Synthesis and Reactivity of NHC-Supported Ni$_2$(μ^2-η^2,η^2-S$_2$)-Bridging Disulfide and Ni$_2$(μ-S)$_2$-Bridging Sulfide Complexes

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Ⓢ Supporting Information

ABSTRACT: The (IPr)Ni scaffold stabilizes low-coordinate, mononuclear and dinuclear complexes with a diverse range of sulfur ligands, including μ^2-η^2,η^2-S$_2$, η^2-S$_2$, μ-S, and μ-SH motifs. The reaction of {(IPr)Ni}$_2$(μ-Cl)$_2$ (**1**, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) with S$_8$ yields the bridging disulfide species {(IPr)ClNi}$_2$(μ^2-η^2,η^2-S$_2$) (**2**). Complex **2** reacts with 2 equiv of AdNC (Ad = adamantyl) to yield a 1:1 mixture of the terminal disulfide compound (IPr)(AdNC)Ni(η^2-S$_2$) (**3a**) and *trans*-(IPr)(AdNC)NiCl$_2$ (**4a**). **2** also reacts with KC$_8$ to produce the Ni–Ni-bonded bridging sulfide complex {(IPr)Ni}$_2$(μ-S)$_2$ (**6**). Complex **6** reacts with H$_2$ to yield the bridging hydrosulfide compound {(IPr)Ni}$_2$(μ-SH)$_2$ (**7**), which retains a Ni–Ni bond. **7** is converted back to **6** by hydrogen atom abstraction by 2,4,6-^{t}Bu$_3$-phenoxy radical. The 2,6-diisopropylphenyl groups of the IPr ligand provide lateral steric protection of the (IPr)Ni unit but allow for the formation of Ni–Ni-bonded dinuclear species and electronically preferred rather than sterically preferred structures.
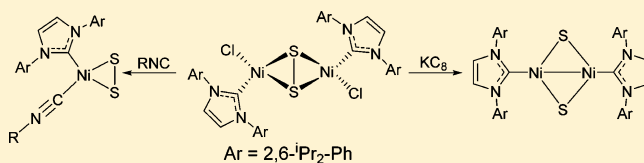
■ INTRODUCTION

Nickel complexes bearing sulfur-based ligands, particularly bridging thiolate (μ-SR) and bridging sulfide (μ-S) species, have received much interest because of their important roles in homogeneous C–S coupling reactions, hydrodesulfurization processes, and small molecule activation chemistry and their prevalence in enzyme active sites. Ni compounds supported by bridging dithiolate, thiosemicarbazone, and cubane-type sulfido ligands are catalytically active for a wide variety of reactions, including hydrogenations of aldehydes, Suzuki coupling, thioesterification, ring cyclization reactions, and copolymerization of CO with ethylene.[1] Heterogeneous Ni–sulfide catalysts for hydrodesulfurization, hydrodenitrogenation, and photocatalytic production of H$_2$ from water have also been studied intensively.[2] In the active sites of nickel CO dehydrogenase, hydrogenase, and acetyl-CoA synthase enzymes, nickel atoms are surrounded by μ-S and μ-SR ligands that are vital for small molecule activation and electron transfer reactions. Model complexes for those active sites have been investigated in depth.[3]

Dinuclear Ni complexes with two bridging thiolate or sulfide ligands, L$_n$Ni$_2$(μ-SR)$_2$ and L$_n$Ni$_2$(μ-S)$_2$, respectively, have been prepared and characterized (Chart 1).[4,5] Bridging sulfide species can be interconverted with bridging disulfide compounds L$_n$Ni$_2$(μ^2-η^2,η^2-S$_2$) by oxidation and reduction.[6] Two additional binding modes have been observed for Ni–disulfide species, the L$_n$Ni$_2$(μ^2-κ^1,κ^1-S$_2$)[7] bridging motif and the L$_n$Ni(η^2-S$_2$) terminal structure.[8] Related L$_n$Ni(η^2-supersulfido) species are also known.[6c] These three latter motifs exhibit limited thermal stability, and little is known about the reactivity of these compounds.

The L$_n$Ni$_2$(μ^2-η^2,η^2-S$_2$) motif has been observed for several L$_n$ ligand manifolds, including bidentate phosphines and

Chart 1. Ni–Disulfides and Related Complexes[a]
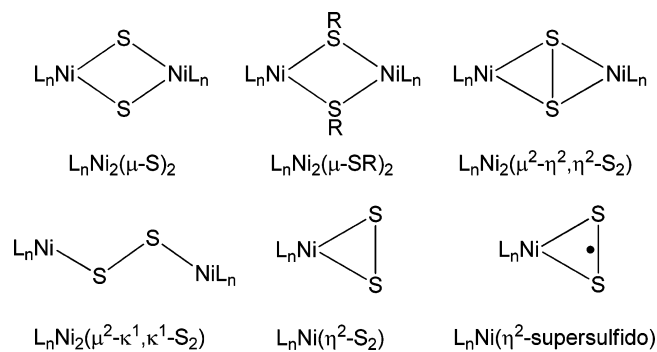
[a]L$_n$Ni$_2$(μ-SR)$_2$ complexes may have a Ni–Ni bond.

diketimines, tridentate phosphines and thioethers, and tetradentate aryl and alkyl amines. L$_n$Ni$_2$(μ^2-η^2,η^2-S$_2$) complexes can be synthesized by several pathways, which are shown schematically in Scheme 1, including (i) salt metathesis of Ni^{II} salts and alkali metal M$_2$S$_2$ reagents, (ii) reaction of L$_n$Ni^I complexes with S$_8$, (iii) two-electron oxidation of L$_n$Ni^{II}(η^2-S$_2$) or L$_n$Ni$_2$(μ-S)$_2$ complexes, (iv) abstraction of S from L$_n$Ni(η^2-S$_2$) supersulfido complexes by PPh$_3$ followed by dimerization, (v) reaction of a L$_n$Ni(η^2-S$_2$) supersulfido complex with an L$_n$Ni^I complex, and (vi) thermally driven homolytic cleavage of an L$_n$Ni^{II}S–CPh$_3$ bond and subsequent dimerization. The only reported reaction of an L$_n$Ni$_2$(μ^2-η^2,η^2-S$_2$) species is the reduction of [{(dippnapht)Ni}$_2$(μ^2-η^2,η^2-S$_2$)]$^{2+}$ (**A**, dippnapht =1,8-bis(diisopropylphosphino)naphthalene, Chart 2) by KC$_8$

