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Mechanistic Insights on the Hydrodesulfurization of Biphenyl-2-thiol with Nickel Compounds

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Abstract: The reactivity of the nickel(I) dimer $[(\text{dippe})\text{Ni}(\mu\text{-H})]_2$ (**1**) with biphenyl-2-thiol was explored with the aim of clarifying the key step of sulfur extrusion during the hydrodesulfurization process using dibenzothiophene (DBT). These reactions were monitored by variable temperature NMR experiments which allowed the complete characterization and isolation of $[(\text{dippe})_2\text{Ni}_2(\mu\text{-H})(\mu\text{-}S\text{-2-biphenyl})]$ (**3**). The latter compound evolves to the terminal nickel-hydride $[(\text{dippe})\text{Ni}\ (\eta^1\text{-}C\text{-2-biphenyl})(\text{H})]$ (**4**) and transient [(dippe)NiS] (**5**), to ultimately yield $[(\text{dippe})_2\text{Ni}_2(\mu\text{-S})]$ (**2**) and biphenyl as the resulting HDS products. The reactivity of **1** and biphenyl-2-thiol was examined using different ratios of reactants, which allowed preparation of $[(\text{dippe})\text{Ni}(\eta^1\text{-}S\text{-biphenyl-2-thiolate})_2]$ (**6**) when using an excess of this substrate. The reactivity of **6** with **1** was addressed, yielding compound **2** and an equivalent amount of biphenyl.

Introduction

The removal of sulfur from petroleum and other fossil feedstocks is extremely relevant worldwide given the necessity to decrease the atmospheric pollution caused by emission of sulfur oxides as a result of internal combustion processes.[1] The industrial process used to remove sulfur-containing compounds is known as catalytic *hydrodesulfurization*, or HDS, and typically uses heterogeneous cobalt or nickel-doped molybdenum sulfide catalysts supported over alumina to do so.[2] The latter catalysts, however, oftentimes face severe difficulties in the removal of alkyl dibenzothiophene (DBT) derivatives, such as 4-methyldibenzothiophene (4-MeDBT) and 4,6-dimethyldibenzothiophene (4,6-Me_2DBT) from the fossil feedstock, substantially reducing the efficacy of the process, the latter compounds being the major residual organosulfur components present in the feedstock.[3]

Numerous mechanistic proposals addressing the HDS of DBT have been reported with the aim of understanding the elementary steps involved, and in doing so improve the efficiency of the catalysts.[1−3] The proposals normally suggest two main reaction routes based on experimental[4] and theoretical[5] observations, the first of which considers hydrogenation of an aromatic ring prior to the C−S bond cleavage of the thiophenic ring, yielding a cyclohexyl-benzene derivative, whereas the second (known as direct desulfurization) proposes the cleavage of a C−S bond to occur first as a result of hydrogenolysis or by elimination through a dihydro-DBT intermediate,[6] leading in both cases to the formation of biphenyl-2-thiol. The latter product is subsequently desulfurized to produce biphenyl as the sulfur-free product. Of note, the step by which sulfur is extruded in the HDS reaction is not yet fully understood, and thus a *direct extrusion* has often been invoked to justify the formation of H_2S as the final fate of sulfur (Scheme 1).[3a,4,5] Some reports of desulfurization of DBT and aromatic thiols by polymetallic complexes have appeared but have only furnished a few mechanistic details.[7]

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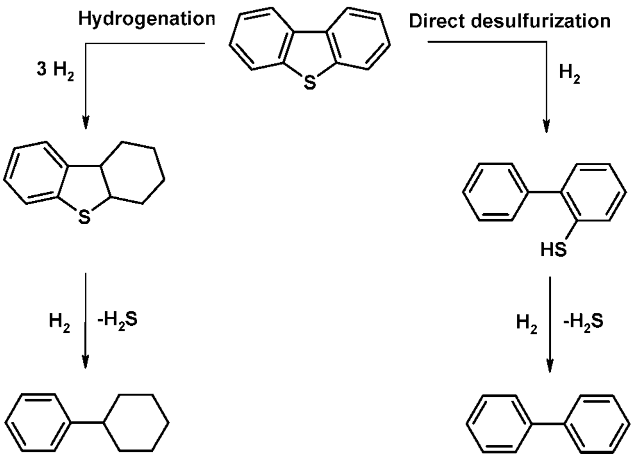
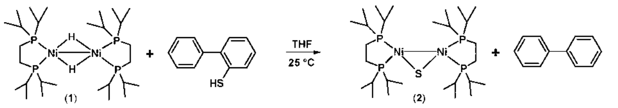
Scheme 1. Routes for the Hydrogenation and Direct Desulfurization of DBT during HDS



With the aim of contributing to the understanding of the above-mentioned extrusion step, we present herein our findings regarding the reactivity of biphenyl-2-thiol in the presence of $[(\text{dippe})\text{Ni}(\mu\text{-H})]_2$ (**1**). In these studies, the facile cleavage of the C−S bond under mild conditions is investigated using VT-NMR experiments as well as isolation of key intermediates, allowing for a better understanding of the sulfur extrusion step and giving insightful information concerning the overall HDS process of DBT.

