

Evidence for the Existence of a Late-Metal Terminal Sulfido Complex

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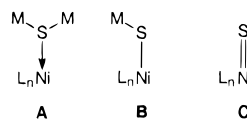
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The transition-metal–sulfur bond is an important linkage in both biological systems¹ and industrial catalysts.² Nickel sulfides, in particular, are key components of natural hydrogenases³ and are active promoters in current hydrotreating catalysts.² Understanding the nature of the metal–sulfur linkages at active sites can offer insight on ways to improve catalysis and provide a better understanding of cluster formation and cluster interconversion reactions in general.

Scheme 1 shows three possible binding modes of a sulfur atom to supported nickel. While numerous examples of binding modes **A**⁴ and **B**⁵ can be found throughout the literature, there exists no sound evidence for a terminal sulfido complex such as **C** in the solution phase.⁶ Additionally, there have been only a few cases for the group 9 and 10 metals where the intermediacy of a terminal sulfido complex has been postulated,⁷ and there has been no experimental evidence to support the existence of such a species. Terminal sulfido complexes of the earlier transition-metals are well-known, and display a wide range of reactivity.⁸ Late-metal analogues might then be anticipated to afford similarly rich chemistry.

Raney nickel, and homogeneous nickel complexes,⁹ have been found to desulfurize a variety of organosulfur substrates. The fate of the sulfur atom in these reactions is usually nickel sulfide, thereby preventing catalysis under traditional laboratory conditions. A number of recent reports from our group,¹⁰ however, indicate that sulfur can be extracted from organic compounds without the formation of nickel sulfide. These results prompted us to further explore the mechanism of these unique desulfur-

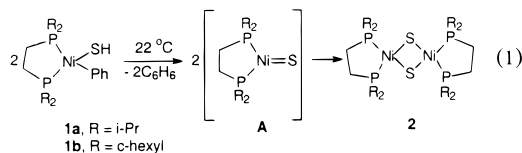
Scheme 1



izations, and to systematically investigate the intermediacy of the three possible binding modes of a sulfur atom to nickel (Scheme 1). In these efforts we have found kinetic and structural evidence that support the chemical feasibility of binding mode **C**, namely a terminal sulfido complex at nickel.

Initial studies were directed toward finding an efficient way to prepare a nickel sulfido complex. Bergman has reported routes to transient $[\text{Cp}_2\text{Ti}=\text{S}]$ and $[\text{Cp}_2\text{Zr}=\text{S}]$ using $\text{Cp}_2\text{Ti}(\text{SH})\text{H}$ ¹¹ and $\text{Cp}_2\text{Zr}(\text{SH})\text{I}$,¹² respectively. The synthetic strategy that we found to be successful with nickel was based on two very different but related findings. It was discovered by Bergman and co-workers that thermolysis of $\text{Cp}^*\text{Zr}(\text{OH})(\text{Ph})$ led to the loss of benzene and formation of the terminal oxo complex, which was subsequently trapped by a variety of substrates.^{12,13} Additionally, Osakada and co-workers found that thermolysis of *trans*- $\text{Ni}(\text{Ar})(\text{SH})(\text{PEt}_3)_2$ ($\text{Ar} = \text{aryl ligand}$) led to decomposition of the metal with formation of $\text{Ar}-\text{H}$ and $\text{S}=\text{PEt}_3$. Curiously, no $\text{Ar}-\text{SH}$ was formed.¹⁴ We wondered whether the loss of arene in this instance was concomitant with the formation of a transient terminal sulfido complex, mimicking the zirconium–oxo chemistry. We therefore prepared a nickel complex containing chelating phosphines and *cis*-(Ar)(SH) groups to examine if elimination of arene would readily occur. Chelating phosphines were used since recent reports have shown that $[\text{L}_2\text{M}(\mu\text{-S})_2]$ complexes (where L_2 is a chelating ligand) are thermally quite stable.^{10b,15} $\text{Li}_2\text{Ni}(\text{SH})(\text{Ph})$ (**1a** and **1b**) [$\text{L}_2 = \text{dippe}$ (1,2-bis(diisopropylphosphino)ethane) (**1a**) and *dcppe* (1,2-bis(dicyclohexylphosphino)ethane) (**1b**)] were prepared and their thermolysis behavior was studied in solution.