Scheme 1. Synthesis of Ni$_2$(μ^2-η^2,η^2-S$_2$) Complexes
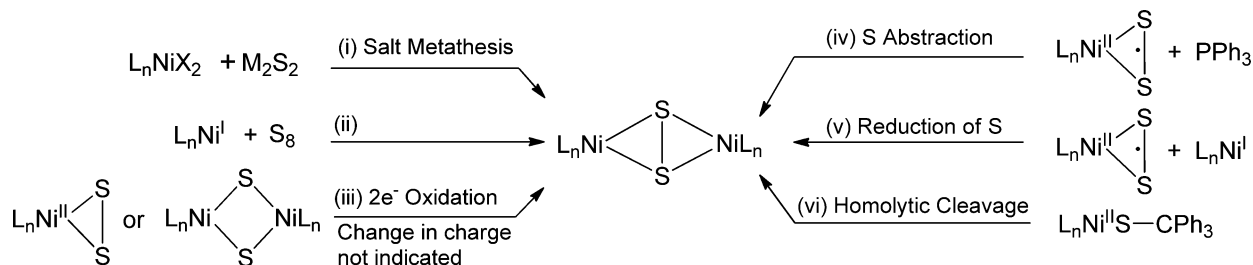
Chart 2. Structural Analogues of Compounds Studied in This Report

dipp = 2,6-^{i}Pr$_2$Ph

Scheme 2

R = Ad (**a**), ^{t}Bu (**b**), o-xylyl (**c**), p-MeO-Ph (**d**)
Ar* = 2,4,6-^{t}Bu$_3$-Ph
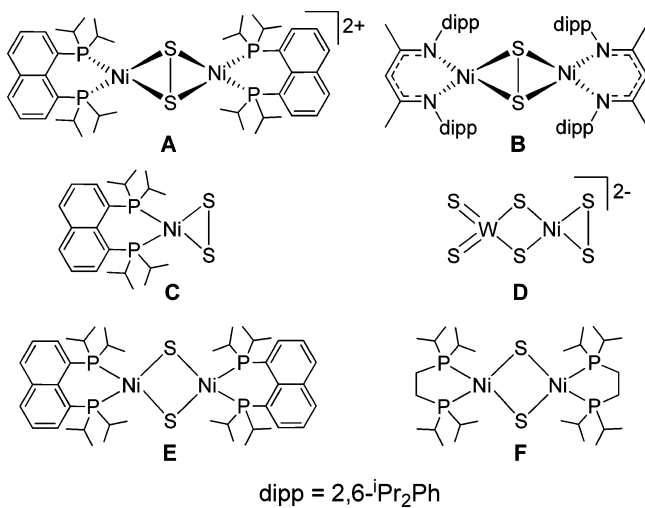
to generate the bridging sulfide complex {(dippnapht)Ni}$_2$(μ-S)$_2$ (**E**, Chart 2).[5a] This reaction shows that in this case the S$_2^{2-}$ unit rather than the Ni^{2+} centers is the site of reduction.

The objective of this work is to identify an ancillary ligand set that enables synthesis of complexes with a variety of Ni−S binding motifs and studies of their reactivity. We report the synthesis of {(IPr)ClNi}$_2$(μ^2-η^2,η^2-S$_2$) (**2**), a bridging disulfide complex supported by a monodentate N-heterocyclic carbene ligand (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene). We also describe the reaction of **2** with isocyanides to produce the terminal disulfide compound (IPr)(RNC)Ni(η^2-S$_2$) (**3**) and the two-electron reduction of **2** to produce the bridging sulfide species{(IPr)Ni}$_2$(μ-S)$_2$ (**6**). Hydrogenation of {(IPr)Ni}$_2$(μ-S)$_2$ (**6**) yields the bridging hydrosulfide complex-{(IPr)Ni}$_2$(μ-SH)$_2$ (**7**), which is converted back to **6** by hydrogen atom abstraction by a phenoxy radical.

■ RESULTS AND DISCUSSION

Synthesis and Structure of {(IPr)ClNi}$_2$(μ^2-η^2,η^2-S$_2$) (2). The reaction of {(IPr)Ni}$_2$(μ-Cl)$_2$ (**1**)[9] with S$_8$ in THF affords the bridging disulfide complex {(IPr)ClNi}$_2$(μ^2-η^2,η^2-S$_2$) (**2**, Scheme 2). Complex **2** was isolated as a dark green powder in 72% yield by precipitation from the reaction mixture with pentane. No intermediates or other products were observed by ^{1}H NMR. Complex **2** does not react further with S$_8$ under these conditions. **2** is thermally stable up to 90 °C, at which temperature it decomposes to the known thiourea IPr=S.[10]

Careful layering of pentane onto a solution of **2** in Et$_2$O at −35 °C yields X-ray quality crystals. The solid-state structure of **2** is shown in Figure 1. The two Ni centers adopt distorted
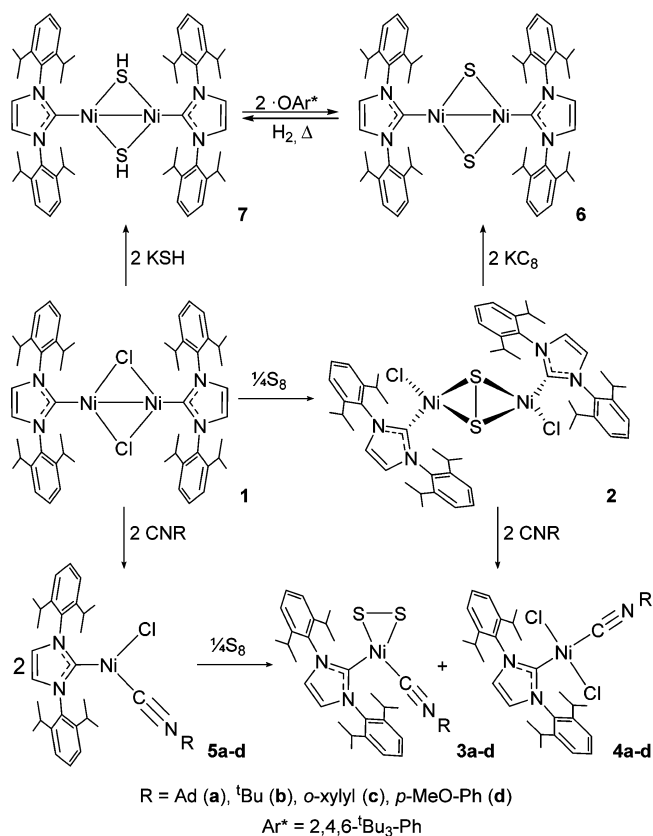
square planar geometries, the principal distortion being the acute S−Ni−S angles (S1−Ni1−S2 = 55.15(11)°; S1−Ni2−S2 = 55.63(11)°). The two square planes share an edge that is composed of the S$_2^{2-}$ moiety, forming a butterfly structure. Complex **2** has approximate C$_2$ symmetry, and the C$_2$ axis bisects the S−S bond. The imidazolin-2-ylidene rings are rotated from the corresponding Ni square planes by 51.43(4)° and 52.05(5)°. The dihedral angle between the two Ni square planes is 107.97(11)°, and the distance between the two nickel atoms is 3.098(2) Å, beyond the limit of a significant Ni−Ni interaction.[11] The distance between the two sulfur atoms is 2.011(4) Å, consistent with a single bond.[12] The Ni−S distances involving the sulfur atoms that are trans to the NHC ligands are ca. 0.06 Å longer than those involving the sulfur atoms that are trans to the chloride ligands, consistent with the larger trans influence and stronger σ-donor properties of the NHC ligands compared to the Cl$^-$ ligand.[13]