Results and Discussion

Reactivity of $[(\text{dippe})\text{NiH}]_2$ (1) with Biphenyl-2-thiol. Equimolecular Reaction. Reaction of **1** with biphenyl-2-thiol in (1:1) ratio at room temperature yielded the compound $[(\text{dippe})_2\text{Ni}_2(\mu\text{-S})]$ (**2**) and free biphenyl, showing that the C−S bond cleavage of biphenyl-2-thiol proceeds under very mild conditions. The $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of **2** confirmed a fluxional behavior for this compound with a coalescence temperature of 25 °C ($\Delta G^{\ddagger} = 22.59$ kcal/mol, Figure S3, Supporting Information). Upon cooling to −20 °C, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this compound in THF-d_8 solution displayed two triplets centered at δ 71.38 and 75.13, with $^2J_{\text{P-P}}$ of 23 Hz, consistent with previously reported data for this unusual Ni(I) compound (eq 1).[8]

 (1)

Sequential VT NMR spectra (^{1}H and ^{31}P) in the interval of −80 to 60 °C were recorded for the addition of 1 equiv of biphenyl-2-thiol to **1** in THF-d_8 (Figure 1). The formation of a major compound at −80 °C was observed, as evidenced by the appearance of a broad singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum centered at δ 68.66 and a simultaneous appearance of a quintet in the hydride region of the ^{1}H NMR spectrum (δ −15.86, $^2J_{\text{P-H}} = 17.2$ Hz). The latter quintet is indicative of a hydride coupled to four phosphorus atoms in the same chemical environment. This species was proposed to be $[(\text{dippe})_2\text{Ni}_2(\mu\text{-H})(\mu\text{-}S\text{-2-biphenyl})]$ (**3**), and could be isolated by crystallization at low temperature. A single crystal X-ray structure confirmed this assignment (Figure 2). A summary of the crystallographic details is presented in Table 1.

Compound **3** can be envisaged as a model for an intermediate during the industrial HDS processes, many of which often use nickel as a promoting metal.[2,3,9] In particular, it depicts a bridging hydride as well as a bridging biphenyl-2-thiolate in between two Ni centers (Ni−Ni bond distance, 2.5124(4) Å). The nickel atoms exhibit different geometries, with Ni(1) being described as displaying a distorted square planar coordination of its surrounding ligands, while Ni(2) exhibits a distorted tetrahedral geometry. In light of this structure, it is proposed that the different geometries around each nickel center promote the fluxional behavior in solution, such that only a singlet is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The latter features (asymmetry around the nickel centers and in the bridging moieties) are rare, and although structures that contain two bridging biphenyl-2-thiolate moieties between metal centers have been reported in the past,[10] to the best of our knowledge only in one other case has the presence of a bridging biphenyl-2-thiolate and a hydride been reported.[11]

Additional analysis of the ^{1}H VT-NMR spectra (Figure 1) provided evidence for the presence of a nickel hydride centered at δ −10.443 (*dd*, $^2J_{\text{P-H}} = 81.0$ Hz) when the solution was cooled to −80 °C. The appearance of the hydride signal was accompanied by the simultaneous appearance of two broad singlets at δ 73.48 and 75.61 in the $^{31}\text{P}\{^1\text{H}\}$ VT-NMR spectrum at the same temperature, and were attributed to the formation of a terminal nickel(II) hydride with formula, $[(\text{dippe})\text{Ni}(\eta^1\text{-}C\text{-2-biphenyl})(\text{H})]$ (**4**), based on similar observations made when expressly preparing compounds of this type.[12] Conversion of **3** into the terminal hydride compound **4** was observed in the VT-NMR experiments while gradually increasing the temperature. The evolution of the latter compound into compound **2** and free biphenyl was also observed in the same experiment as the temperature was increased to 60 °C, suggesting compounds **3** and **4** to be consecutive intermediates of the HDS process. Scheme 2 illustrates these conclusions.

The formation of compound **3** is proposed to occur in the first step of the reaction, which involves the net elimination of molecular hydrogen from the bridging nickel(I) dimer and addition of the S−H to the bimetallic system, the details of which are not known. A cooperative effect between the metals in the different coordination geometries exhibited in **3** (*vide supra*) could be implicated after this step, as stripping of the biphenyl moiety from the sulfur atom is accompanied by cleavage of the dimer, which results in 1e oxidation of the two nickel(I) centers generating both the terminal hydride compound **4** and a nickel sulfide, $[(\text{dippe})\text{Ni}{=}\text{S}]$ (**5**). Formation of this sulfide has been reported previously by our group in closely related desulfurization experiments and is known to undergo rapid association to yield new bridged compounds.[13] Reductive elimination of biphenyl from compound **4** provides a clear rationale for the formation of free biphenyl and a highly reactive

