe center that bears little resemblance to known compounds (Chart 1). Furthermore, the exact site of H₂ activation remains controversial.^{8–11} One reason to expect H₂ binding at Fe is the wealth of precedent for ferrous H₂ complexes.^{12–16}

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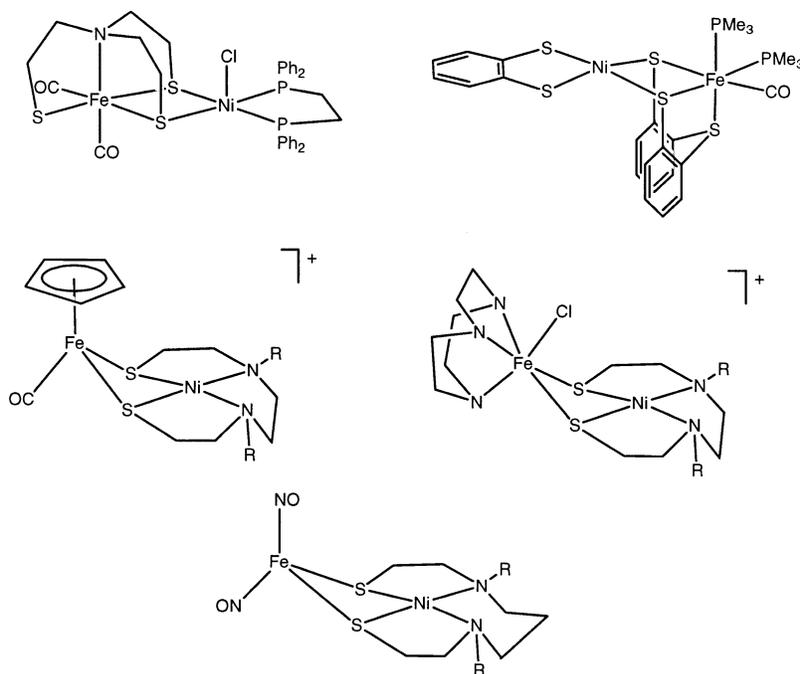
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Chart 2. Structural Models for the Ni-Fe Hydrogenase Metalloenzyme Active Site^a

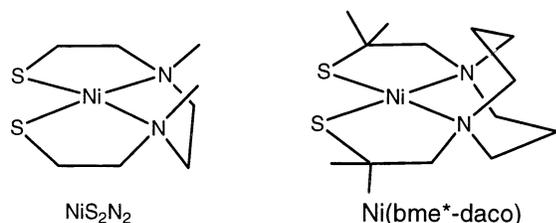
^a See text for references.

Representative synthetic models for the NiFe-hydrogenase active site are shown in Chart 2. The primary focus has been on the preparation of the Ni(μ -SR)₂Fe centers, which are observed in the enzyme structure. Commonly such bimetallic complexes are prepared by the interaction of iron reagents with diaminodithiolates of Ni(II). These diaminodithiolate building blocks comprise a fairly large class of complexes.¹⁷ The Ni(SR)₂(NR₃)₂ coordination set simulates the Ni(SR)₄ site seen crystallographically in the enzymes.^{18–21} Two unresolved deficiencies with the applicability of Ni(SR)₂(NR₃)₂ as a subunit in these models are (i) that the naturally occurring nickel thiolate is distorted toward the tetrahedral geometry, whereas the nickel is typically planar in its diaminodithiolates, and (ii) the naturally occurring Ni(SR)₄ site is probably anionic. The other half of the bimetallic active site features an Fe(CN)₂(CO) subunit, as established by combined crystallographic and spectroscopic studies. Many examples of Fe-CN-CO species have been examined recently,^{22–24} some even linked to a nickel thiolate.²⁵ Bimetallic derivatives of Ni(SR)₂(NR₃)₂ complexes are also relevant to the recently characterized active site of acetyl CoA synthase (ACS, Chart 1), which features a diamido-dithiolato nickel center linked to copper via two thiolato bridges. ACS is responsible for forming acetyl groups, which may occur via methyl transfer from nickel to a Cu-bound CO ligand.²⁶

Several years ago we started to explore the synthesis of *fac*-L₃Fe(II) complexes of the NiS₂N₂ in a search for complexes that would exhibit some reactivity at one of the two metals. Initial studies focused on (Me₃TACN)-Fe²⁺ derivatives (Me₃TACN = *N,N,N'*-trimethyltriazacyclononane). We synthesized the species [(Me₃TACN)-FeCl(NiS₂N₂)]⁺ via the reaction of (Me₃TACN)FeCl₂²⁷ with standard Ni(SR)₂(NR₃)₂ building blocks, but the resulting bimetallic complex, which was high spin, showed little affinity for π -acid ligands.²⁸ In a revised approach, we synthesized the low-spin complex [CpFe(CO)(NiS₂N₂)]⁺ via the reaction of [CpFe(CO)₂(CH₂-CMe₂)]BF₄ again using the NiS₂N₂ building block. The resulting salt {CpFe(CO)[NiS₂N₂]}BF₄, also characterized crystallographically,²⁹ was found to be substitutionally inert. The lack of suitable reactivity in these Ni-Fe species led us to redirect our efforts toward Ru analogues with the knowledge that Ru(II) typically exhibits a high affinity for π -acid ligands and H₂.³⁰ In this paper

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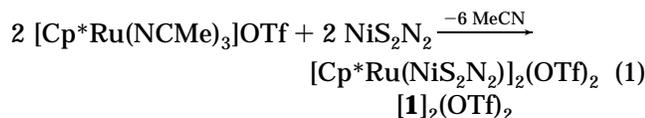
Chart 3. Structures of NiS₂N₂ and Ni(bme*-daco) Metalloligands^a^a See text for references.

we summarize these results, focusing especially on (C₅R₅)Ru⁺ and (C₆R₆)Ru²⁺ derivatives of the NiS₂N₂ metalloligands. We demonstrate that the Ru center, used as a surrogate for the naturally occurring Fe, is reactive toward π -acid ligands.