Nickel thiols of type **1** were synthesized by the addition of NaSH to $\text{L}_2\text{Ni}(\text{Cl})(\text{Ph})$. It was found that mild heating of **1** in THF solutions led to loss of benzene (1 equiv observed by ¹H NMR spectroscopy) and production of the bridged sulfido dimers **2** in quantitative yields by NMR spectroscopy (eq 1). Complex



2a was also synthesized independently by the addition of 2 equiv of $(\text{dippe})\text{Ni}(\text{SH})_2$ to $[(\text{dippe})\text{NiH}]_2$. A single-crystal X-ray structure of **2a** shows the “bent”¹⁶ Ni_2S_2 core of the bridged sulfido dimer (see Supporting Information).

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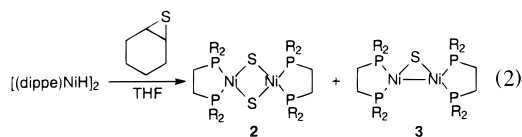
Table 1. Kinetic Data for Benzene Loss from (dcpe)Ni(Ph)(SH) (**1b**) in THF Solution

[1b], M	T, °C	k, s ⁻¹ ^a
0.00030	30.4	1.94(2) × 10 ⁻⁵
0.00030	37.9	4.66(2) × 10 ⁻⁵
0.00030	48.0	1.56(1) × 10 ⁻⁴
0.00030	56.1	4.06(2) × 10 ⁻⁴
0.00030	64.8	1.03(1) × 10 ⁻³
0.00030	60.2	5.14(4) × 10 ⁻⁴
0.00030 ^b	60.2	3.57(4) × 10 ⁻⁴
0.00030 ^c	60.2	4.94(6) × 10 ⁻⁴
0.012 ^d	22	5.0(8) × 10 ⁻⁶
0.037 ^d	22	4.8(10) × 10 ⁻⁶
0.034 ^{d,e}	22	5.0(4) × 10 ⁻⁶
0.034 ^{d,f}	22	4.5(2) × 10 ⁻⁶

^a Errors are listed at the 95% confidence level, $k \pm \sigma$. Rate measurements by UV-vis unless otherwise noted. ^b (dcpe)Ni(Ph)(SD) used. ^c NaOH (s) added. ^d Rate measurements by NMR spectroscopy. ^e 0.34 M **6** added. ^f 1.0 M **6** added.

The formation of dimer **2** from **1** presumably proceeds by way of the terminal sulfido complex **A**. The kinetics of eq 1 was examined to establish the order of the reaction. Thermolysis of solutions of **1b** in THF to form **2b** was examined in the concentration range 3–37 mM and 22–65 °C. The disappearance of **1b** was found to follow first-order kinetics for 3–5 half-lives (Table 1). Added base (NaOH) had no effect upon the observed rate constant. The monodeuterated complex (dcpe)Ni(Ph)(SD) reacted more slowly than its protio analogue, with $k_H/k_D = 1.44$ at 60 °C. An Eyring plot of the rate data determined over a 43 °C range provides activation parameters of $\Delta H^\ddagger = 23.1 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = -4.2 \pm 2.5$ eu. These results are consistent with a unimolecular rate determining step involving the loss of benzene and formation of a terminal sulfido intermediate.

