Deep Hydrodesulfurization in Homogeneous Solution: Access to a Transition-Metal Insertion Complex of 4,6-Dimethyldibenzothiophene

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Summary: Alkylated dibenzothiophenes are among the most difficult compounds to desulfurize in the hydroprocessing of crude oil, and information leading to their efficient removal is of tremendous value. Homogeneous nickel and platinum complexes were found to desulfurize alkylated dibenzothiophenes in the solution phase proceeding through well-characterized transition-metal insertion complexes.

The removal of organosulfur compounds from fossil fuels represents one of the largest-scale industrial processes catalyzed by transition metals today. In this procedure, crude oil distillates are treated with high pressures of hydrogen gas (150−2250 psi) over a hot heterogeneous catalyst (320−440 °C) to remove sulfur residuals prior to further processing.[1] Because of new regulations designed to limit the sulfur content in diesel fuels, much interest has been focused on the problems of “deep” hydrodesulfurization (HDS) or production of gas oils containing less than 0.05 wt % sulfur.[2] The major obstacle in producing fuels with such a low sulfur content is the difficulty in desulfurizing alkylated dibenzothiophenes, especially those which are substituted in the 4 and the 4,6 positions.

Figure 1 shows a gas-chromatographic analysis of sulfur impurities found in crude oil at various conversions in HDS.[2c,d] The spectra acutely display the lack of reactivity of the alkylated dibenzothiophenes toward desulfurization. Indeed, as noted by Topsøe and coworkers, “an important challenge is to find more active catalysts for deep HDS, and this challenge can be stated without much oversimplification as that of finding more active catalysts for HDS of (substituted) 4-methyldibenzothiophene and (substituted) 4,6-dimethyldibenzothiophene.”[2d] Tremendous industrial effort, therefore, has been focused on understanding the structure/reactivity differences of dibenzothiophene (**1**), 4-methyldibenzothiophene (**2**), and 4,6-dimethyldibenzothiophene (**3**) in attempts to design a more efficient catalyst for the hydroprocessing of crude oil.[3]

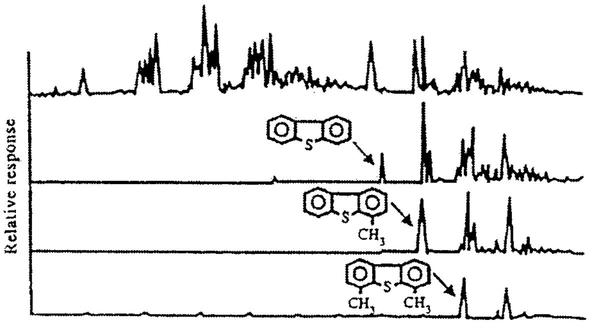
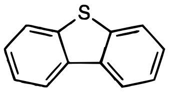


Figure 1. Gas-chromatographic traces showing the removal of organosulfur compounds from oil.[2c,d] The upper trace represents the feed, and the traces in descending order represent products with increasing conversions in HDS. The data illustrate the relatively low reactivity of 4,6-dimethyldibenzothiophene. Reprinted with permission from ref 2c, copyright 1996 American Chemical Society.



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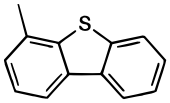

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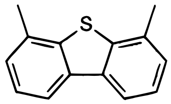

3

Few homogeneous HDS studies of dibenzothiophenes substituted in the 4 and the 4,6 positions have been reported[4] due to the lack of reactivity of the sterically hindered carbon−sulfur bonds in these substrates. In fact, since the first report of insertion of a transition metal into the C−S bond of a thiophenic molecule nearly 40 years ago,[5] there has been only one report of a soluble transition-metal complex structurally characterized as having inserted into the less-hindered carbon−sulfur bond of **2**[4a] and there is one report of a low yield (15%) desulfurization of **3** using Ni^0 reducing agents plus acid.[4c,6] This lack of reactivity of transition metals toward the carbon−sulfur bonds in **2** and **3** has been discouraging, since the initial carbon−sulfur bond cleavage is thought to be one of the fundamental steps toward the desulfurization of thiophenes.[7] The discovery of a transition-metal complex that could insert into the C−S bonds of alkylated dibenzothiophenes would, therefore,

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(6) A report has appeared in the literature since the initial submission of this article in which the (Et$_3$P)$_2$Pt fragment is believed to have inserted nonspecifically into the C−S bonds of **2** forming a 1:1 mixture of thiametallacycle isomers. The C−S insertion complexes were not structurally characterized but were found to release 3-methylbiphenyl under desulfurization conditions, see: Iretskii, A.; García, J. J.; Picazo, G.; Maitlis, P. M. *Catal. Lett.* **1998**, 51, 129−131.