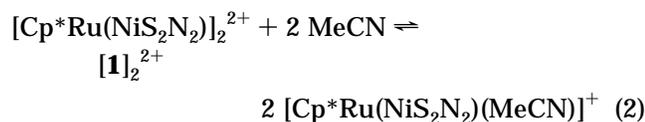
Results and Discussion

The overall synthetic methodology followed in this work entails treatment of various ruthenium electrophiles with nickel complexes of either of two diamino dithiolates, which are shown in Chart 3.

Synthesis of [Cp*Ru(NiS₂N₂)]₂(OTf)₂ (1**)₂(OTf)₂.** Treatment of MeCN solutions of [Cp*Ru(MeCN)₃]OTf with NiS₂N₂ furnished dark brown [Cp*Ru(NiS₂N₂)]₂(OTf)₂ (**1**)₂(OTf)₂ in excellent yield (eq 1).

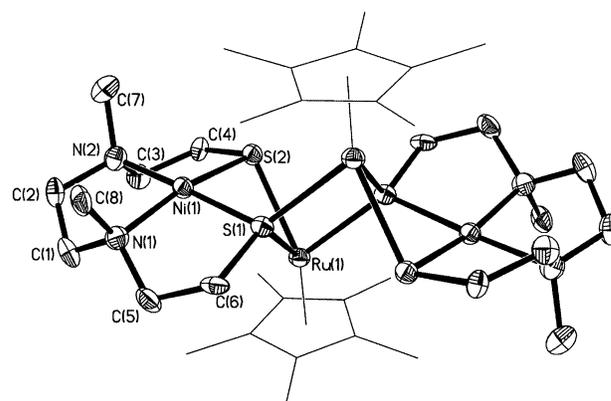


The salt **1**₂(OTf)₂ is moderately air-stable in the solid state but rapidly oxygenates when exposed to air in solution (see below). ¹H NMR spectroscopic analysis of **1**₂(OTf)₂ in CD₃CN showed broadened signals that were shifted downfield of those in the free NiS₂N₂. Upon cooling the solution to -30 °C, two subspectra can be resolved, which we attribute to [Cp*Ru(NiS₂N₂)(CD₃CN)]⁺ and [Cp*Ru(NiS₂N₂)]₂²⁺ (eq 2).



The high-temperature ¹H NMR spectrum is simple, due to rapid monomer–dimer equilibria, with the equilibrium favoring the monomer [Cp*Ru(NiS₂N₂)(NCMe)]⁺ (Supporting Information). The ESI-MS spectrum of **1**₂(OTf)₂ shows a parent ion with *m/z* = 501 corresponding to Cp*Ru(NiS₂N₂)⁺, i.e., one-half of the dimer unit. Signals for [Cp*Ru(NiS₂N₂)(NCMe)]⁺ were not observed.

Crystallographic analysis of **1**₂(OTf)₂ reveals a centrosymmetric dication with the Ru centers being quasi-octahedral and the NiS₂N₂ coordination sphere being relatively planar (Figure 1, Table 1). The Ru and Ni centers are linked via the two μ -SR units. All three Ru–S distances fall in a narrow range of 2.4736(16)–

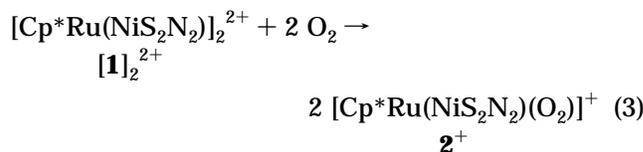
**Figure 1.** Molecular structure of the dication in [Cp*Ru(NiS₂N₂)]₂(OTf)₂, **1**₂(OTf)₂, with thermal ellipsoids drawn at the 50% probability level.**Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**₂(OTf)₂**

Ru(1)–S(1)	2.4736(16)	S(1)–Ru(1)–S(1A)	73.81(7)
Ru(1)–S(2)	2.4672(17)	S(2)–Ru(1)–S(1A)	81.61(6)
Ru(1)–S(1A)	2.4396(17)	S(1)–Ni(1)–S(2)	88.15(7)
Ni(1)–S(1)	2.1401(18)	N(1)–Ni(1)–N(2)	88.6(2)
Ni(1)–S(2)	2.1761(17)	C(6)–S(1)–Ru(1)	122.1(2)
Ni(1)–N(1)	1.938(5)	C(6)–S(1)–Ni(1)	98.9(2)
Ni(1)–N(2)	1.943(5)	Ru(1)–S(1)–Ni(1)	83.41(5)
S(1)–Ru(1)–S(2)	74.84(5)	Ru(1A)–S(1)–Ni(1)	124.10(7)

2.4396(17) Å. The Ni environment of the NiS₂N₂ moiety is similar to that observed in [Ni(NiS₂N₂)]₂²⁺.³¹

Complex **1**₂²⁺ proved to be unreactive toward PhCCH, cyclohexene, Et₃SiH, H₂O, protic acids, and H₂ in both MeCN and MeNO₂, although it does react with O₂, S₈, CO, and CNMe as described below. Reactions of **1**₂²⁺ with more aggressive reagents such as LiAlH₄, NaBH₄, and NaOMe led to decomposition into NiS₂N₂ and unidentified ruthenium-containing products. Reaction of [Cp*RuCl]₄ with 4 equiv of NiS₂N₂ in MeCN produced the chloride salt of **1**₂²⁺, as indicated by ¹H NMR spectroscopy.

Reactivity of **1₂(OTf)₂ with O₂ and S₈.** Exposure of an MeCN solution of **1**₂(OTf)₂ to air quantitatively afforded the red-brown peroxy species [Cp*Ru(NiS₂N₂)(η^2 -O₂)]OTf (**2**)OTf (eq 3).