Two close structural analogues of **2**, {(dippnapht)Ni}$_2$(μ^2-η^2,η^2-S$_2$) (**A**)[5a] and {(dipp-nacnac)Ni}$_2$(μ^2-η^2,η^2-S$_2$) (**B**, dipp-nacnac = CH{(CMe)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)}$_2$),[6c] have been re-
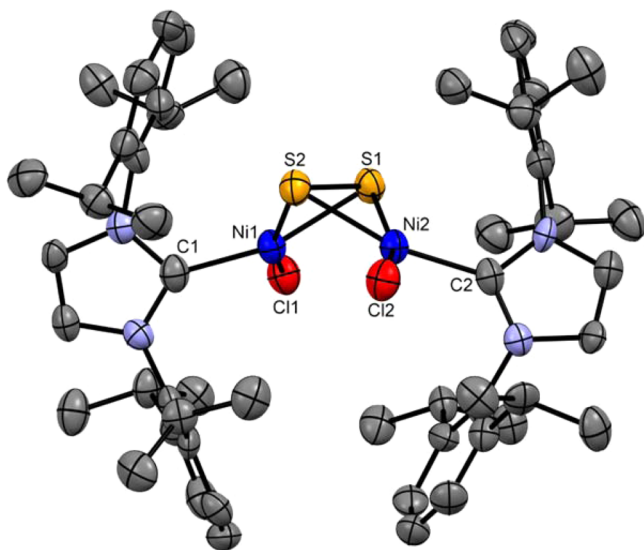
Figure 1. Molecular structure of {(IPr)ClNi}$_2$(μ^2-η^2,η^2-S$_2$) (**2**). Hydrogen atoms are omitted. Selected bond distances (Angstroms) and angles (degrees): Ni(1)−Ni(2) = 3.098(2), S(1)−S(2) = 2.011(4), Ni(1)−S(1) = 2.198(3), Ni(1)−S(2) = 2.143(3), Ni(2)−S(1) = 2.123(3), Ni(2)−S(2) = 2.184(3), Ni(1)−C(1) = 1.893(10), Ni(2)−C(2) = 1.891(10), Ni(1)−Cl(1) = 2.156(3), Ni(2)−Cl(2) = 2.143(3); Ni(1)−S(1)−Ni(2) = 91.58(11), Ni(1)−S(2)−Ni(2) = 91.43(12), S(1)−Ni(1)−S(2) = 55.15(11), S(1)−Ni(1)−Cl(1) = 100.73(12), S(2)−Ni(1)−C(1) = 106.1(3), C(1)−Ni(1)−Cl(1) = 96.1(3), S(1)−Ni(2)−S(2) = 55.63(11), S(2)−Ni(2)−Cl(2) = 101.14(12), S(1)−Ni(2)−C(2) = 106.6(3), C(2)−Ni(2)−Cl(2) = 95.5(3).

ported (Chart 2). The Ni$_2$S$_2$ core of **2** is more contracted than those of **A** or **B**. The S−S distance of **2** is ca. 0.040 Å shorter than those in **A** and **B**, the Ni−S distances trans to IPr in **2** fall in between the Ni−S distances in **A** and **B**, and the Ni−S distances trans to chloride in **2** are the shortest overall. Additionally, the dihedral angle between the Ni−S−S−Ni planes of **2** is 4.25° and 25.96° smaller, and the Ni−Ni distance in **2** is ca. 0.14 and 0.50 Å shorter than the corresponding values for **A** and **B**. Examination of space-filling models for **A** and **B** shows that the ^{i}Pr and dipp substituents on the P and N donor atoms on opposite sides of the molecule are in close contact, suggesting that steric repulsion between these groups results in the expansion and flattening of their Ni$_2$S$_2$ cores. In contrast, the dipp substitutents in **2** are located on the flanking N atoms rather than the donor C atom. Examination of a space-filling model for **2** reveals less crowding around the Ni centers and a small gap between the two IPr ligands, indicative of little steric crowding between them. These comparisons suggest that the more compact structure of **2** is electronically preferred.

Reaction of {(IPr)ClNi}$_2$(μ^2-η^2,η^2-S$_2$) (2) with Isocyanides. Complex **2** reacts with 2 equiv of adamantyl isocyanide (AdNC) in Et$_2$O to afford a 1:1 mixture of (IPr)(AdNC)Ni(η^2-S$_2$) (**3a**) and *trans*-(IPr)(AdNC)NiCl$_2$ (**4a**). No intermediates were observed by ^{1}H NMR. **3a** was selectively precipitated from the reaction mixture by addition of pentane and isolated in 88% yield, and **4a** was isolated subsequently from the filtrate in 76% yield. Close control of stoichiometry is required to obtain clean conversion of **2** to **3a** and **4a** because the product mixture reacts further with AdNC to yield free IPr, Ni(CNAd)$_4$, and other products.
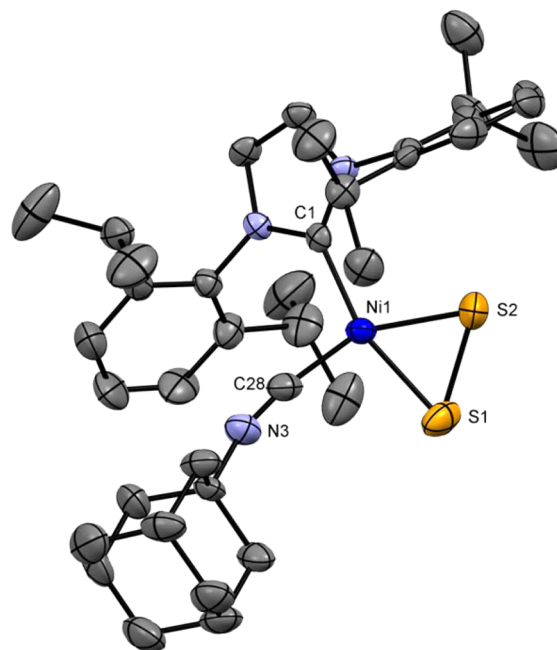

Figure 2. Molecular structure of (IPr)(AdNC)Ni(η^2-S$_2$) (**3a**). Hydrogen atoms are omitted. Selected bond distances (Angstroms) and angles (degrees): S(1)−S(2) = 2.113(2), Ni−S(1) = 2.159(2), Ni−S(2) = 2.137(2), Ni−C(1) = 1.904(5), Ni−C(28) = 1.823(6), C(28)−N(3) = 1.152(7); S(1)−Ni−S(2) = 58.92(7), C(1)−Ni−C(28) = 105.0(2), C(1)−Ni−S(2) = 100.60(15), C(28)−Ni−S(1) = 95.7(2), Ni−C(28)−N(3) = 171.3(5).

Careful layering of pentane onto a solution of **3a** in Et$_2$O at −35 °C yields X-ray quality crystals (Figure 2). In the solid state, **3a** adopts an approximate square planar geometry, with the principal distortion being the acute S−Ni−S angle of 58.92(7)°. The imidazolin-2-ylidene ring is rotated from the Ni square plane by 41.9(6)°, and the isocyanide is slightly bent away from the IPr ligand with a Ni−C−N angle of 171.3(5)° due to steric interference between these groups. The S−S distance (2.113(2) Å) is 0.1 Å longer than that in **2** but still consistent with a single bond. Two close structural analogues of **3a** exist, one supported by a dippnapht ligand (**C**),[5a] and the other by a chelating tetrathiotungstate ligand (**D**, Chart 2).[8b] The structures of the Ni(η^2-S$_2$) cores of **3a**, **C**, and **D** are very similar.