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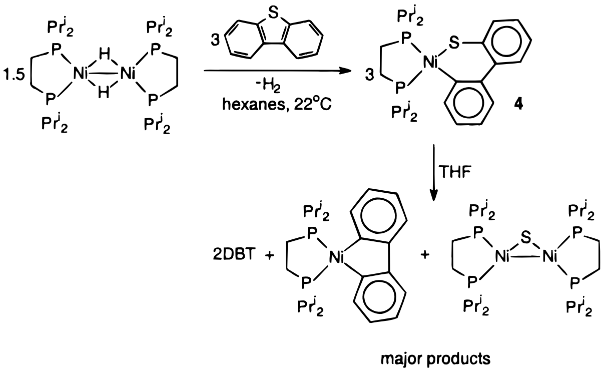
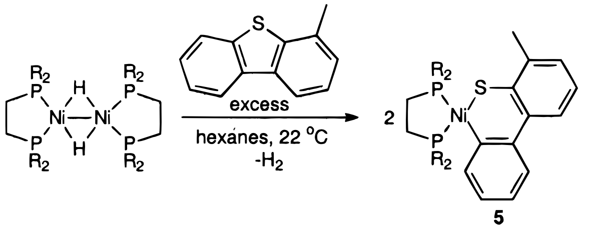
offer insight into ways to improve HDS catalysis. Access to a *series* of sterically hindered dibenzothiophene adducts in the homogeneous phase will provide a means to undertake a much needed structure/reactivity study to provide information on how alkylation of dibenzothiophenes in the 4 and 4,6 positions affect adsorption and reactivity on a catalyst surface. We would now like to report the first clear example of insertion of a transition metal into the C−S bond of **3,** the solid-state structures of the analogous insertion complexes of **1** and **2**, and two rare examples of desulfurization of **3** that do not require the use of external saline hydrides or acid sources.

It has recently been communicated by our lab[8] that a dinuclear nickel−hydride complex was able to mediate cleavage of both of the C−S bonds in dibenzothiophene (DBT) at room temperature via the intermediacy of the C,S-insertion complex **4** (eq 1). The success of the nickel system toward unsubstituted dibenzothiophene prompted us to explore reactions with dibenzothiophenes substituted in the 4 and 4,6 positions.



(1)

Reaction of [(dippe)NiH]$_2$ with **2** at room temperature (19 h, 26% yield) provided a similar C−S insertion adduct (**5**) in which the nickel bisphosphine fragment inserted into the C−S bond distal to the methyl group (eq 2). X-ray analysis[9] revealed an extremely low biphenyl twist between the two aromatic rings (28.9°), which presumably arises from steric interactions of the dippe ligand with the methylated ring of the dibenzothiophene unit. Reaction of **2** with excess nickel (1.5 equiv or 3Ni per S) under 1 atm of H_2 (40 °C, 3 days) leads to high yields (>90%) of the desulfurized 3-phenyltoluene, again proceeding via the intermediacy of the C−S insertion complex **5**. No such nickel-insertion complex could be seen in similar reactions with **3** at room temperature. However, reaction of 1.5 equiv of [(dippe)NiH]$_2$ at 90 °C with **3** under an atmosphere of H_2 in THF-d_8 did lead to the formation of the desulfurized 3,3′-dimethylbiphenyl as the organic product, as detected by ^{1}H NMR spectroscopy (eq 3).



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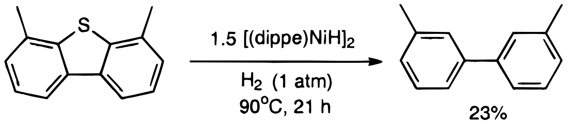
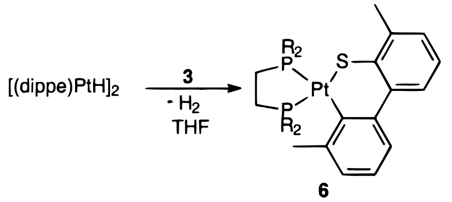


(3)

No intermediate C−S insertion complex of **3** could be detected in the ^{31}P{^{1}H} NMR spectrum under these conditions. The only nickel-containing product that could be identified was Ni(dippe)$_2$. In support of a homogeneous species being responsible for the desulfurization (rather than nickel metal), the reaction affords similar yields (19%) of 3,3′-dimethylbiphenyl when repeated in the presence of 1000 equiv of Hg to absorb any heterogeneous particles.[10] Additionally, a control experiment showed that [(dippe)NiH]$_2$ under an atmosphere of H_2 in THF does not undergo decomposition at 90 °C. This control experiment clearly demonstrates that at elevated temperatures **3** must be interacting with either [(dippe)NiH]$_2$ or a species in equilibrium with this dimer. The instability of the organometallic intermediates in the nickel reaction, coupled with recent achievements in platinum HDS models,[11] encouraged us to examine the analogous platinum hydride dimer for HDS activity.