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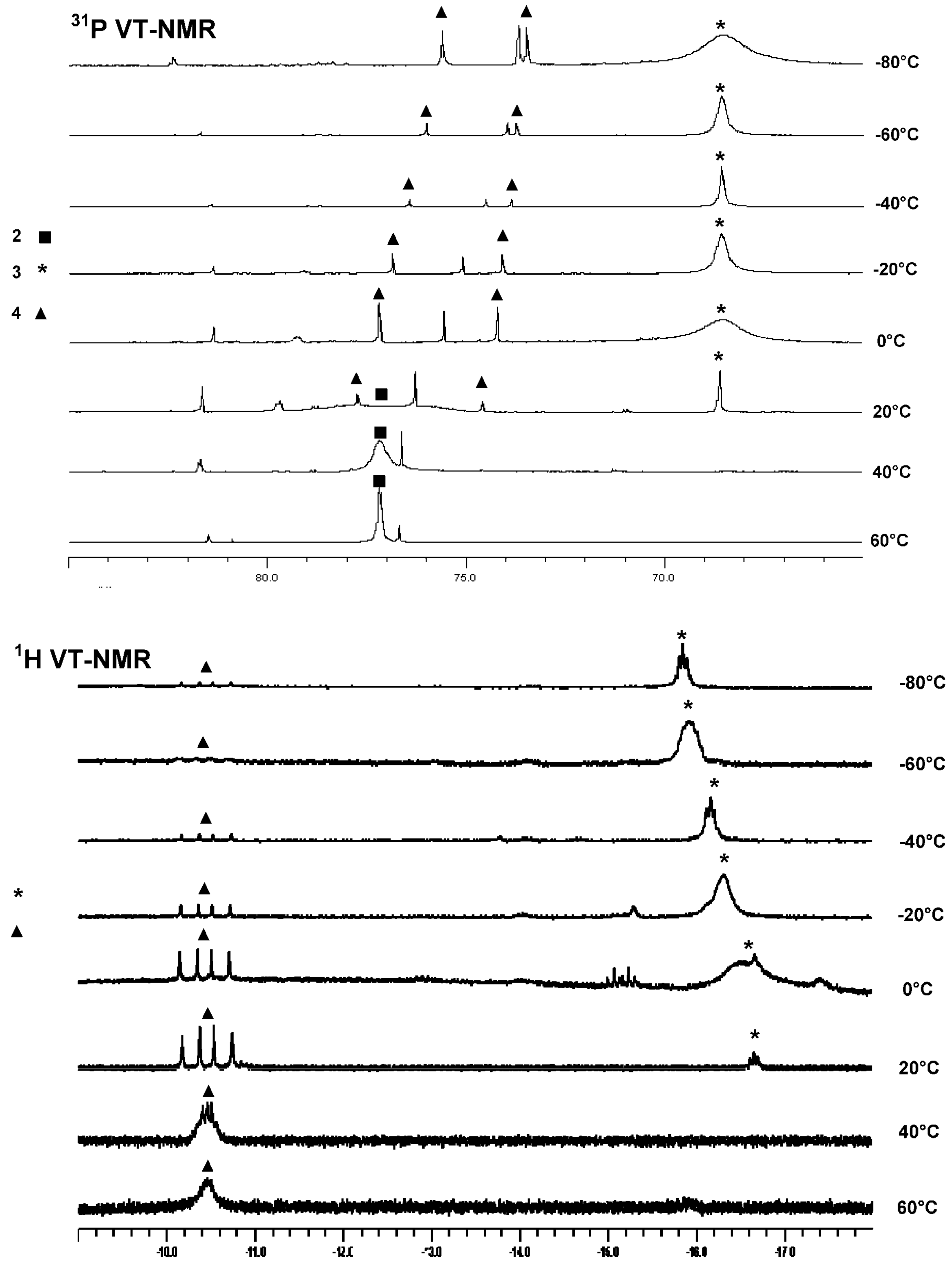


Figure 1. $^{31}P\{^1H\}$ and ^1H VT-NMR experiments in THF-d_8 of the equimolecular reaction of **1** with biphenyl-2-thiol.

14e [(dippe)Ni^0] fragment from which the sulfide [$(dippe)_2Ni_2(\mu$-S)], **2**, is ultimately produced. The latter nickel(I) dinuclear compound acts as the final fate of sulfur in this reaction scheme[3a] and is consistent with the general mechanism for the hydrogenolysis of biphenyl-2-thiol on the industrial scale, as illustrated in Scheme 1. These observations inherently provide direct evidence for the role that nickel may play in the heterogeneous catalyst surface as a dopant, by allowing bimetallic interactions with HDS metals in order to promote desulfurization of the thiols present in the fossil feedstock.

Reactivity of [(dippe)NiH]$_2$ (1) and 2 equiv of Biphenyl-2-thiol. Exploration of reactivity using compound **1** and 2 equiv of biphenyl-2-thiol at room temperature was undertaken in the aim of studying the effect that a larger amount of this substrate would have on the outcome of the HDS reaction. Formation of **2** was observed in this reaction as

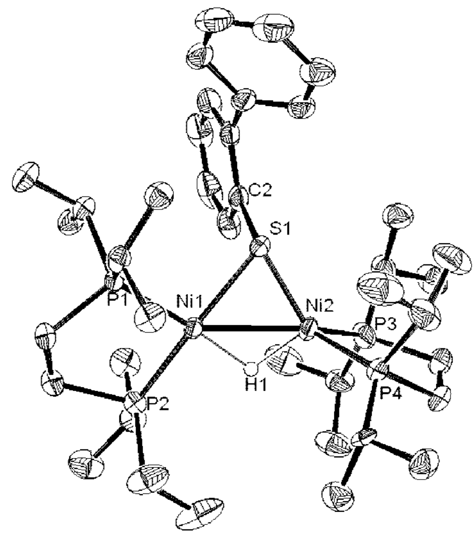
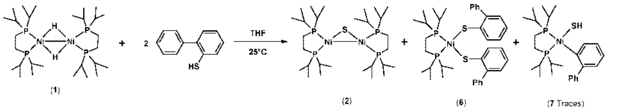