ESI-MS analysis confirms the formula (*m/z* = 533.1). Aside from the methylene signals, the ¹H NMR spectrum shows a singlet for the two NMe groups and a singlet for Cp* shifted 0.12 ppm upfield vs **1**₂²⁺. Crystallographic analysis confirms the close similarity of the Ru–Ni bimetallic unit in **2**⁺ and **1**₂²⁺ (Figure 2, Table 2). In principle, the species [Cp*Ru(L)(NiS₂N₂)] could exist as four possible isomers; however only one isomer (Chart 4) was observed for **2**⁺. In terms of the relative stereochemistry, the Cp* ligands in **1**₂²⁺ are axial, while the Cp* in **2**⁺ is equatorial. Cations [Ni(NiS₂N₂)]₂²⁺ and Fe(NO)₂[Ni(S₂N₂)] (S₂N₂' = *N,N*-

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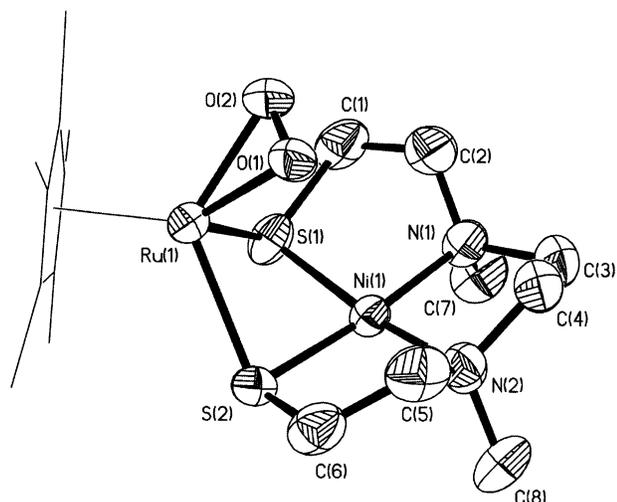
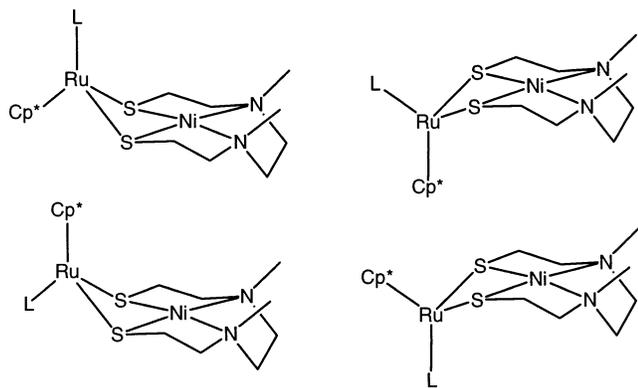


Figure 2. Molecular structure of the cation of $[\text{Cp}^*\text{Ru}(\text{NiS}_2\text{N}_2)(\eta^2\text{-O}_2)](\text{OTf})$, $[\mathbf{2}](\text{OTf})$, with thermal ellipsoids drawn at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[\mathbf{2}]\text{OTf}$

Ru(1)–O(1)	2.054(6)	O(2)–Ru(1)–S(1)	86.1(3)
Ru(1)–O(2)	2.041(6)	S(1)–Ni(1)–S(2)	87.74(8)
Ru(1)–S(1)	2.418(2)	N(1)–Ni(1)–N(2)	89.3(2)
Ru(1)–S(2)	2.4086(19)	N(1)–Ni(1)–S(1)	90.45(16)
O(1)–O(2)	1.371(8)	N(2)–Ni(1)–S(2)	90.75(17)
Ni(1)–S(1)	2.144(2)	C(1)–S(1)–Ru(1)	111.8(3)
Ni(1)–S(2)	2.130(2)	C(1)–S(1)–Ni(1)	96.8(3)
Ni(1)–N(1)	1.939(5)	Ru(1)–S(1)–Ni(1)	82.84(7)
Ni(1)–N(2)	1.925(5)	C(6)–S(2)–Ru(1)	114.0(3)
O(1)–Ru(1)–O(2)	39.1(2)	Ni(1)–S(2)–Ru(1)	83.36(6)
S(1)–Ru(1)–S(2)	75.71(7)	C(6)–S(2)–Ni(1)	98.5(3)
O(1)–Ru(1)–S(2)	95.6(3)		

Chart 4. Possible Isomers of $[\text{Cp}^*\text{Ru}(\text{L})(\text{NiS}_2\text{N}_2)]^{\text{a}}$



^a The one in the upper left is observed.

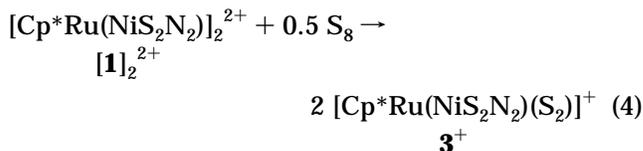
diethyl-3,7-diazanonane-1,9-dithiolate) adopt similar conformations.^{31,32} The NiS_2N_2 ligand adopts a bowl-like cavity under the $\eta^2\text{-O}_2$ ligand. In comparison to $[\mathbf{1}]_2^{2+}$, the Ru(1)–S(1) and Ru(1)–S(2) distances of $\mathbf{2}^+$ are 0.056–0.059 Å shorter. The O–O distance of 1.371–(8) Å is similar to those observed in $[\text{Cp}^*\text{Ru}(\text{dppe})(\eta^2\text{-O}_2)]^+$ (1.398(5) Å)^{33,34} and $[\text{Cp}^*\text{Ru}(\text{dppm})(\eta^2\text{-O}_2)]^+$ (1.37–(1) Å),³⁴ although the Ru–O distances are slightly longer. The O_2 ligand was not displaced by CO and was also unreactive toward H_2 in refluxing MeCN solution.

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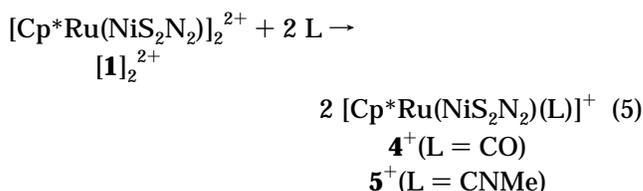
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Complex $[\mathbf{1}]_2(\text{OTf})_2$ also reacts with elemental sulfur at room temperature in MeCN solution to give the brown persulfide $[\text{Cp}^*\text{Ru}(\text{NiS}_2\text{N}_2)(\eta^2\text{-S}_2)]\text{OTf}$, $[\mathbf{3}]\text{OTf}$ (eq 4).