Crystals of **4a** were grown by layering pentane onto a THF solution of **4a** (Figure 3). In the solid state, **4a** exhibits a square planar geometry and a trans arrangement of the AdNC and IPr ligands. The imidazolin-2-ylidene ring is rotated from the Ni square plane by 88.6(6)°. Several other *trans*-(IPr)(L)NiCl$_2$ complexes have been characterized, in which L = IPr,[14] *N,N*-diisopropyl-imidazolin-2-ylidene,[15] 2,6-lutidine,[16] PPh$_3$,[14] or PMe$_3$[17] and all are structurally similar to **4a**.

Alternate Synthesis of (IPr)(AdNC)Ni(η^2-S$_2$) (3a) and *trans*-(IPr)(AdNC)NiCl$_2$ (4a). Complexes **3a** and **4a** can be prepared by an alternate route involving sequential reaction of **1** with AdNC and S$_8$ (Scheme 2). The reaction of **1** with 2 equiv of AdNC in Et$_2$O yields the 3-coordinate Y-shaped complex (IPr)(AdNC)NiCl (**5a**), which precipitates from the reaction mixture as a pale yellow powder in 94% yield. The analogous *tert*-butyl and benzyl isocyanide complexes were previously prepared by this route and characterized crystallographically, and the magnetic moment of **5a** in solution (μ_{eff} = 1.9 μ_B) is similar to those of these species.[17] The reaction of **5a**
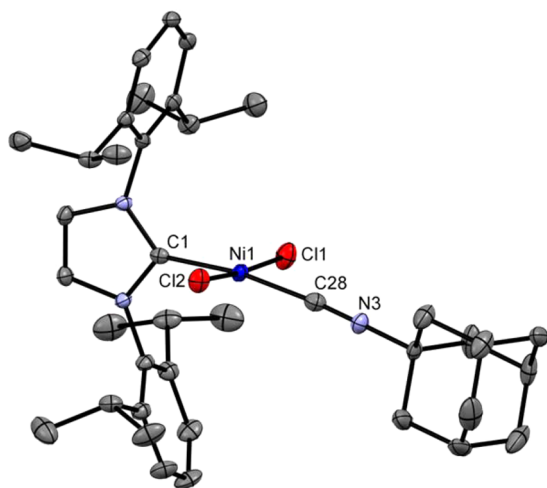
Figure 3. Molecular structure of *trans*-(IPr)(AdNC)NiCl$_2$ (**4a**). Hydrogen atoms are omitted. Selected bond distances (Angstroms) and angles (degrees): Ni–C(1) = 1.9022(14), Ni–C(28) = 1.871(2), Ni–Cl(1) = 2.1614(4), Ni–Cl(2) = 2.1747(4), C(28)–N(3) = 1.150(2); C(1)–Ni–Cl(1) = 92.02(4), C(1)–Ni–Cl(2) = 90.52(5), Cl(1)–Ni–C(28) = 90.18(5), Cl(2)–Ni–C(28) = 88.12(5), Ni–C(28)–N(3) = 175.97(14).

with S$_8$ in THF produces a 1:1 mixture of **3a** and **4a** quantitatively (by NMR), and **3a** and **4a** are isolated in yields comparable to those from the reaction of **2** with AdNC. **5a** reacts with excess AdNC to yield {(IPr)NiCl$_2$}$_2$, free IPr, and Ni(CNAd)$_4$,[17] and therefore, close control of stoichiometry is important for clean conversion of **1** to **5a**. However, neither **3a** nor **4a** react further with S$_8$.

^{1}H NMR studies show that **1** and **2** react with *tert*-butyl (**b**), *o*-xylyl (**c**), and *p*-methoxyphenyl (**d**) isocyanides in the same manner as with AdNC, as shown in Scheme 2. The AdNC complexes exhibited the most favorable solubility properties and therefore lent themselves to the highest isolated yields and full characterization. While the mechanistic details of the conversion of **2** to **3a–d** and **4a–d** are unknown, these reactions show that the disulfide unit is quite robust.

IR Spectra of Isocyanide Complexes. The isocyanide ν_{CN} bands for **3a** and **4a** (2136 and 2210 cm^{-1}, respectively) appear at higher frequencies than the value for free AdNC (2123 cm^{-1}). Therefore, **3a** and **4a** are examples of nonclassical isocyanide complexes in which the isocyanide acts as a σ-donor, but π-back-bonding is minimal.[18] This binding mode is consistent with the poor back-bonding properties of d^8 Ni^{II} centers. **4a** exhibits a larger coordination shift in ν_{CN} (87 cm^{-1}) than **3a** (13 cm^{-1}), due to the stronger electron-withdrawing effect of the two Cl ligands in **4a** versus the (η^2-S$_2$) ligand in **3a**. In contrast, the ν_{CN} value for **5a** (2108 cm^{-1}) is 15 cm^{-1} lower than the free AdNC value, due to π-back-bonding from the d^9 Ni^I center.

Reduction of {(IPr)ClNi}$_2$(μ^2-η^2,η^2-S$_2$) (2) by KC$_8$. As noted above, the two-electron reduction of disulfide complex **A** (Chart 2) with KC$_8$ yields the bridging sulfide complex **E**. DFT analysis of **2** indicates that the LUMO has significant S–S σ^* character (see Supporting Information), which suggests that two-electron reduction should induce a similar S–S bond cleavage reaction.[19] Indeed, the reaction of **2** with 2 equiv of KC$_8$ in THF affords {(IPr)Ni}$_2$(μ-S)$_2$ (**6**), which was isolated as X-ray quality crystals in 90% yield by recrystallization from Et$_2$O and pentane (Scheme 2).

In the solid state, **6** adopts a bimetallic structure with nearly planar nickel centers (sum of angles Ni1 = 356.42(6)°, Ni2 = 352.65(6)°, Figure 4). The two imidazolin-2-ylidene rings are
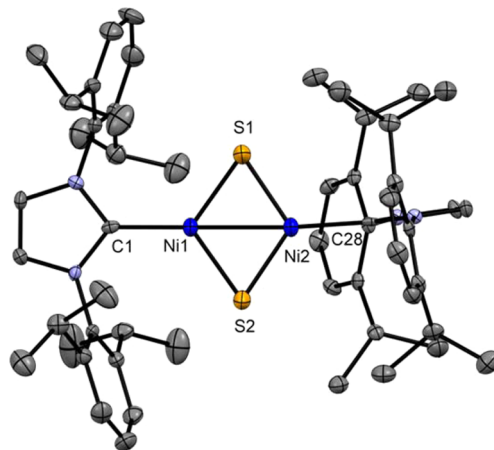

