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# Room-Temperature Desulfurization of Dibenzothiophene Mediated by $[(i\text{-Pr})_2\text{PCH}_2)_2\text{NiH}]_2$

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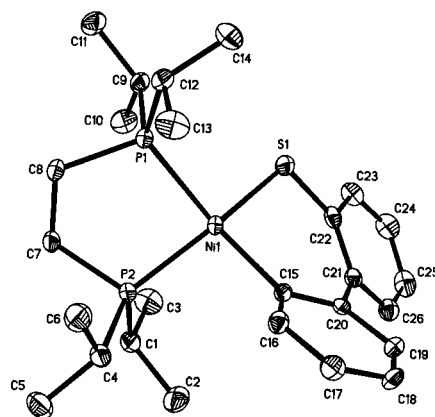
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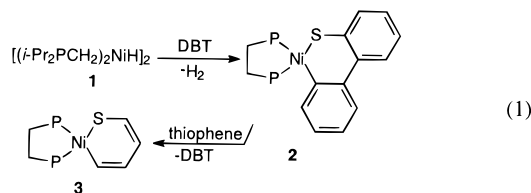
Nickel, due to its inexpensive nature, is a highly practical catalyst for numerous chemical transformations.<sup>1</sup> Nickel is also currently used as a promoter in the heterogeneous process of hydrodesulfurization (HDS).<sup>2</sup> A detailed understanding of the reactivity of the catalyst with dibenzothiophenes (DBTs) is crucial to the optimization of HDS technology, as these substrates are among the most difficult to remove in the hydroprocessing of crude oil.<sup>3</sup> In homogeneous models, organometallic nickel complexes in conjunction with added hydride reagents have been shown to desulfurize a variety of DBTs affording the corresponding biphenyls as the organic products.<sup>4</sup> Although these reactions proceed quite efficiently, the use of external hydride sources makes these reactions unsuitable for use at the industrial level. Furthermore, there has been no structural characterization of the organometallic fragments produced upon sulfur extrusion, leaving pertinent mechanistic information relevant to the desulfurization process at nickel unresolved. In attempts to obtain such information, we embarked on synthesizing an organometallic nickel complex which could activate the C–S bond of DBT. To our surprise, *this complex was able to mediate activation of both C–S bonds of DBT at room temperature, yielding novel organometallic compounds which have been structurally characterized.*

Recently, a platinum bisphosphine complex was found to be capable of insertion into one C–S bond of DBT.<sup>5</sup> This result, coupled with the general success of polynuclear complexes in the desulfurization of various thiophenes,<sup>6</sup> led us to prepare a dinuclear nickel phosphine complex.  $[(\text{dippe})\text{NiH}]_2$  (**1**) [dippe =  $(i\text{-Pr}_2\text{PCH}_2)_2$ ] was synthesized in a procedure similarly used to prepare the known  $[(\text{Cy}_2\text{PCH}_2)_2\text{NiH}]_2$  complex.<sup>7,8</sup> This



**Figure 1.** ORTEP drawing of **2**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

hydride dimer reacted with DBT (with the loss of  $\text{H}_2$ ) in hexanes at room temperature, and the resulting C–S insertion product (dippe) $\text{Ni}(\eta^2\text{-C,S-DBT})$  (**2**) precipitated from solution (eq 1).<sup>9</sup> An ORTEP drawing of **2** displaying the common biphenyl



twist<sup>10</sup> ( $34.8^\circ$ ) can be seen in Figure 1. This insertion complex was found to be labile in solution as seen when **2** was dissolved in neat thiophene producing free DBT plus the new C–S insertion complex **3**<sup>11</sup> (eq 1) in quantitative yield.

Over the course of 5 days (room temperature), a solution of **2** in  $\text{THF-}d_8$  converts to four new organometallic products as detected in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. These products have been identified as (dippe) $\text{Ni}(2,2'\text{-biphenyl})$  (**4**),  $[\text{Ni}_2(\mu\text{-S})(\text{dippe})_2]$  (**5**),  $[(\text{dippe})\text{Ni}(\mu\text{-S})]_2\text{Ni}(2,2'\text{-biphenyl})$  (**6**), and  $(\text{dippe})_2\text{Ni}$  (**7**) (eq 2).