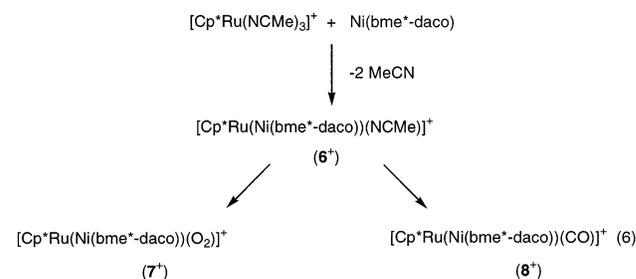
The ^1H NMR data for $\mathbf{3}^+$ resemble that for the dioxygen complex $\mathbf{2}^+$. Further supporting the structure proposed for $\mathbf{3}^+$, the FAB-MS showed a parent ion for $[\text{Cp}^*\text{Ru}(\text{NiS}_2\text{N}_2)(\text{S}_2)]^+$ ($m/z = 565$) and the fragment $[\text{Cp}^*\text{Ru}(\text{NiS}_2\text{N}_2)]^+$ ($m/z = 501$).

Reactions of $[\mathbf{1}]_2(\text{OTf})_2$ with CO and MeNC. Acetonitrile solutions of $[\mathbf{1}]_2(\text{OTf})_2$ react with CO and MeNC to give the corresponding adducts $[\text{Cp}^*\text{Ru}(\text{NiS}_2\text{N}_2)\text{L}]\text{OTf}$, $[\mathbf{4}]\text{OTf}$ for L = CO and $[\mathbf{5}]\text{OTf}$ for L = MeNC (eq 5).



The IR spectrum of $\mathbf{4}^+$ exhibits ν_{CO} at 1901 cm^{-1} , the low value of which is indicative of the excellent electron-donating power of the NiS_2N_2 ligand. For comparison, ν_{CO} for the structurally related phosphine complexes $[\text{Cp}^*\text{Ru}(\text{PMe}_3)_2(\text{CO})]^+$ and $[\text{Cp}^*\text{Ru}(\text{dppe})(\text{CO})]^+$ occur at 1935 and 1975 cm^{-1} ,^{35,36} respectively. FAB-MS shows peaks for $[\text{Cp}^*\text{Ru}(\text{NiS}_2\text{N}_2)(\text{CO})]^+$ as well as $[\text{Cp}^*\text{Ru}(\text{NiS}_2\text{N}_2)]^+$. The MeNC adduct $[\mathbf{5}]\text{OTf}$ proved to be spectroscopically similar to $\mathbf{4}^+$, the ν_{CN} again occurring at relatively low energy at 2070 cm^{-1} . Addition of excess of MeNC with $[\mathbf{1}]_2^{2+}$ gave the bis(adduct) $[\text{Cp}^*\text{Ru}(\text{NiS}_2\text{N}_2)(\text{CNMe})_2]^+$, which was characterized spectroscopically. Telling ^1H NMR data are the presence of diastereotopic CNMe signals as well as signals consistent with an unsymmetrically bound NiS_2N_2 .

$[\text{Cp}^*\text{Ru}(\text{Ni}(\text{bme}^*\text{-daco}))(\text{MeCN})]\text{OTf}$ ($[\mathbf{6}]\text{OTf}$). In this series of experiments we examined a bulkier version of the NiS_2N_2 species $\text{Ni}(\text{bme}^*\text{-daco})$, where $\text{bme}^*\text{-daco}$ = [1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane] (Chart 3). The goal was to generate a stable monomeric analogue of $[\mathbf{1}]_2^{2+}$. Solutions of $[\text{Cp}^*\text{Ru}(\text{NCMe})_3]^+$ and $\text{Ni}(\text{bme}^*\text{-daco})$ react readily in MeCN solution to produce dark brown $[\text{Cp}^*\text{Ru}(\text{NCMe})(\text{Ni}(\text{bme}^*\text{-daco}))]^+$ ($\mathbf{6}^+$) (eq 6). FAB-MS analysis shows a



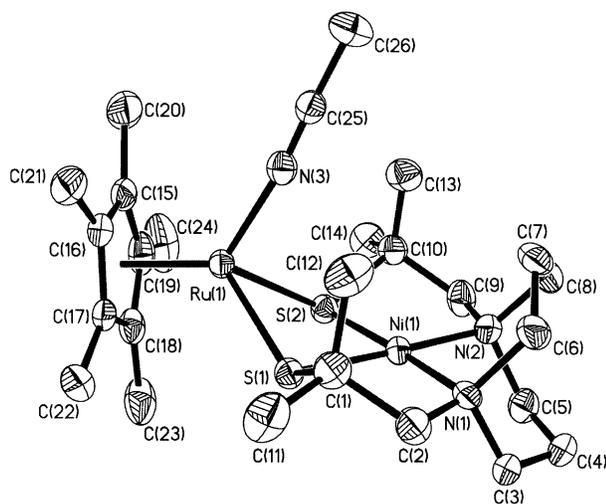


Figure 3. Molecular structure of the cation of [Cp*Ru(Ni(bme*-daco))(NCMe)]OTf, [6]OTf, with thermal ellipsoids drawn at the 50% probability level.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [6]OTf

Ru(1)–S(1)	2.4346(18)	N(3)–C(25)–C(26)	177.4(5)
Ru(1)–S(2)	2.4628(18)	C(25)–N(3)–Ru(1)	172.2(3)
Ru(1)–N(3)	2.051(4)	S(1)–Ni(1)–S(2)	85.39(8)
Ni(1)–S(1)	2.1519(17)	N(1)–Ni(1)–N(2)	92.79(16)
Ni(1)–S(2)	2.1548(17)	C(1)–S(1)–Ru(1)	123.80(15)
Ni(1)–N(1)	1.983(3)	C(1)–S(1)–Ni(1)	97.03(15)
Ni(1)–N(2)	1.977(4)	Ni(1)–S(1)–Ru(1)	93.75(8)
S(1)–Ru(1)–S(2)	73.21(6)	C(10)–S(2)–Ru(1)	125.37(14)
S(1)–Ru(1)–N(3)	99.04(11)	C(10)–S(2)–Ni(1)	97.22(15)
N(3)–Ru(1)–S(2)	96.84(11)	Ni(1)–S(2)–Ru(1)	92.89(7)