Figure 2. ORTEP representation of **3**. The location of hydride H1 was determined by isotropic refinement. Ellipsoids are shown at the 50% probability level. Selected bond distances (Å): Ni(1)−Ni(2) 2.5124(4); Ni(1)−H(1) 1.63(3); Ni(2)−H(1) 1.52(3); Ni(1)−S(1) 2.2687(6); Ni(2)−S(1) 2.1443(6); Ni(1)−P(1) 2.1736(6); Ni(1)−P(2) 2.1434(6); Ni(2)−P(3) 2.1444(7); Ni(2)−P(4) 2.1448(7). Selected bond angles (°): P(1)−Ni(1)−S(1) 94.50(2); S(1)−Ni(1)−H(1) 88.4(10); H(1)−Ni(1)−P(2) 87.2(10); P(2)−Ni(1)−P(1) 91.01(2); S(1)−Ni(2)−P(3) 126.02(3); S(1)−Ni(2)−H(1) 96.2(11); P(4)−Ni(2)−H(1) 111.9(11); P(3)−Ni(2)−H(1) 111.7(11); Ni(2)−Ni(1)−H(1) 35.6(10).

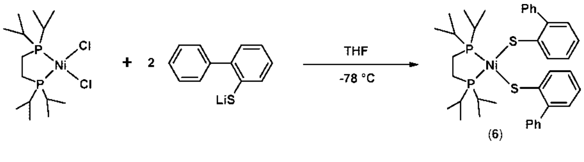
expected, although to our surprise, the appearance of two additional byproducts (compounds **6** and **7**) was also observed (eq 2). No change in the distribution of products was observed even after prolonged heating at 100 °C for 5 d (**2** (45%), **6** (54%), and **7** (1%)).



(2)

Compound **6** was formulated as a monometallic product containing two biphenyl-2-thiolate moieties coordinated to a nickel(II) center, displaying a singlet in the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture (THF-d_8, δ 78.39). **7** was detected as a trace byproduct, which gave rise to two doublets with $^2J_{P-P} = 39.4$ Hz centered at δ 69.11 and 78.56 in the same spectrum. The magnitude of the coupling constants of the two phosphorus environments in **7** was consistent with that of a Ni(II) complex and was assigned to [(dippe)Ni(SH)(η^1-biphenyl)] (**7**), the C−S oxidative addition product. Compound **7** gave rise to a broad signal in the ^1H NMR spectrum of the mixture located at δ −1.03, and this was assigned in turn to the sulfhydryl group attached to the nickel(II) center.

In the aim of providing proof for the formulation of compound **6**, independent preparation was accomplished by reacting lithium biphenyl-2-thiolate (LiS-biphenyl) with [(dippe)NiCl$_2$], at −78 °C. This reaction resulted in the formation of a red solid which displayed a singlet at δ 78.39 in the $^{31}P\{^1H\}$ NMR spectrum (THF-d_8 solution, eq 3).



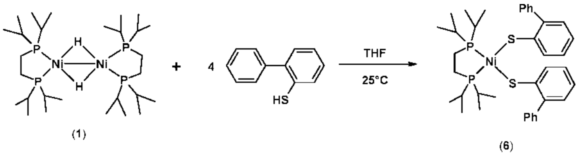
(3)

Single crystals suitable for X-ray structure determination were grown from a THF solution at room temperature. Figure 3 shows the ORTEP representation of this compound, exhibiting a square planar geometry around the nickel(II) center. Crystallographic details related to this determination are presented in Table 1.

The reaction of **1** with 2 equiv of biphenyl-2-thiol was also followed by $^{31}P\{^1H\}$ and ^1H VT-NMR, as described above for the equimolecular reaction, going from −80 to 60 °C. Figure 4 shows the progressive change in the signals in the $^{31}P\{^1H\}$ VT-NMR spectra.

Formation of compound **6** was detected as the first process, indicated by the appearance of a singlet at δ 78.39 in the $^{31}P\{^1H\}$ NMR spectrum at the low temperature limit of −80 °C. On raising the temperature to −20 °C, the growth of a new singlet at δ 68.66 for **3** was observed, accompanied by the simultaneous appearance of a hydride signal in the ^1H NMR spectrum at δ −15.865. The conversion of **6** into the S−H oxidative addition compound **3** suggests that the HDS route proposed for the equimolecular system is the natural end-route of the HDS process. The fact that this should take place (i.e., the conversion of **6** into **3**) was interpreted as an indication of the overall reactivity that **6** may exhibit in the presence of trace hydride compounds in the reaction mixture. Therefore, the reactivity of **6** with **1** was examined. Scheme 3 shows that formation of **2** and biphenyl is observed, suggesting compound **3** to be an intermediate in the reaction of the hydride dimer with the bis-thiolate precursor, again an indication of the bimetallic character that these nickel-mediated transformations have.