Figure 4. Molecular structure of {(IPr)Ni}$_2$(μ-S)$_2$ (**6**). Hydrogen atoms are omitted. Selected bond distances (Angstroms) and angles (degrees): Ni(1)–Ni(2) = 2.3666(5), S(1)–S(2) = 3.4186(8), Ni(1)–S(1) = 2.0972(6), Ni(1)–S(2) = 2.0950(6), Ni(2)–S(1) = 2.0911(6), Ni(2)–S(2) = 2.0890(6), Ni(1)–C(1) = 1.923(2), Ni(2)–C(28) = 1.899(2); Ni(1)–S(1)–Ni(2) = 68.81(2), Ni(1)–S(2)–Ni(2) = 68.89(2), S(1)–Ni(1)–S(2) = 109.26(2), S(1)–Ni(2)–S(2) = 109.73(2), C(1)–Ni(1)–S(1) = 123.55(6), C(1)–Ni(1)–S(2) = 123.27(6), C(28)–Ni(2)–S(1) = 125.04(6), C(28)–Ni(2)–S(2) = 117.88(6).

perpendicular to each other: one is coplanar with the planar, diamond-shaped Ni$_2$S$_2$ core and the other is perpendicular to it. The structure has approximate C$_{2v}$ symmetry with the mirror planes lying along the Ni–Ni vector. The S–S distance is 3.4186(8) Å, indicating that the S–S bond in **2** has been completely cleaved,[11,12] while the Ni–Ni distance is very short (2.3666(5) Å), indicative of a significant Ni–Ni bonding interaction.[20] These pronounced structural changes result in Ni–S–Ni angles (68.81(2)°, 68.89(2)°) that are significantly more acute than those in **2** (~91.5°). The average Ni–S distance in **6** is ca. 0.07 Å shorter than that in **2**, consistent with the higher formal charge of the sulfur in **6** (two S^{2-} ligands) versus **2** (one S$_2^{2-}$ ligand).

Two analogues of **6** that contain chelating diphosphine ligands in place of IPr have been reported, compounds **E** and **F** (Chart 2).[5b] The Ni$_2$S$_2$ core of **6** is more contracted than those in **E** and **F**. Complex **6** exhibits a significantly shorter Ni–Ni distance, by 0.9174 and 0.5744 Å, respectively, and shorter Ni–S bonds, on average by ca. 0.08 and 0.10 Å, respectively. The diamond core of **6** is flatter and features a much longer S–S distance (by 0.580 and 0.342 Å, respectively) and more acute Ni–S–Ni angles (by 29.44° and 15.16°, respectively) compared to those in **E** and **F**. Similar to complexes **A** and **B**, **E** and **F** have bulky ^{i}Pr groups on the P donor atoms, and space-filling models show that the ^{i}Pr groups on opposite sides of the molecule are in close contact. This observation suggests that steric repulsion between these groups results in the expansion of the Ni$_2$S$_2$ core. In contrast, there is less crowding around the Ni centers and a small gap between the two IPr ligands in **6**. This difference suggests that the Ni–Ni-bonded structure of **6** is electronically preferred but precluded by steric crowding in **E** and **F**.[21]

Reaction of {(IPr)Ni}$_2$(μ-S)$_2$ (6) with H$_2$. Bridging sulfide and hydrosulfide species, {L$_n$M}$_2$(μ-S)$_2$ and {L$_n$M}$_2$(μ-SH)$_2$, are closely related and can be interconverted through acid/base reactions, with a concomitant change in the overall charge.[22] Interestingly, 6 and its neutral hydrosulfide analogue {(IPr)-Ni}$_2$(μ-SH)$_2$ (7) can be interconverted through hydrogenation and H atom abstraction reactions. Complex 6 reacts with 1 atm of H$_2$ over 24 h at 70 °C in benzene to produce {(IPr)Ni}$_2$(μ-SH)$_2$ (7) in 85% yield. This reaction is accompanied by a color change from turquoise to yellow and the growth of a ^{1}H NMR resonance at δ = −4.81 (s, 2H), corresponding to the μ-SH units in 7. No intermediates in the conversion of 6 to 7 were observed by ^{1}H NMR. Complex 7 can also be prepared by the salt metathesis reaction of 1 with 2 equiv of KSH in a MeOH and THF mixture, followed by a recrystallization from Et$_2$O and pentane to produce X-ray quality crystals in 92% yield (Scheme 2). However, 6 does not react with common H atom donor sources such as Bu$_3$SnH, dihydroanthracene, or terpinenes.

In the solid state, 7 assumes a bimetallic structure with planar Ni centers (sum of angles 359.64(4)°, Figure 5). The SH
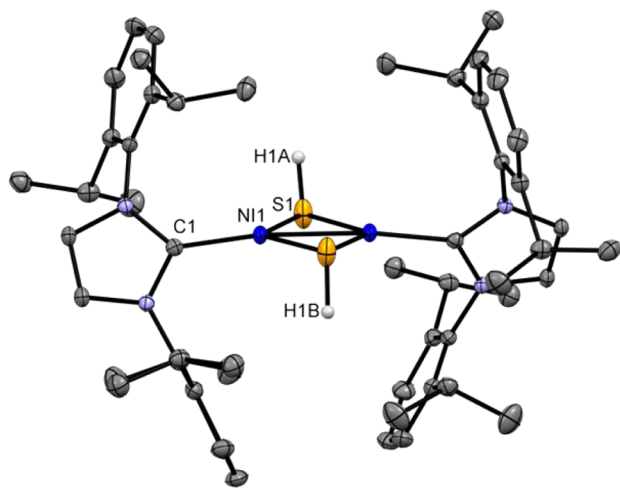

Figure 5. Molecular structure of {(IPr)Ni}$_2$(μ-SH)$_2$ (7). Hydrogen atoms except those on S are omitted. H1 is disordered over two sites (A, B; above and below the Ni$_2$S$_2$ plane). Selected bond distances (Angstroms) and angles (degrees): Ni−Ni' = 2.3601(7), Ni−S = 2.1945(4), Ni−S' = 2.2042(4), Ni−C(1) = 1.8677(12), S−S' = 3.7119(6); Ni−S−Ni' = 64.891(12), S−Ni−S' = 115.096(12), C(1)−Ni−S = 123.82(4), C(1)−Ni−S' = 120.72(4).

hydrogens were located and their positions refined isotropically. The Ni$_2$(SH)$_2$ core forms a diamond with H atoms disordered over both sides of the Ni$_2$S$_2$ plane. The Ni−S distances are ca. 0.1 Å longer in 7 than in 6, as expected for the conversion from a formally Ni^{II} to a Ni^{I} species. Due to the longer Ni−S distances in 7, the Ni−S−Ni angles are 4° more acute and the S−S distance is 0.3 Å longer. The conformation of 7 is quite different from that of 6, with the imidazolin-2-ylidene rings in 7 rotated from the Ni$_2$S$_2$ plane by 59.4° in opposite directions. This conformation positions the diisopropylphenyl rings directly above the μ-SH groups, and the resulting anisotropic shielding explains the high-field shift of the μ-SH ^{1}H NMR resonance. The Ni−Ni distance is 2.3601(7) Å, which is typical for Ni(I)−Ni(I) species that have antiferromagnetically coupled Ni centers (2.314(1)−2.559(2) Å).[9,23]

Few hydrogenations of sulfide ligands have been reported. A terminal titanium sulfido species, Cp*$_2$(py)Ti=S, is hydrogenated to produce the terminal thiol−hydride complex Cp*$_2$TiH(SH).[24] The Rh(I)[25] and Ir(I)[26] bridging sulfide complexes, [{MeC(CH$_2$PPh$_2$)$_3$Rh}$_2$(μ-S)$_2$]$^{2+}$ and [Cp$_2$Mo(μ-S)$_2$Ir(PPh$_3$)$_2$]$^+$, produce M(H)(μ-SH)$_2$M(H) species upon double hydrogenation. Ni alkyl and aryl thiolate complexes are also known to react with H$_2$ to produce thiols, an important step in the hydrodesulfurization processes, and Ni hydride species are viable catalysts for and have been characterized as intermediates in these reactions.[27] Here, in contrast, no hydride intermediates were observed in the conversion of 6 to 7.