Complexes **4** and **5** are the major products formed in the reaction (1:1 ratio) and account for 82% of all organometallic products. Free DBT is also seen in the  $^1\text{H}$  NMR spectrum (2 equiv per **4** or **5**). Compounds **4**, **6**, and **7** have all been

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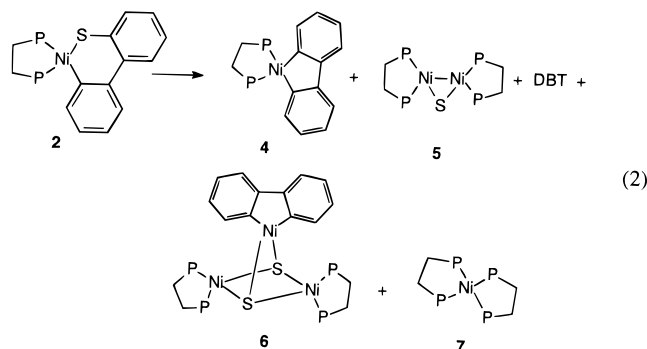
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(8) The quintet at  $\delta$  –9.81 ( $J$  = 24.2 Hz) in the  $^1\text{H}$  NMR spectrum is characteristic of nickel–bisphosphine hydride dimers.

(9) Analytical data for **2**:  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$ )  $\delta$  7.53–7.43 (m, 2H), 7.39 (d,  $J$  = 7.3 Hz, 1H), 7.17 (d,  $J$  = 6.4 Hz, 1H), 7.00–6.83 (m, 4H), 2.77 (br s, 1H), 2.41 (br s, 1H), 2.25–0.84 (m, 24 H), 0.63 (br s, 3H), 0.12 (br s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-78^\circ\text{C}$ , 100 MHz)  $\delta$  156.11 (dd,  $J$  = 27.7, 25.8 Hz), 147.44 (s), 143.03 (s), 138.95 (s), 133.59 (d,  $J$  = 8.1 Hz), 128.81 (s), 125.25 (s), 124.68 (s), 123.94 (s), 122.05 (s), 121.42 (s), 25.02 (d,  $J$  = 27.2 Hz), 23.78 (d,  $J$  = 20.2 Hz), 22.06–21.46 (m), 19.99–19.66 (m), 18.91–17.10 (m), 15.46–15.26 (m), 14.81 (s);  $^{31}\text{P}\{^1\text{H}\}$  (THF- $d_8$ ,  $-78^\circ\text{C}$ , 162 MHz)  $\delta$  75.55 (d,  $J$  = 10.2 Hz), 74.39 (d,  $J$  = 10.2 Hz). Anal. Calcd (found) for  $\text{C}_{26}\text{H}_{40}\text{NiP}_2\text{S}$ : C, 61.57 (61.80); H, 7.74 (7.98).

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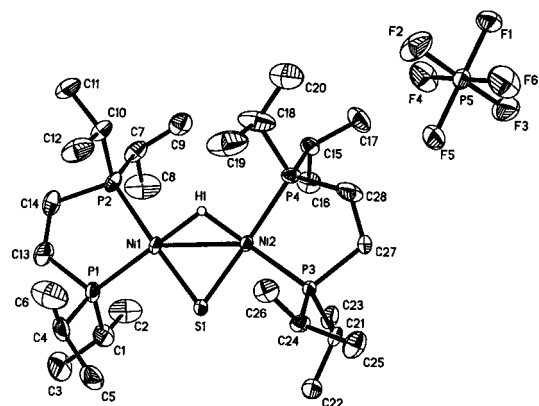
(11) Analytical data for **3**:  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ,  $25^\circ\text{C}$ )  $\delta$  7.46 (t,  $J$  = 10 Hz, 1H), 7.37 (t,  $J$  = 11.1 Hz, 1H), 6.91–6.82 (m, 1H), 6.58 (t,  $J$  = 8.1 Hz, 1H), 2.46 (oct,  $J$  = 7.5 Hz, 2H), 2.32 (oct,  $J$  = 6.9 Hz, 2H), 1.94 (sext,  $J$  = 8.7 Hz, 2H), 1.78 (sext,  $J$  = 8.1 Hz, 2H), 1.31–1.15 (m, 24H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-35^\circ\text{C}$ , 100 MHz)  $\delta$  142.01 (dd,  $J$  = 68.8, 27.7 Hz), 125.85 (s), 121.59 (d,  $J$  = 13.3 Hz), 120.03 (s), 24.24–23.67 (m), 22.40 (t,  $J$  = 19.6 Hz), 19.76 (dd,  $J$  = 22.3, 13.7 Hz), 18.65 (s), 18.32 (s), 17.90 (s), 17.79 (s);  $^{31}\text{P}\{^1\text{H}\}$  (THF- $d_8$ ,  $25^\circ\text{C}$ , 162 MHz)  $\delta$  82.33 (d,  $J$  = 20.4 Hz), 73.24 (d,  $J$  = 20.4 Hz). Anal. Calcd (found) for  $\text{C}_{18}\text{H}_{36}\text{NiP}_2\text{S}$ : C, 52.98 (53.36); H, 9.11 (8.96).