Reactivity of [(dippe)NiH]$_2$ (1) in the Presence of 4 equiv of Biphenyl-2-thiol. Following our previous discussion on the reactivity of compound **1** in the presence of excess biphenyl-2-thiol, 1 equiv of **1** was reacted in the presence of 4 equiv of the latter substrate. The selective formation of **6** was observed by NMR spectroscopy (eq 4), consistent with the prior observation while using a 1:2 ratio and suggested the formation of the bis-thiolate to be the initial step of reactivity preceding HDS as discussed above.



(4)

To note, the model reactions presented here include a metal coordinated to soft phosphorus and sulfur atoms. The best evidence for the interaction of a substrate with MoS$_2$ have been provided by STM studies by Lauritsen et al.,[14] in which they show that an edge vacancy is created by sulfur removal. This geometry places the metal between two "soft" sulfur donors, very similar to our model compounds.

Conclusions

The current work provides insight into the HDS reaction of biphenyl-2-thiol. Biphenyl-2-thiol is proposed as an organic intermediate formed during the HDS of DBT and precedes the

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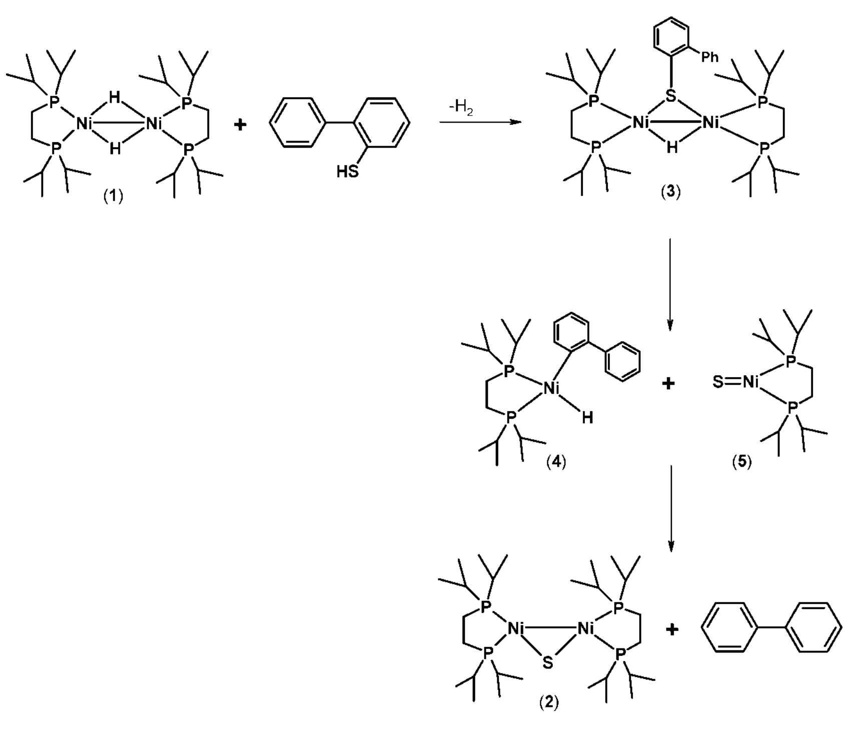
Table 1. Summary of Crystallographic Data for Compounds **3** and **6**

	3	6
empirical formula	$C_{40}H_{74}Ni_2P_4S$	$C_{38}H_{50}NiP_2S_2$
formula weight	828.35	691.55
temperature (K)	100.0(1)	105.0(1)
wavelength (Å)	0.71073	0.71073
crystal system	monoclinic	orthorhombic
space group	$P2_1/c$	$Fdd2$
unit cell dimensions	$a = 22.369(3)$ Å	$a = 30.896(4)$ Å
	$b = 10.9191(15)$ Å	$b = 50.891(7)$ Å
	$c = 19.087(3)$ Å	$c = 9.0942(13)$ Å
	$\beta = 110.827(2)°$	$\beta = 90°$
volume (Å^3)	4357.4(10)	14299(3)
Z	4	16
density (calcd) (gcm^{-3})	1.263	1.285
μ (mm^{-1})	1.085	0.775
F(000)	1784	5888
crystal color	black	red
crystal size (mm^3)	0.26 × 0.24 × 0.20	0.16 × 0.16 × 0.06
θ range (deg)	1.95−32.57	2.07−32.58
no. reflns collected	77743	47236
no. independent reflns	15799 [R(int) = 0.0608]	12856 [R(int) = 0.0837]
observed reflns	10710	9768
absorption correction	multiscan	multiscan
max and min transmission	0.8122 and 0.7657	0.9550 and 0.8861
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	15799/8/468	12856/1/396
GOF on F^2	1.020	1.012
final R indices [$I > 2\sigma(I)$]	R1 = 0.0447, wR2 = 0.0931	R1 = 0.0471, wR2 = 0.0768
R índices (all data)	R1 = 0.0791, wR2 = 0.1079	R1 = 0.0758, wR2 = 0.0863

Scheme 2. Reaction Scheme for the HDS Process Undertaken over Biphenyl-2-thiol Using **1**.



extrusion step by which hydrogen sulfide is produced while undergoing hydrogenolysis. Nickel is commonly used as a dopant in the MoS_2 catalyst for this process, and as encountered in this work, formation of an asymmetric compound with distinct coordination geometries, namely [(dippe)Ni(μ-H)(μ-*S*-2-biphenyl)] (**3**), may suggest that bimetallic assistance of metal centers during HDS could be involved in the ultimate success of the process. Compound **3** plays a key role for this matter. The scission of this compound into monomeric entities then drives the extrusion of sulfur from the thiol and results in the formation of [(dippe)$_2$Ni$_2$(μ-S)] (**2**) and free biphenyl as the final HDS products.