Hydrogen Atom Abstraction from {(IPr)Ni}$_2$(μ-SH)$_2$ (7). Compound 7 reacts with 2,4,6-^{t}Bu$_3$-phenoxy radical[28] to produce 6 and the parent phenol in quantitative yield on the NMR scale (Scheme 2). This reaction proceeds with similar high yields on the preparatory scale. Compound 6 does not react further with excess phenoxy radical. Similar H atom transfer and abstraction reactivity was reported recently for the bridging diselenide complex [(Me$_4$[12]aneN$_4$)$_2$Ni$_2$(μ^2-η^2,η^2-Se$_2$)]$^{2+}$.[29] This species reacts with 9,10-dihydroanthracene to produce the monomeric selenol [(Me$_4$[12]aneN$_4$)NiSeH]$^+$, which reacts with 2,4,6-^{t}Bu$_3$-phenoxy radical to regenerate the bridging diselenide.

CONCLUSIONS

The (IPr)Ni scaffold stabilizes low-coordinate, mononuclear and dinuclear complexes with a diverse range of sulfur ligands, including μ^2-η^2,η^2-S$_2$, η^2-S$_2$, μ-S, and μ-SH. The 2,6-diisopropylphenyl groups of the IPr ligand provide lateral steric protection of the (IPr)Ni unit but also allow for the formation of Ni−Ni-bonded dinuclear species and electronically preferred rather than sterically preferred structures. This contrasts with the dominant influence of steric effects on the structures of analogous compounds containing diphosphine ligands. The reaction of {(IPr)Ni}$_2$(μ-Cl)$_2$ (1) with S$_8$ yields the bridging disulfide species {(IPr)ClNi}$_2$(μ^2-η^2,η^2-S$_2$) (2), which exhibits a compact butterfly core structure. Complex 2 reacts with 2 equiv of AdNC to produce the terminal disulfide complex (IPr)(AdNC)Ni(η^2-S$_2$) (3a) and *trans*-(IPr)(AdNC)-NiCl$_2$ (4a). AdNC breaks up the dimer into two mononuclear species, but the S−S bond is maintained. In contrast, two-electron reduction of 2 with KC$_8$ yields the bridging sulfide complex {(IPr)Ni}$_2$(μ-S)$_2$ (6). The added electrons cleave the S−S bond, and the unusual sterics of IPr allow the two Ni centers to come into close proximity and form a Ni−Ni bond. The reaction of 6 with H$_2$ yields the bridging hydrosulfide compound {(IPr)Ni}$_2$(μ-SH)$_2$ (7), which retains a Ni−Ni bond. Complex 7 is converted back to 6 through hydrogen atom abstraction by a phenoxy radical. This work raises interesting questions related to the bonding of these nickel species and the mechanisms of their reactions, and future studies are needed to elucidate these matters.

EXPERIMENTAL SECTION

General Procedures. Unless stated otherwise, all operations were performed in an MBraun Lab Master drybox under an atmosphere of purified nitrogen.[30] Anhydrous Et$_2$O and THF were purchased from Fisher, stirred over sodium metal, and filtered through activated alumina.[31] Anhydrous benzene was purchased from Sigma-Aldrich, stirred over sodium metal, and filtered through activated alumina. Pentane and toluene were purchased from Sigma-Aldrich and dried by passage through activated alumina and Q-5 columns. C$_6$D$_6$ was

purchased from Cambridge Isotope Laboratories, degassed by freeze–pump–thaw cycles, and dried over CaH_2 or activated 4 Å molecular sieves. Celite and 4 Å molecular sieves were activated by evacuation overnight at 180 °C. $\{(IPr)Ni\}_2(\mu\text{-}Cl)_2$,[9b] KC_8,[32] and 2,4,6-$^tBu_3$-phenoxy radical[28] were prepared according to literature preparations. All other chemicals were used as received. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN) or Robertson Microlit (Ledgewood, NJ). NMR spectra were recorded on a Bruker 400 or 500 MHz NMR spectrometer. Chemical shifts were determined by reference to the solvent resonance (^1H, residual C_6D_5H in C_6D_6 δ 7.16; ^{13}C, C_6D_6 δ 128.1), and coupling constants are reported in hertz. Infrared spectra were measured as Fluorolube-S20 mulls between CaF_2 plates using a Thermo NEXUS 670 Near-, Far-, and Mid-FTIR with ATR Accessory.

X-ray Data Collection and Structure Refinement. X-ray diffraction data for **2** was collected on a Bruker SMART APEX system with a charged coupled device (CCD) detector and a Mo-target X-ray tube (λ = 0.71073 Å). X-ray diffraction data **3a**, **4a**, **6**, and **7** were collected on a Bruker D8 VENTURE with a PHOTON 100 CMOS detector system equipped with a microfocus Mo-target X-ray tube (λ = 0.71073 Å). All data were collected at 100 K using a routine of ϕ and ω scans to survey an entire sphere of reciprocal space and indexed using the SMART or APEX2 program suits. Data were corrected for absorption effects using empirical methods as implemented in SADABS. Space groups were determined based on systematic absences and intensity statistics. The structures were solved and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 6.14) software package (XL refinement program version 2014/7[33]). All non-hydrogen atoms were refined anisotropically. Compound **3a** exhibited disorder in the Ad group, which was modeled by parts and using restraints on one part. Compound **3a** also crystallized with two molecules of THF in the unit cell, one of which was modeled by parts, and the second was removed by the Squeeze command. Compound **4a** crystallized with one-half a molecule of pentane in the unit cell, which could not be modeled, and was removed by the Squeeze command. All hydrogen atoms were refined isotropically and fixed at calculated positions except for the H on S1 in **7**, which was located in the difference map, disordered over two positions, and refined isotropically. All structures are drawn with thermal ellipsoids at 50% probability. Crystallographic data and details of the data collection and structure refinement for all structures are listed in Table S4, Supporting Information. For further details on refinement, description of disorder modeling, and an extensive list of geometric parameters, see the Supporting Information.