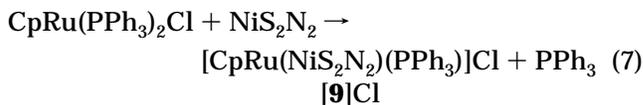
parent ion at $m/z = 585.1$ for [Cp*Ru(Ni(bme*-daco))]⁺. The ¹H NMR spectrum of 6⁺, while complex, exhibits signals that can be reasonably assigned to those expected for the bme*-daco ligand at δ 4.5–1.8. The geminal methyl groups appear as singlets at δ 1.57 and 1.13 and the Cp* methyl resonance is observed as a sharp singlet at δ 1.56. The coordinated MeCN rapidly exchanges in CD₃CN solution.

Crystallographic analysis demonstrates that 6⁺, unlike [1]₂²⁺, consists of isolated Ru-Ni species wherein the thiolato ligands are only doubly bridging (Figure 3, Table 3). The Cp*Ru moiety adopts the usual piano-stool geometry as seen in [1]₂²⁺ and 2⁺. The Ru centers feature an MeCN ligand with a Ru–N–C angle of 172.2–(3)° and Ru(1)–N(3) distance of 2.051(4) Å. The Ni center sits in the pocket of the bme*-daco ligand in a square planar arrangement, as observed for the NiS₂N₂ ligands in the structures of [1]₂²⁺ and 2⁺.

Complex 6⁺ reacts rapidly with air in solution to give the peroxo complex [Cp*Ru(Ni(bme*-daco))(η²-O₂)]OTf ([7]OTf), which proved structurally similar to 2⁺ (Supporting Information). Carbonylation of solutions of 6⁺ gave the adduct [Cp*Ru(Ni(bme*-daco))(CO)]OTf, [8]-OTf ($\nu_{\text{CO}} = 1914 \text{ cm}^{-1}$).

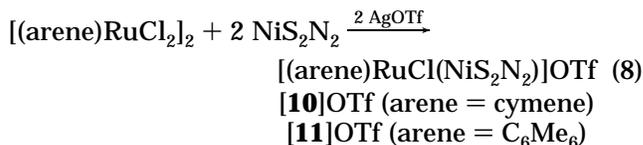
[CpRu(PPh₃)(NiS₂N₂)]Cl. The phosphine ligands in CpRu(PPh₃)₂Cl are known to be labile,³⁷ and this encouraged us to examine the reaction of (NiS₂N₂) and CpRu(PPh₃)₂Cl, a reaction that afforded the PPh₃ ad-

duct [CpRu(NiS₂N₂)(PPh₃)]Cl ([9]Cl), isolated as brick red crystals (eq 7).



Analysis by ¹H NMR spectroscopy and ESI-MS confirmed the formula. The PPh₃ ligand in 9⁺ is not labile: complex 9⁺ showed no reaction toward CO or NaBH₄. No reaction occurred between NiS₂N₂ and CpRu(PPh₃)₂H, indicating that the phosphine ligands in the hydrido complex are nonlabile (presumably due to the absence of π -donor ligands). We then examined the reaction of NiS₂N₂ with CpRu(PPh₃)₂SH, which is known to readily undergo CO-for-PPh₃ ligand exchange,³⁷ but this reaction instead afforded Cp₄Ru₄S₄, resulting from the thermally induced condensation of CpRu(PPh₃)₂SH.³⁸

[(arene)Ru(Cl)(NiS₂N₂)]PF₆. Treatment of NiS₂N₂ with sources of (arene)RuCl⁺ (arene = C₆Me₆, cymene) gave the expected adducts [(arene)RuCl(NiS₂N₂)]⁺, isolated as their OTf[−] salts (eq 8).



These cationic complexes proved thermally and chemically robust, and spectroscopic evidence supports the expected symmetric structures.

Summary

This project explored the preparative accessibility of thiolato-bridged Ni-Ru derivatives, as a starting point for the further development of functional models for bio-organometallic reaction centers. In particular the NiFe-hydrogenases and acetyl CoA synthase (ACS) both feature four-coordinate Ni centers bound to a second metal that is proposed to bind π -acids as either substrates (ACS) or constitutive ligands. Although many derivatives of Ni(SR)₂(amine)₂ are known, the resulting bimetallic complexes studied to date are unreactive with respect to the binding of π -acid ligands.

On the basis of the present results, the NiS₂N₂ species could be expected to serve more generally as a supporting ligand in organometallic chemistry, e.g., in place of diphosphines. In terms of their affinity for (cyclopentadienyl)ruthenium(II) centers, the NiS₂N₂ species serve as innocent spectator ligands, although one that is more basic than typical Ph₂P-derived chelating diphosphines.²² The high basicity of the NiS₂N₂ is further indicated by the tendency of [Cp*Ru(NiS₂N₂)]⁺ to dimerize via formation of μ_3 -thiolato ligands.

The reactivity of [Cp*Ru(NiS₂N₂)]⁺ toward dioxygen differs from the corresponding oxygenations of NiS₂N₂ and Ni(bme*-daco), which afford sulfinato (RSO₂[−]) and sulfenato (RSO[−]) complexes.^{39–42} It is well known that

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Table 4. Details of Data Collection and Structure Refinement for [1]₂(OTf)₂, [2]OTf, and [6]OTf