Experimental Section

All manipulations were carried out using standard Schlenk and glovebox techniques under argon (Praxair 99.998). THF and benzene (Aldrich) were dried and distilled from dark-purple solutions of sodium/benzophenone ketyl. Toluene (Aldrich) was

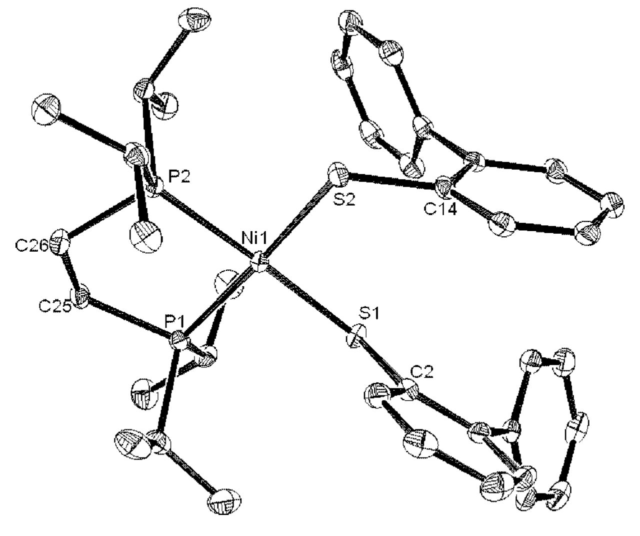


Figure 3. ORTEP representation of **6**. Ellipsoids are shown at the 50% probability level. Selected bond distances (Å): Ni(1)−P(1) 2.1728(7); Ni(1)−P(2) 2.1831(7); Ni(1)−S(1) 2.2298(7); Ni(1)−S(2) 2.2252(7). Selected bond angles (deg): P(1)−Ni(1)−S(2) 174.84(3); P(2)−Ni(1)−S(1) 172.58(3); P(1)−Ni(1)−S(1) 86.06(3); P(2)−Ni(1)−S(2) 87.46(3); P(1)−Ni(1)−P(2) 88.60(3); S(1)−Ni(1)−S(2) 98.16(3).

dried and distilled from sodium. Deuterated solvents were dried and distilled before use from sodium/benzophenone ketyl. ^{1}H and ^{31}P{^{1}H} NMR spectra were acquired on an AVANCE400 spectrometer in THF-d_8 unless otherwise stated. Chemical shifts (δ, ppm) in the ^{1}H NMR spectra are reported relative to the residual proton signals of the deuterated solvent, and ^{31}P{^{1}H} NMR spectra are relative to external 85% H_3PO_4. Biphenyl-2-thiol was obtained from John C. DiCesare, Department of Chemistry, University of Tulsa, Tulsa, Oklahoma, and was used without further purification. *n*-Butyllithium was purchased from Aldrich. The syntheses of [(dippe)$NiCl_2$][15] and [(dippe)NiH]$_2$[8] were carried out following the reported procedures.

Equimolecular Reaction of 1 with Biphenyl-2-thiol at Room Temperature, Selective Preparation of [(dippe)$_2$Ni$_2$(μ-S)] (2). A THF-d_8 solution of compound **1** (0.050 g, 0.077 mmol) was prepared in the glovebox, and to it was added biphenyl-2-thiol (0.0143 g, 0.077 mmol) at room temperature. The color of the solution immediately changed from wine-red to dark-brown. All H_2 gas produced from reaction was vented to the glovebox for a period of 5 min, during which evolution of gas ceased completely and the remaining reaction mixture was transferred to a NMR tube equipped with J-Young valve. Analysis of the NMR spectra indicated the formation of **2** as the sole product. ^{1}H NMR (400 MHz, THF-d_8, −20 °C): δ 1.016−1.250 (m, 48H, CH_3 of the isopropyl group), 1.466 (br, 4H, CH_2CH_2 of dippe), 1.637 (d, $^2J_{H-P}$ = 8.0 Hz, 4H, CH_2CH_2 of dippe), 2.097 (br, 4H, CH of the isopropyl group), 2.184 (m, 4H, C−H of the isopropyl group). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8, −20 °C): δ 71.39 (t, J_{P-P} = 23.0 Hz), 75.13 (t, J_{P-P} = 23.0 Hz). Anal. Calcd (found) for $C_{28}H_{64}Ni_2P_4S$: 50.73 (49.89) C, 9.57 (9.97) H.

VT-NMR Experiments of the Reaction of 1 with Biphenyl-2-thiol. Compound **1** (0.050 g, 0.077 mmol) was dissolved in THF-d_8 in an NMR tube, and the solution was cooled to 78 °C in a dry ice/acetone bath for a period of 10 min. Biphenyl-2-thiol (0.0143 g, 0.077 mmol) was slowly added at low temperature. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded every 20 °C as the reaction mixture was warmed from −80 to 60 °C in the NMR probe.