{(IPr)ClNi}₂(μ^2-η^2,η^2-S₂) (2). A suspension of S_8 (0.0283 g, 0.883 mmol) in THF (3 mL) was added dropwise at room temperature over 10 s to a stirred, pale green solution of $\{(IPr)Ni\}_2(\mu\text{-}Cl)_2$ (**1**, 0.313 g, 0.324 mmol) in THF (8 mL). The color of the mixture changed to a dark forest green over the course of 5 s. The mixture was stirred for 45 min and filtered through Celite. The filtrate was concentrated to 4 mL under reduced pressure, chilled to −35 °C, layered with pentane (13 mL), and chilled to −35 °C overnight to induce precipitation. A dark green powder was collected by filtration. This process was repeated to give several crops of product. Yield: 0.225 g (72%). X-ray quality crystals of **2** were grown by slow diffusion of pentane into an Et_2O solution of **2**. ^1H NMR (22 °C, 400 MHz C_6D_6): δ 7.35 (t, J = 8.0, 4H, p-$C_6{}^iPr_2H_3$), 7.28 (dd, J = 8.0 and 1.6, 8H, m-$C_6{}^iPr_2H_3$), 6.41 (s, 4H, $C_3N_2H_2$), 3.28 (sept, J = 6.4, 4H, PhC*H*Me₂), 2.55 (sept, J = 6.8, 4H, PhC*H*Me₂), 1.59 (d, J = 7.2, 12H, PhCH(C*H*₃)₂), 1.42 (d, J = 6.6, 12H, PhCH(C*H*₃)₂), 0.96 (d, J = 6.8, 12H, PhCH(C*H*₃)₂), 0.93 (d, J = 7.2, 12H, PhCH(C*H*₃)₂). $^{13}C\{^1H\}$ NMR (22 °C, 500 MHz, C_6D_6): δ 171.8 (Ni−C*N₂*), 146.9 (o-$C_6{}^iPr_2H_3$), 146.5 (o-$C_6{}^iPr_2H_3$), 136.6 (i-$C_6{}^iPr_2H_3$), 130.3 (p-$C_6{}^iPr_2H_3$), 125.4 (Ni−CN₂*C₂H₂*), 125.0 (m-$C_6{}^iPr_2H_3$), 124.5 (m-$C_6{}^iPr_2H_3$), 29.1 (PhC*H*(CH₃)₂), 28.9 (PhC*H*(CH₃)₂), 26.3 (PhCH(C*H*₃)₂), 25.8 (PhCH(C*H*₃)₂), 24.3 (PhCH(C*H*₃)₂), 23.7 (PhCH(C*H*₃)₂). IR (CaF₂, fluorolube): ν (cm^{-1}) 3163, 3123, 3087, 2962, 2927, 2867, 1592, 1558, 1467, 1456, 1402, 1384, 1361, 1331, 1276, 1198, 1149, 1125, 1041, 967. Anal. Calcd for $Ni_2Cl_2S_2N_4C_{54}H_{72}$: C, 62.98; H, 7.06; N, 5.04. Found: C, 62.43; H, 6.90; N, 5.15.

Synthesis of (IPr)(AdNC)Ni(η^2-S₂) (3a). A solution of AdNC (0.0343 g, 0.213 mmol) in Et_2O (2 mL) was chilled to −35 °C and then added dropwise to a chilled, stirred solution of **2** (0.108 g, 0.105 mmol) in Et_2O (8 mL). There was an immediate color change to orange. The solution was stirred for 30 min and filtered through Celite. The volatiles were removed by vacuum, and the resulting solid was redissolved in Et_2O (7 mL). The filtrate was chilled to −35 °C, and a fluffy yellow solid precipitated, which was collected by filtration. This process was repeated to give several crops of product. Yield: 0.0620 g (88%). X-ray quality crystals of **3a**·2(THF) were grown by liquid diffusion of pentane into a THF solution of **3a**. ^1H NMR (22 °C, 500 MHz C_6D_6): δ 7.27 (t, J = 7.5, 2H, p-$C_6{}^iPr_2H_3$), 7.15 (d, J = 7.5, 4H, m-$C_6{}^iPr_2H_3$), 6.55 (s, 2H, $C_3N_2H_2$), 3.06 (sept, J = 6.5, 4H, PhC*H*Me₂), 1.61 (d, J = 7, 12H, PhCH(C*H*₃)₂), 1.59 (br, 3H, NC(CH₂)₃(C*H*)₃(CH₂)₃), 1.49 (br, 6H, NC(C*H*₂)₃(CH)₃(CH₂)₃), 1.18 (dd, J = 13.5 and 12, 6H, NC(CH₂)₃(CH)₃(C*H*₂)₃), 1.11 (d, J = 7, 12H, PhCH(C*H*₃)₂). $^{13}C\{^1H\}$ NMR (22 °C, 500 MHz, C_6D_6): δ 185.8 (Ni−C*N₂*), 146.2 (o-$C_6{}^iPr_2H_3$), 137.3 (i-$C_6{}^iPr_2H_3$), 130.2 (p-$C_6{}^iPr_2H_3$), 124.3 (Ni−CN₂*C₂H₂*), 124.1 (m-$C_6{}^iPr_2H_3$), 43.2 (NC-(*C*H₂)₃(CH)₃(CH₂)₃), 35.4 (NC(CH₂)₃(*C*H)₃(CH₂)₃), 29.1 (PhC*H*Me₂), 29.0 (NC(CH₂)₃(CH)₃(*C*H₂)₃), 25.4 (PhCH(C*H*₃)₂), 24.0 (PhCH(C*H*₃)₂). IR (CaF₂, fluorolube): ν (cm^{-1}) 2960, 2930, 2865, 2329, 2136 (ν_{CN}, AdNC), 1456, 1398, 1126, 1041. Anal. Calcd for $Ni_1S_2N_3C_{32}H_{51}$: C, 67.85; H, 7.64; N, 6.25. Found: C, 67.65; H, 7.36; N, 5.92.

Synthesis of *trans*-(IPr)(AdNC)NiCl₂ (4a). **4a** was isolated from **3a** by selective precipitation from the reaction mixture of **2** with AdNC. After **3a** was precipitated, the filtrate was concentrated in THF (2 mL), chilled to −35 °C, layered with pentane (4 mL), and chilled to −35 °C overnight. Red crystals were collected by filtration. Yield: 0.0543 g (76%). X-ray quality crystals of **4a**·0.5Pent were grown by liquid diffusion of pentane into an Et_2O solution of **4a**. ^1H NMR (22 °C, 500 MHz C_6D_6): δ 7.33 (s, 6H, m/p-$C_6{}^iPr_2H_3$), 6.71 (br, 2H, $C_3N_2H_2$), 3.40 (sept, J = 6.5, 4H, PhC*H*Me₂), 1.73 (d, J = 6.5, 12H, PhCH(C*H*₃)₂), 1.30 (br, 3H, NC(CH₂)₃(C*H*)₃(CH₂)₃), 1.09 (d, J = 6.5, 12H, PhCH(C*H*₃)₂, and br, 6H, NC(C*H*₂)₃(CH)₃(CH₂)₃), 0.94 (dd, J = 31 and 10.5, 6H, NC(CH₂)₃(CH)₃(C*H*₂)₃). $^{13}C\{^1H\}$ NMR (22 °C, 500 MHz, C_6D_6): δ 147.4 (o-$C_6{}^iPr_2H_3$), 130.7 (p-$C_6{}^iPr_2H_3$), 124.4 (m-$C_6{}^iPr_2H_3$), 41.3 (NC(CH₂)₃(CH)₃(*C*H₂)₃), 35.0 (NC-(*C*H₂)₃(CH)₃(CH₂)₃), 29.2 (PhC*H*Me₂), 28.6 (NC-(CH₂)₃(*C*H)₃(CH₂)₃), 26.6 (PhCH(C*H*₃)₂), 23.6 (PhCH(C*H*₃)₂). IR (CaF₂, fluorolube): ν (cm^{-1}) 3180, 3070, 2966, 2912, 2865, 2210 (ν_{CN}, AdNC), 1965, 1592, 1467, 1405, 1383, 1360, 1345, 1333, 1307, 1199. Anal. Calcd for $Ni_1Cl_2N_3C_{38}H_{51}$: C, 67.17; H, 7.57; N, 6.18. Found: C, 67.43; H, 7.82; N, 5.94.