Attempts at trapping the terminal sulfido with traditional reagents such as olefins or nitriles failed, but this could be due to the instability of the resulting metallacycles. To test this hypothesis, we attempted to prepare a four-membered thia-metallacycle containing the bisphosphine ligand systems. Reaction of [(dippe)NiH]₂ with cyclohexene sulfide did not lead to the resulting metallacycle but instead to loss of alkene and formation of sulfur bridged dimers **2** and **3**^{10b} (eq 2). Similar reactivity has

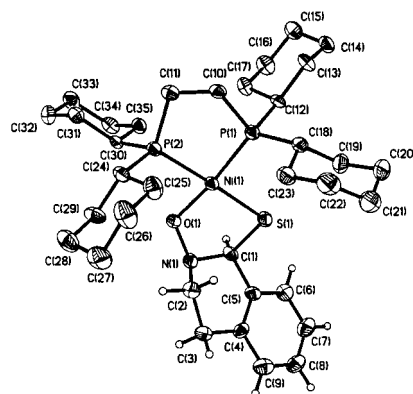
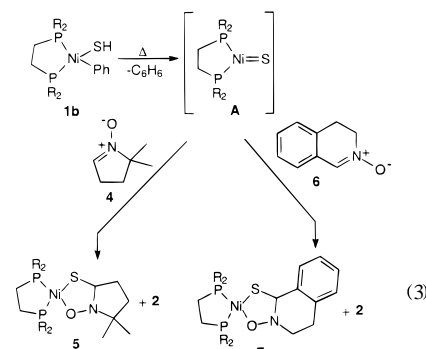


been seen by Hillhouse with (bipy)Ni(COD) and ethylene sulfide, where at 20 °C the majority of the nickel is precipitated as nickel sulfide with release of ethylene as the organic product.^{9a}

Nitrone traps are known to be effective for thioketones¹⁷ and proved to be efficient traps of the nickel sulfido **A** as well. 5,5'-Dimethyl-1-pyrroline *N*-oxide (**4**) reacted with **1b** to form a new, asymmetric product (**5**) as determined by ³¹P{¹H} NMR spectroscopy (eq 3).¹⁸ Importantly, the rate of disappearance of **1b** was found to be independent of the presence of nitron trap or its concentration, a result consistent with a nonassociative reaction. Furthermore, the trapping reaction with nitron was found to be competitive with the dimerization process, for the product distribution was found to depend on nitron concentration. Reaction of **1b** with a 0.34 M THF solution of **4** afforded products

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(18) ³¹P{¹H} NMR (THF-*d*₆): δ 80.37 (d, $J = 30.5$ Hz), 70.61 (d, $J = 30.5$ Hz).

**Figure 1.** ORTEP drawing of **7**. Ellipsoids shown at 30% probability level. Hydrogen atoms on the phosphine ligand are omitted for clarity.

2b and **5** in a 5:1 ratio, whereas reaction with a 1 M solution of **4** afforded the same products in a 1:1 ratio. These observations are consistent with a rate-determining step for the formation of **A**, followed by a competition between dimerization or reaction with the nitron trap.¹⁹ The relatively low yields obtained for **5** along with similarities in solubility of **4**, **5**, and **2b** prevented the structural characterization of the nitron adduct. However, reaction of **1b** with 20 equiv (0.025 M) of the more reactive nitron, 3,4-dihydroisoquinoline *N*-oxide (**6**),^{20,21} afforded the trapped sulfido product **7** in much higher yields (17:1 ratio of **7** to **2b**). The ³¹P{¹H} NMR spectrum of **7** is almost identical to that of **5** (THF-*d*₆, δ 79.77 (d, $J = 30.9$ Hz), 74.50 (d, $J = 30.9$ Hz)), and the higher yields permitted the isolation of X-ray quality crystals. An ORTEP drawing of the single-crystal X-ray structure of **7** is shown in Figure 1, and confirms the mode of addition as a formal 1,3-dipolar cycloaddition.²²

In summary, we have provided both kinetic and structural evidence that supports the existence of a late-metal terminal sulfido complex. The chemical feasibility of such an intermediate may have important mechanistic implications in homogeneous and heterogeneous desulfurization reactions, as well as in the reaction chemistry of sulfided clusters in general.

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Supporting Information Available: A listing of experimental procedures, plots of kinetic data, and tables of data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(19) Alternatively, **A** could react with **1b** to generate **2b**, although this pathway is more complicated than a simple dimerization of transient **A** as loss of a second molecule of benzene by a different mechanism must be involved.

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(22) In control experiments, the sulfido dimers **2** do not react with **4** or **6** at room temperature to yield any observable products by NMR spectroscopy.