Preparation of [(dippe)$_2$Ni$_2$(μ-H)(μ-S-2-biphenyl)] (3). A THF-d_8 solution of **1** (0.050 g, 0.077 mmol) was prepared and cooled to −78 °C following the procedure described above and biphenyl-2-thiol (0.0143 g, 0.077 mmol) then added. The color of the solution immediately changed from wine-red to green. ^{1}H and ^{31}P{^{1}H} NMR spectra were immediately determined at −80 °C as compound **3** decomposes rapidly. ^{1}H NMR (400 MHz, THF-d_8, −80 °C): δ −15.865 (quint, $^2J_{H-P}$ = 17.2 Hz, 1H, Ni−H), 0.870−1.236 (br, 48H, CH_3 of the isopropyl group), 1.471 (br, 8H, CH_2CH_2 of dippe), 1.922 (m, 8H, CH of the isopropyl group), 6.778 (bs, 1H), 6.851 (bs, 1H), 7.203 (d, $^3J_{H-H}$ = 6.0 Hz, 2H), 7.283 (m, 2H), 7.722 (d, $^3J_{H-H}$ = 6.0 Hz, 2H), 7.931 (bs, 1H). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8, −80 °C): δ 68.66 (bs).

Reaction of 1 with 4 equiv of Biphenyl-2-thiol at Room Temperature; Selective Preparation of [(dippe)Ni(η^1-S-biphenyl-2-thiolate)$_2$] (6). A THF-d_8 solution of **1** (0.050 g, 0.077 mmol) was prepared at room temperature as described above and biphenyl-2-thiol (0.0572 g, 0.310 mmol) added. The color of the solution immediately changed from wine-red to red and a red precipitate was produced. Analysis of the NMR spectra of the mixture showed **6** to be the sole product. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 1.09−1.291 (m, 12H, CH_3 of the isopropyl group), 1.616 (d, $^2J_{H-P}$ = 11.2 Hz, 4H, CH_2CH_2 of dippe), 2.271 (m, 4H, CH of the isopropyl group), 6.711 (m, 1H), 6.804 (d, $^3J_{H-H}$ = 3.6 Hz, 2H), 7.068 (t, $^3J_{H-H}$ 7.0 Hz, 1H), 7.142 (t, $^3J_{H-H}$ = 7.4 Hz, 2H), 7.225

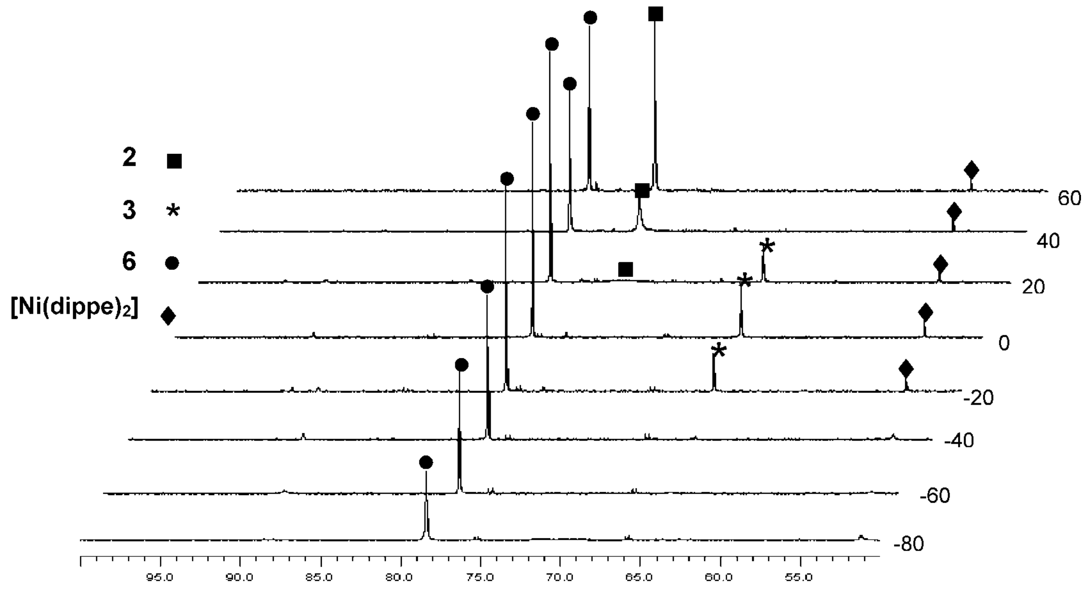
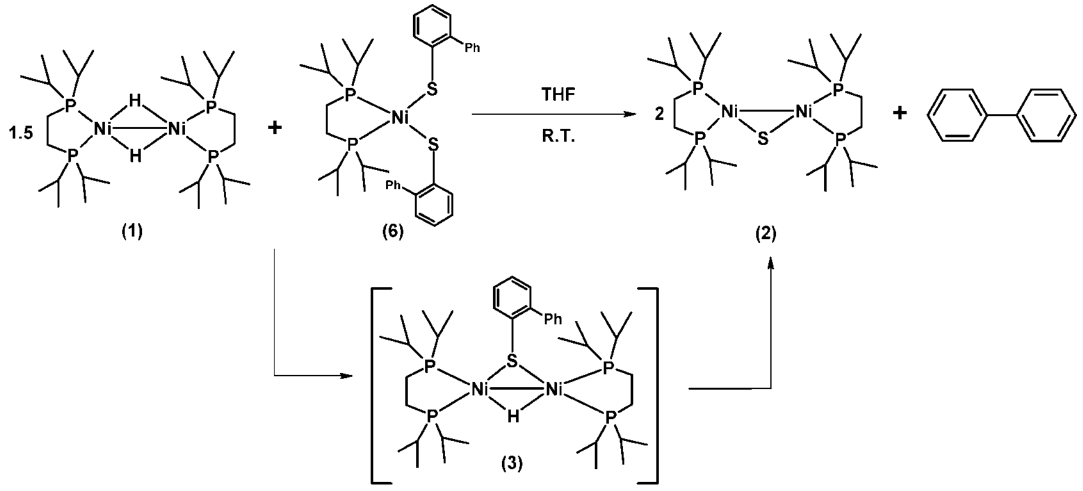