Synthesis of (IPr)(AdNC)NiCl (5a). A solution of AdNC (0.0268g, 0.166 mmol) in Et_2O (1 mL) was chilled to −35 °C and added dropwise to a chilled, stirred solution of **1** (0.0778 g, 0.0805 mmol) in Et_2O (4 mL). The color of the solution changed to red, and after 1 h a beige solid precipitated. The solution was chilled to −35 °C, and a pale yellow solid was collected by filtration. Yield: 0.0976 g (94%). ^1H NMR (22 °C, 500 MHz C_6D_6): δ 7.29 (br, 3H, NC(CH₂)₃(C*H*)₃(CH₂)₃), 6.91 (br, 4H, $C_3N_2H_2$), 5.97 (br, 12H, PhCH(C*H*₃)₂), 2.86 (br, 6H, NC(C*H*₂)₃(CH)₃(CH₂)₃), 1.55 (br, 4H, m-$C_6{}^iPr_2H_3$), 1.33 (br, 12H + 2H, PhCH(C*H*₃)₂ and m-$C_6{}^iPr_2H_3$), 0.99 (br, 6H, NC(CH₂)₃(CH)₃(C*H*₂)₃), 0.25 (br, 4H, PhC*H*(CH₃)₂). IR (CaF₂, fluorolube): ν (cm^{-1}) 2910, 2858, 2108 (ν_{CN}, AdNC), 1457, 1396, 1200. μ_{eff} = 1.9 μ_B in C_6D_6. Anal. Calcd for $Ni_1Cl_1N_3C_{38}H_{51}$: C, 70.87; H, 7.98; N, 6.53. Found: C, 70.66; H, 8.19; N, 6.31.

Synthesis of {(IPr)Ni}₂(μ-S)₂ (6). A suspension of KC_8 (0.0546 g, 0.404 mmol) in THF (3 mL) was chilled to −35 °C and added dropwise to a chilled, stirred solution of **2** (0.193 g, 0.187 mmol) in THF (4 mL). The mixture was stirred for 3 h, warmed to room temperature, and filtered through Celite, resulting in a blue-black solution. The volatiles were removed by vacuum, and the resulting solid was extracted with pentane (4 × 10 mL), providing a turquoise solution. The volatiles were removed by vacuum, and the resulting turquoise solid was dissolved in Et_2O (3 mL), chilled to −35 °C, layered with pentane (7 mL), and chilled to −35 °C overnight. Dark blue crystals were collected by filtration. This process was repeated to

give several crops of product. Yield: 0.162 g (90%). Complex **6** decomposes over the course of hours in CH_2Cl_2 at room temperature. X-ray quality crystals of **6** were grown by liquid diffusion of pentane into an Et_2O solution of **6**. ^{1}H NMR (22 °C, 500 MHz C_6D_6): δ 7.18 (d, J = 7.5, 8H, m-$C_6{}^iPr_2H_3$), 6.99 (t, J = 7.5, 6H, p-$C_6{}^iPr_2H_3$), 5.30 (s, 4H, $C_3N_2H_2$), 3.31 (br, 8H, PhCHMe$_2$), 1.71 (br, 24H, PhCH-(CH_3)$_2$), 1.17 (br, 24H, PhCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (22 °C, 500 MHz, C_6D_6): δ 153.0 (o-$C_6{}^iPr_2H_3$), 130.8 (p-$C_6{}^iPr_2H_3$), 127.1 (i-$C_6{}^iPr_2H_3$), 125.4 (m-$C_6{}^iPr_2H_3$), 115.5 (Ni−C$N_2C_2H_2$), 41.1 (PhCHMe$_2$), 26.5 (PhCH(CH_3)$_2$), 26.2 (PhCH(CH_3)$_2$). Multiple chemical analyses of spectroscopically pure, crystalline samples of **6** gave poor results (see Supporting Information).

Synthesis of {(IPr)Ni}$_2$(μ-SH)$_2$ (7). A solution of KSH (0.0256 g, 0.355 mmol) in THF (1 mL) and methanol (6 mL) was chilled to −35 °C and added dropwise to a chilled, stirred solution of **1** (0.168 g, 0.174 mmol) in THF (2 mL) and Et_2O (5 mL). The color of the solution turned to orange, then to red, and finally to a murky yellow-green. The solution was stirred for 1 h and warmed up to room temperature. The volatiles were removed by vacuum, producing a yellow-green film, which was extracted with pentane (20 mL) and filtered through Celite. The filtrate was dried by vacuum, and the residue was dissolved in Et_2O (3 mL), chilled to −35 °C, layered with pentane (7 mL), and chilled to −35 °C overnight to produce yellow-green crystals that were collected by filtration. Yield: 0.528 g (92%). X-ray quality crystals were grown by liquid diffusion of pentane into an Et_2O solution of **7**. ^{1}H NMR (22 °C, 500 MHz C_6D_6): δ 7.25 (t, J = 7.5, 4H, p-$C_6{}^iPr_2H_3$), 7.15 (d, J = 8, 8H, m-$C_6{}^iPr_2H_3$), 6.53 (s, 4H, $C_3N_2H_2$), 3.05 (sept, J = 7, 8H, PhCHMe$_2$), 1.50 (d, J = 6.5, 24H, PhCH(CH_3)$_2$), 1.09 (d, J = 6.5, 24H, PhCH(CH_3)$_2$), −4.81 (s, 2H, SH). ^{13}C{^{1}H} NMR (22 °C, 500 MHz, C_6D_6): δ 189.5 (Ni−CN_2), 146.8 (o-$C_6{}^iPr_2H_3$), 137.8 (i-$C_6{}^iPr_2H_3$), 129.2 (p-$C_6{}^iPr_2H_3$), 123.8 (m-$C_6{}^iPr_2H_3$), 123.3 (Ni−C$N_2C_2H_2$), 28.9 (PhCHMe$_2$), 25.1 (PhCH-(CH_3)$_2$), 24.2 (PhCH(CH_3)$_2$). IR (CaF$_2$, fluorolube): ν (cm^{-1}) 3125, 3069, 2965, 2868, 2474 (ν_{CN}, SH), 1592, 1538, 1467, 1388, 1362, 1327, 1301, 1198, 1125. Anal. Calcd for Ni$_2$S$_2$N$_4$C$_{54}$H$_{74}$: C, 67.51; H, 7.76; N, 5.83. Found: C, 67.48; H, 7.70; N, 5.87.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details and characterization data for new complexes, crystallographic data (as cif files). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.
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