	[1] ₂ (OTf) ₂	[2]OTf	[6]OTf
chemical formula	C ₁₉ H ₃₃ F ₃ N ₂ NiO ₃ RuS ₃	C ₁₉ H ₃₃ F ₃ N ₂ NiO ₃ RuS ₃	C ₂₇ H ₄₆ F ₃ N ₃ NiO ₃ RuS ₃
temp (K)	193(2)	193(2)	193(2)
cryst size (mm)	0.66 × 0.06 × 0.04	0.47 × 0.20 × 0.08	0.30 × 0.10 × 0.07
space group	P1	P2 ₁ /c	P2 ₁ /c
a (Å)	9.252(2)	12.950(5)	11.084(10)
b (Å)	11.413(3)	15.019(5)	18.259(16)
c (Å)	13.835(3)	27.320(9)	16.519(15)
α (deg)	101.343(4)	90	90
β (deg)	99.102(4)	91.271(7)	92.401(8)
γ (deg)	101.017(4)	90	90
V (Å ³)	1376.5(6)	5312(3)	3340(5)
Z	2	8	4
D _{calcd} (Mg m ⁻³)	1.569	1.707	1.252
μ (Mo Kα, mm ⁻¹)	0.71073	0.71073	0.71073
max./min. transmn	0.9950/0.8532	0.7744/0.6440	0.9890/0.8661
no. of reflns measd/indep	8562/5035	39985/12786	21653/7944
no. of data/restraints/params	5035/0/323	12786/1047/835	7944/0/380
GOF	0.896	0.968	0.939
R _{int}	0.0665	0.0671	0.0623
R ₁ [I > 2σ] (all data) ^a	0.0491 (0.1047)	0.0588 (0.1513)	0.0456 (0.0964)
wR ₂ [I > 2σ] (all data) ^b	0.1032 (0.1197)	0.1547 (0.1919)	0.0943 (0.1079)
max. peak/hole (e ⁻ /Å ³)	1.019/-0.691	1.340/-0.609	1.727/-1.202

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

η^2 -O₂ ligands are nucleophilic,^{43,44} so it is not surprising that oxygen atom transfer from the peroxy ligand to the thiolate is not observed.

Experimental Section

General Considerations. All air-sensitive manipulations employed standard Schlenk line and drybox techniques. Solvents were dried using a solvent purification system similar to that described by Grubbs et al.⁴⁵ Published procedures were followed in the preparation of NiS₂N₂ (S₂N₂²⁻ = SCH₂CH₂-NMeCH₂CH₂NMeCH₂CH₂S),³¹ Ni(bme*-daco),⁴⁶ [Cp*Ru(NC-Me)₃OTf],⁴⁷ CpRu(PPh₃)₂Cl,⁴⁸ and [(arene)RuCl₂]₂ (arene = cymene or C₆Me₆).⁴⁹ Elemental analyses were conducted by the Microanalytical Laboratory in the School of Chemical Sciences. ¹H NMR spectra were acquired on a Unity Varian 400 or a Unity Varian 500 NMR spectrometer. Infrared spectra were acquired on a Mattson Infinity Gold FT-IR spectrometer using solution cells with CaF₂ plates. Fast atom bombardment (FAB) and electrospray ionization-mass spectrometry (ESI-MS) were acquired using a Micromass 70 VSE double-focusing sector instrument and a Micromass Quattro QHQ quadrupole-hexapole-quadrupole instrument, respectively.

[Cp*Ru(NiS₂N₂)₂(OTf)₂] ([1]₂(OTf)₂). A solution of 252 mg (0.495 mmol) of [Cp*Ru(NCMe)₃OTf] in 10 mL of MeCN was added to a solution of 134 mg (0.506 mmol) of NiS₂N₂ in 15 mL of MeCN. After 1 h, the resulting dark brown solution was reduced in volume to ca. 5 mL. The concentrate was layered with 15 mL of Et₂O and stored at -20 °C overnight. Dark

brown crystals precipitated from solution and were collected and washed with Et₂O. Yield: 260 mg (81%). ¹H NMR (CD₃CN, 20.1 °C): δ 3.72 (br, m, 2H), 3.12 (br, m, 2H), 2.61 (m, 4H), 2.51 (s, 6H), 3.38 (br, m, 2H), 2.15 (m, 2H), 1.56 (br, s, 15H). ¹H NMR (CD₃CN, 60.1 °C): δ 3.72 (m, 2H), 3.13 (m, 2H), 2.65–2.57 (m, 4H), 2.51 (s, 6H), 2.39 (m, 2H), 2.18 (m, 2H), 1.61 (s, 15H). FAB-MS (MeCN): *m/z* 501 [Cp*Ru(NiS₂N₂)]⁺. Anal. Calcd for C₁₉H₃₃F₃N₂NiO₃RuS₃: C, 35.09; H, 5.11; N, 4.31. Found: C, 35.13; H, 5.22; N, 4.37.

[Cp*Ru(NiS₂N₂)(η^2 -O₂)]OTf ([2]OTf). A solution of 100 mg (0.077 mmol) of [1]₂(OTf)₂ in 10 mL of MeCN was stirred in air for 1.5–2.0 h, resulting in a color change from dark brown to red-brown. The solvent volume was reduced under vacuum to ca. 2 mL and then layered with 15 mL of Et₂O, which was cooled to -20 °C for 8 h to produce red-brown crystals. Yield: 94 mg (95%). ¹H NMR (CD₃CN): δ 4.25 (m, 2H), 3.40 (m, 2H), 2.72 (m, 4H), 2.59 (s, 6H), 2.57 (m, 4H), 1.49 (s, 15H, Cp*). ESI-MS (MeCN): *m/z* 533 [Cp*Ru(NiS₂N₂)(η^2 -O₂)]⁺. Anal. Calcd for C₁₉H₃₃F₃N₂NiO₅RuS₃: C, 33.44; H, 4.87; N, 4.10. Found: C, 33.80; H, 5.08; N, 4.29.

[Cp*Ru(NiS₂N₂)(η^2 -S₂)]OTf ([3]OTf). A solution of 142 mg (0.109 mmol) of [1]₂(OTf)₂ and 10.0 mg (0.312 mmol) of S₈ was prepared in 15 mL of MeCN. After 2 h, the solvent volume was reduced to ca. 2 mL, and the concentrate was treated with 10 mL of Et₂O to give a brown precipitate of crude [3]OTf. Yield: 104 mg (74%). Dark brown single crystals were grown by diffusion of Et₂O into an MeCN solution of [3]OTf. ¹H NMR (CD₃CN): δ 4.09 (m, 2H), 3.30 (m, 2H), 2.62–2.49 (m, 6H), 2.52 (s, 6H), 2.39 (m, 2H), 1.41 (s, 15H). FAB-MS (MeCN): *m/z* 565 [Cp*Ru(NiS₂N₂)(S₂)]⁺; 501 [Cp*Ru(NiS₂N₂)]⁺. Anal. Calcd for C₁₉H₃₃F₃N₂NiO₃RuS₅: C, 31.94; H, 4.65; N, 3.92. Found: C, 32.03; H, 4.62; N, 4.11.