Figure 4. ^{31}P{^{1}H} VT-NMR follow-up of the reaction **1** with 2 equiv of biphenyl-2-thiol, dissolved in THF-d_8.

Scheme 3. Reactivity of **6** in the Presence of **1**, at Room Temperature



(d, $^{3}J_{\mathrm{H-H}} = 7.2$ Hz, 2H), 7.875 (d, $^{3}J_{\mathrm{H-H}} = 7.6$ Hz, 1H). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8, 25 °C): δ 78.39 (s).

Independent Preparation of [(dippe)Ni(η^1-S-biphenyl-2-thiolate)$_2$] (6). A 50 mL Schlenk flask was charged with biphenyl-2-thiol (0.0286 g, 0.154 mmol) and dissolved in THF (10 mL). The solution was cooled to −78 °C in a dry ice/acetone bath and *n*-butyllithium (1.6 M, 0.115 mL) was slowly added under constant stirring over a period of 5 min. A suspension of [(dippe)NiCl$_2$] (0.030 g, 0.0766 mmol) in THF (10 mL) was also added slowly to the mixture and then allowed to warm to room temperature. The color of the solution changed from orange to red after a period of 15 min. The solution was stirred for 30 min and filtered through a frit charged with neutral alumina. The solvent was removed *in vacuo* from the filtrate, leaving a solid red residue which was redissolved in a small amount of THF and stored in a freezer at −30 °C, yielding single crystals suitable for X-ray diffraction studies. ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ 1.09−1.291 (m, 12H, CH$_3$ of the isopropyl group), 1.616 (d, $^{2}J_{\mathrm{H-P}}$ =11.2 Hz, 4H, CH$_2$CH$_2$ of dippe), 2.271 (m, 4H, CH of the isopropyl group), 6.711 (m, 1H), 6.804 (d, $^{3}J_{\mathrm{H-H}} = 3.6$ Hz, 2H), 7.068 (t, $^{3}J_{\mathrm{H-H}} = 7.0$ Hz, 1H), 7.142 (t, $^{3}J_{\mathrm{H-H}} = 7.4$ Hz, 2H), 7.225 (d, $^{3}J_{\mathrm{H-H}} = 7.2$ Hz, 2H), 7.875 (d, $^{3}J_{\mathrm{H-H}} = 7.6$ Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 25 °C) 145.82 (s), 145.61 (s), 145.28 (s), 138.40 (s), 131.40 (s), 129.48 (s), 127.54 (s), 126.20 (s), 126.03 (s), 122.69 (s), 26.79 (t, $^{1}J_{\mathrm{C-P}} = 13$ Hz), 20.31 (s), 18.97 (s). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8, 25 °C): δ 78.39 (s). Anal. Calcd (found) for $C_{38}H_{50}NiP_2S_2$: 65.99 (64.55) C, 7.28 (7.33) H. E.I. = *m*/*z* 690.

Crystal Structure Determinations. A single crystal was placed onto the tip of a 0.1 mm diameter glass fiber in each structure determination and then mounted on a Bruker SMART APEX II CCD Platform diffractometer for data collection. The latter was performed at 100.0(1) K in the case of **3** and 105.0(1) K in the case of **6**.[16] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal sets of 20 frames. The data collections were carried out using Mo Kα radiation (graphite monochromator) with frame times of 30 s for **3** and 90 s for **6** and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed, and four major sections of frames were collected with 0.50° steps in ω at four different ϕ settings and a detector position of −33° in 2θ. The intensity data were corrected for absorption.[17] Final cell constants were calculated from the *xyz* centroids of a sampling of strong reflections from the actual data collection after integration.[18] Each structure was solved using SIR97[19] and refined using SHELXL-97.[20] The space groups $P2_1/c$ for **3** and *Fdd*2 for **6** were determined on the basis of systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The bridging hydride atom in **3** was found from the difference Fourier map and refined independently from all atoms with an individual isotropic displacement parameter. The final full matrix least-squares refinement converged to R1 values of 0.0447 for **3** and 0.0471 for **6** (F^2, $I > 2\sigma(I)$) and wR2 values of 0.1079 for **3** and 0.0863 for **6** (F^2, all data).

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Supporting Information Available: Selected NMR spectra for **2**, **3**, and **6**; VT-NMR spectra of **2**; crystallographic data and cif files of compounds **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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