identified by X-ray crystallography, and independent synthetic routes to **4** and **7** have also been developed (see the Supporting Information). Attempts at crystallizing complex **5** were unsuccessful, but its protonated form  $[\text{Ni}_2(\mu\text{-S})(\mu\text{-H})(\text{dippe})_2][\text{PF}_6]$  (**8**) could be synthesized independently from  $(\text{dippe})\text{Ni}(\text{SH})_2$ , **1**, and  $\text{KPF}_6$  and proved amenable to crystallization. An ORTEP drawing of **8** can be seen in Figure 2.

Treatment of **8** with potassium *tert*-butoxide in THF generated complex **5**, providing additional support for the assignment of its structure. Complex **5** is fluxional at room temperature, and the broad resonance seen for the phosphines decoalesces into two apparent triplets ( $\delta$  77.86 and 73.64) in the  $^{31}\text{P}\{\text{H}\}$  spectrum at  $-35^\circ\text{C}$ . The related dinuclear complexes  $[\text{Pt}_2(\mu\text{-H})(\mu\text{-S})(\text{dppe})_2][\text{PF}_6]^{12}$  ( $\text{dppe}$  = bis(diphenylphosphino)ethane) and  $[\text{Pt}_2(\mu\text{-H})(\mu\text{-CO})(\text{dppe})_2][\text{BF}_4]^{13}$  have also been observed to display fluxional behavior. The bridging sulfide moiety found in complexes **5** and **8** is a common structural feature of homogeneous desulfurization products previously found for thiophene and benzothiophene substrates.<sup>6</sup> We now report that the desulfurization of dibenzothiophene yields a similar species.

We propose that the reversible loss of free DBT from the C–S insertion product generates reactive bisphosphine nickel(0) fragments which can further react with **2** to yield the observed products. It is interesting to note that no dimeric species of the type  $[(\text{dippe})\text{Ni}(\text{DBT})]_2$  was observed by NMR spectroscopy. This contrasts with the thermal chemistry displayed by  $(\text{Et}_3\text{P})_2\text{Pt}(\eta^2\text{-C,S-DBT})^5$  and  $[\text{Cp}^*\text{Rh}(\eta^2\text{-C,S-DBT})]^{14}$  both of which form  $\mu\text{-S}$  dimers. The mechanism by which the minor product **6** (14% of organometallics) is formed remains unclear and is under further study. It was established, however, that reaction of the dinuclear complex  $[(\text{dippe})\text{Ni}(\mu\text{-S})]_2$  with **4** at room temperature only slowly (weeks) produces



**Figure 2.** ORTEP drawing of **8**. Ellipsoids are shown at the 30% probability level. All hydrogen atoms except the bridging hydride are omitted for clarity.

**6.** The nucleophilicity of the bridging sulfur atoms in  $[(\text{R}_3\text{P})_2\text{M}(\mu\text{-S})]_2$  complexes has been well documented.<sup>15</sup> It was thought that reaction of such a species with **4** may have been the origin of **6**, but the rate of this reaction is inconsistent with such a pathway operating during the desulfurization of **2**.

Reaction of **4** with 1 atm of  $\text{H}_2$  at room temperature quantitatively yields **1** and free biphenyl, demonstrating the potential power of homogeneous nickel complexes in catalytic desulfurization. Here, we have shown that a hydride, a proton, or a hydrogen atom source are not required in the desulfurization of DBT, only in the release of free biphenyl. The experimental conditions used here represent marked improvements over those employed in the one cited example of homogeneous desulfurization of DBT ( $170^\circ\text{C}$ , 30 atm of  $\text{H}_2$ ) in the absence of added hydride or acid sources.<sup>16</sup> We have also been able to structurally characterize the organometallic products of the desulfurization of DBT at nickel. Further hydrogenation experiments with **5** as well as reactivity studies of **1** with thiophene, benzothiophene, and methyl-substituted DBTs will be presented in a full paper.

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**Supporting Information Available:** A listing of experimental procedures, data collection parameters, bond lengths, bond angles, fractional atomic coordinates, and anisotropic thermal parameters (23 pages). See any current masthead page for ordering and Internet access instructions.

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