[Cp*Ru(NiS₂N₂)(CO)]OTf ([4]OTf). A 15 mL solution containing 104 mg (0.080 mmol) of [1]₂(OTf)₂ was purged with CO for 30 min, resulting in a color change from dark brown to deep red. The solvent volume was reduced to ca. 1 mL, and the concentrate was layered with 20 mL of Et₂O, which after 8 h produced red-brown crystals of [4]OTf at -20 °C. Yield: 80 mg (75%). ¹H NMR (CD₃CN): δ 4.00 (m, 2H), 3.43 (m, 2H), 2.80 (m, 4H), 2.62 (s, 6H), 2.58 (m, 2H), 2.18 (m, 2H), 1.75 (s, 15H). IR (MeCN): ν_{CO} 1901 cm⁻¹. FAB-MS (MeCN): *m/z* 529 [Cp*Ru(NiS₂N₂)(CO)]⁺; 501 [Cp*Ru(NiS₂N₂)]⁺. Anal. Calcd for C₂₀H₃₃F₃N₂NiO₄RuS₃: C, 35.41, H, 4.90, N, 4.13. Found: C, 35.66, H, 5.03, N, 4.27.

[Cp*Ru(NiS₂N₂)(CNMe)]OTf ([5]OTf). To a solution of 86.0 mg (0.066 mmol) of [1]₂(OTf)₂ in 10 mL of MeCN was

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added 0.20 mL (0.18 mmol) of a 0.91 M stock solution of CNMe in MeCN. The solution initially became red for 2 min and then turned red-brown. After stirring for 2 h, the solvent volume was reduced to ca. 1 mL, and the solution was then layered with 10 mL of Et₂O to produce brown crystals. Yield: 55 mg (60%). ¹H NMR (CD₃CN): δ 4.00 (2H, m), 3.87 (3H, s), 3.27 (2H, m), 2.64 (4H, m), 2.54 (6H, s), 2.44 (2H, m), 1.87 (2H, m), 1.67 (15H, s). IR (KBr): ν_{CN} 2070 cm⁻¹. FAB-MS (MeCN): *m/z* 542.0 [Cp*₂Ru(NiS₂N₂)(CNMe)]⁺, 501.0 [Cp*₂Ru(NiS₂N₂)]⁺. Anal. Calcd for C₂₁H₃₆F₃N₃NiO₃RuS₃: C, 36.48; H, 5.25; N, 6.08. Found: C, 37.02; H, 5.54; N, 6.14.

[Cp*₂Ru(NiS₂N₂)(CNMe)₂]OTf ([10]OTf). To a solution of 100 mg (0.077 mmol) of [1]₂(OTf)₂ in 10 mL of MeCN was added 1.00 mL (0.46 mmol) of a 0.46 M solution of CNMe in MeCN. The solution was stirred for 6 h and during this time became red. The volume was then reduced and 15 mL of Et₂O was added. A red crystalline solid was produced after 1 day at -20 °C, collected by filtration, and dried in vacuo. Yield: 99.0 mg (88%). ¹H NMR (CD₃CN): 3.74 (s, 3H, Me), 3.45 (s, 3H, Me), 3.21 (m, 2H), 3.04 (m, 1H), 2.98 (m, 1H), 2.96 (s, 3H, Me), 2.82 (s, 3H, Me), 2.64 (m, 1H), 2.58 (m, 1H), 2.49–2.36 (m, 4H), 2.19 (m, 1H), 2.09 (m, 1H), 1.73 (s, 15H, Cp*). IR (MeCN): ν_{CN} 2159; 2125 cm⁻¹. FAB-MS (MeCN): *m/z* 583.1 [Cp*₂Ru(NiS₂N₂)(CNMe)₂]⁺; 501.1 [Cp*₂Ru(NiS₂N₂)]⁺.

[Cp*₂Ru(Ni(bme*-daco))(NCMe)]OTf ([6]OTf). In a glovebox, a solution of 27.0 mg (0.053 mmol) of [Cp*₂Ru(NCMe)₃]OTf in 2 mL of MeCN was added to a solution of 19.0 mg (0.055 mmol) of Ni(bme*-daco) in 3 mL of MeCN. The dark solution was stirred for 2 h followed by reduction of the solvent volume to ca. 1 mL. Layering with 6 mL of Et₂O afforded red-brown crystals of [6]OTf. Yield: 40 mg (98%). ¹H NMR (CD₃CN): δ 4.53 (m, 1H), 3.59 (dt, 2H), 2.92 (m, 2H), 2.61 (dt, 2H), 2.54–2.44 (m, 6H), 1.83 (m, 3H), 1.57 (s, 6H, 2 Me), 1.56 (s, 15H, C₅Me₅), 1.13 (s, 6H, 2 Me). FAB-MS (CH₃CN): *m/z* 585.1 [Cp*₂RuNi(bme*-daco)]⁺. Anal. Calcd for C₂₇H₄₆F₃N₃NiO₃RuS₃: C, 41.92; H, 5.99; N, 5.43. Found: C, 41.35; H, 5.90; N, 5.28.

[Cp*₂Ru(Ni(bme*-daco))(η²-O₂)]OTf ([7]OTf). A 5 mL solution of 20 mg (0.029 mmol) of [6]OTf in MeCN was stirred in air for 30 min. The solvent was then removed under vacuum, producing a red-brown solid, which was recrystallized from a 10:1 mL mixture of MeCN/Et₂O at -20 °C overnight. Yield: 18 mg (80%). ¹H NMR (CD₃CN): δ 3.82 (m, 1H), 3.54 (m, 2H), 3.18 (m, 2H), 2.78 (m, 4H), 2.66–2.42 (m, 6H), 1.88, (m, 1H), 1.73 (s, 6H, 2 Me), 1.43 (s, 15 H, Cp*), 1.37 (s, 6H, 2 Me). An analytically pure sample of this compound was not obtained.

[Cp*₂Ru(Ni(bme*-daco))(CO)]OTf ([8]OTf). A 5 mm NMR tube charged with a 1 mL of CD₃CN solution containing 10.0 mg (0.013 mmol) of [6]OTf was purged with CO for 1 h, during which time the dark solution became red. ¹H NMR (CD₃CN): δ 4.44 (m, 1H), 3.60 (m, 2H), 2.94 (m, 2H), 2.68–2.51 (m, 8H), 2.06–1.85 (m, 3H), 1.75 (s, 15H, Cp*), 1.65 (s, 6H, 2 Me), 1.13 (s, 6H, 2 Me). IR (CD₃CN): ν_{CO} = 1914 cm⁻¹. Anal. Calcd for C₂₆H₄₃F₃N₂NiO₄RuS₃: C, 40.95; H, 5.95; N, 3.67. Found: C, 40.18; H, 5.64; N, 3.98.

[CpRu(NiS₂N₂)(PPh₃)Cl] ([9]Cl). A solution of 100 mg (0.138 mmol) of CpRu(PPh₃)₂Cl and 37.0 mg (0.140 mmol) of NiS₂N₂ in 15 mL of MeCN was heated at reflux for 12 h. After removal of the solvent, the red residue was washed with 30 mL of Et₂O. Brick red crystals were grown after 48 h by slow diffusion of Et₂O into a solution of [9]Cl in 4 mL of MeCN at

room temperature. Yield: 70 mg (69%). ¹H NMR (CD₃CN): δ 7.43–7.26 (15H, m, Ph), 4.51 (5H, s, C₅H₅), 4.04 (2H, m), 3.89 (2H, m), 3.62 (2H, m), 3.42 (2H, m), 3.28 (2H, m), 2.83 (6H, s, 2 Me), 2.69 (2H, m). ³¹P NMR: δ 52.6. FAB-MS (MeCN): *m/z* 693.0 [CpRu(NiS₂N₂)(PPh₃)]⁺, 430.9 [CpRu(NiS₂N₂)]⁺. Anal. Calcd for C₃₁H₃₈ClN₂NiRuPS₃: C, 51.08; H, 5.25; N, 3.84. Found: C, 49.99; H, 5.55; N, 3.88.

[(cymene)RuCl(NiS₂N₂)]OTf ([10]OTf). A 5 mL MeCN solution of 29.0 mg (0.11 mmol) of AgOTf was added dropwise to a solution of 34 mg (0.06 mmol) of [(cymene)RuCl₂]₂ in 5 mL of MeCN. The solution became light yellow with a white precipitate and was stirred for another 20 min, then allowed to settle. The yellow solution was filtered and transferred to a 10 mL solution of 30 mg (0.11 mmol) of NiS₂N₂ in MeCN. The brown solution became cherry-red immediately upon the addition. After 2 h, the solution was reduced in volume to ca. 1 mL, layered with 10 mL of Et₂O, and stored at -20 °C overnight to afford a red powder. Yield: 57 mg (80%). ¹H NMR (CDCl₃): δ 5.45 (2H, d, *J* = 6.0 Hz), 5.31 (2H, d, *J* = 6.0 Hz), 4.70 (2H, m), 3.84 (2H, m), 3.61–3.44 (6H, m), 3.06 (6H, s, 2 N-Me), 2.94 (2H, m), 2.81 (1H, septet, *J* = 6.8 Hz), 2.15 (3H, s, Me), 1.20 (6H, d, *J* = 6.8 Hz, 2 Me). FAB-MS (MeCN): *m/z* 535.0 [(C₁₀H₁₄)Ru(NiS₂N₂Cl)]⁺. Anal. Calcd for C₁₉H₃₂ClF₃N₂NiO₃RuS₃: C, 33.32; H, 4.71; N, 4.09. Found: C, 33.44; H, 5.08; N, 4.19.

[(C₆Me₆)Ru(NiS₂N₂)Cl]OTf ([11]OTf). Complex [11]OTf was prepared in a manner similar to [10]OTf by reacting 100 mg (0.15 mmol) of [(C₆Me₆)RuCl₂]₂ in 5 mL of MeCN and 77 mg (0.30 mmol) of AgOTf in 5 mL of MeCN. The resulting slurry was filtered into a solution of 79.0 mg (0.30 mmol) of NiS₂N₂ in 10 mL of MeCN. After 2 h, the solvent was reduced in vacuo to ca. 1 mL and layered with Et₂O. After 1 day, a red powder precipitated. Yield: 58 mg (70%). ¹H NMR (CD₃CN): δ 4.40 (m, 2H), 3.23 (m, 2H), 2.73 (m, 2H), 2.57 (s, 6H), 2.53 (m, 2H), 2.42–2.30 (m, 4H), 1.98 (s, 18H, C₆Me₆). FAB-MS (MeCN): *m/z* 563.0 [(C₆Me₆)Ru(NiS₂N₂Cl)]⁺. Anal. Calcd for C₂₁H₃₆ClF₃N₂NiO₃RuS₃: C, 35.38; H, 5.09; N, 3.93. Found: C, 35.30; H, 5.17; N, 4.18.

Crystallography. Crystals were mounted on thin glass fibers using oil (Paratone-N, Exxon). Data were collected at 193(2) K on a Siemens CCD diffractometer. Crystal and refinement details are given in Table 4. All structures were solved using SHELXTL and direct methods; correct atomic positions were deduced from an *E* map or by an unweighted difference Fourier synthesis. H atom *U*s were assigned as 1.2 times the *U*_{eq}'s of adjacent C atoms. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement of *F*² was indicated by the maximum shift/error for the last cycle.

Acknowledgment. This research was supported by NIH.

Supporting Information Available: Atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for [1]₂(OTf), [2]OTf, [6]OTf, and [7]OTf. Variable-temperature ¹H NMR spectrum of [1]₂²⁺. A molecular structure of [7]OTf is included with thermal ellipsoids drawn at the 30% probability level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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