Reaction of excess **3** with [(dippe)PtH]$_2$[12] in THF (10 h, 120 °C) resulted in the clean formation of a new product (**6**) (eq 4), as detected by NMR spectroscopy. The new product was assigned as the C−S insertion product based on the observation of two inequivalent phosphine resonances in the ^{31}P NMR spectrum and the uniqueness of all signals for the 4,6-dimethyldibenzothiophene ligand in the ^{1}H and ^{13}C NMR spectra. No platinum−hydride resonances were detected in the ^{1}H NMR spectrum, ruling out the possibility of a C−H-activated product, and no dramatic upfield shifts consistent with an η^2-arene complex were observed spectroscopically. **6** was selectively crystallized in 40% isolated yield by cooling the THF solution to 0 °C. An X-ray structure analysis revealed the first example of a transition-metal insertion product of **3** as shown in Figure 2 (Table 1).[13]



(4)

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(9) Crystallographic data for all structures will be deposited with the Cambridge Crystallographic Data Centre, Nos. 101106 and 101404.

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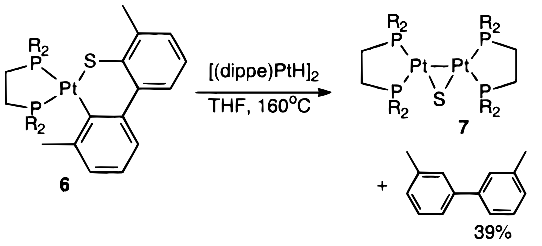
Table 1. Crystallographic Data for Compounds 5, 6, 8, and 9

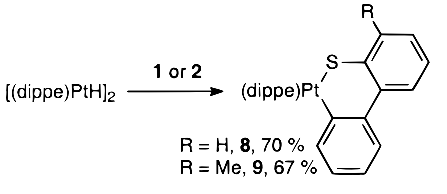
	6	**9**	**8**	**5**
chemical formula	$C_{28}H_{44}P_2PtS{\cdot}0.5$hexane	$C_{27}H_{42}P_2PtS$	$C_{26}H_{40}P_2PtS$	$C_{27}H_{42}NiP_2S$
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$Pna2_1$
Z	4	2	8	4
a, Å	13.3227(4)	8.1406(2)	16.2512(3)	9.1750(6)
b, Å	17.5229(6)	9.0505(2)	17.2377(3)	19.1716(1)
c, Å	13.5940(4)	18.8618(5)	19.7362(3)	15.7144(1)
β, deg	99.2810(10)	85.1910(10)	102.7760(10)	90
vol, Å^3	3132.0(2)	1363.73(6)	5391.9(2)	2764.2(3)
ρ_{calc}, g cm^{-3}	1.512	1.597	1.581	1.248
temp, °C	−80	−80	−80	−80
Measurement of Intensity Data				
diffractometer	Siemens SMART			
radiation	Mo Kα 0.710 73 Å			
frame range/time, deg/s	0.3/30	0.3/10	0.3/10	0.3/60
2θ range, deg	3.82−56.98	4.36−56.42	3.18−56.58	3.36−46.5
no. of data collected	18 470	8525	30 388	11 153
agreement between equivalent data (R_{int})	0.0576	0.0322	0.0506	0.0679
no. of params varied	312	289	557	289
abs cor	empirical (SADABS)			
$R_1(F_o)$, $wR_2(F_o^2)$ ($F_o > 4\sigma(F_o)$)	0.0371, 0.0764	0.0442, 0.1004	0.0498, 0.0721	0.0537, 0.1004

Reaction of **6** with 1 equiv of $[(dippe)PtH]_2$ in THF-d_8 (25 h, 160 °C) led to the formation of 3,3′-dimethylbiphenyl (39%). Initially, two triplets were seen in the ^{31}P spectrum (δ 86.80 (t, $J_{P-P} = 9.2$ Hz), 73.21 (t, $J_{P-P} = 8.9$ Hz)), but the organometallic species responsible for these resonances decomposed under the extreme reaction conditions. This compound is assigned as $[(dippe)Pt]_2(\mu\text{-}S)$ (**7**) (eq 5) based upon the similarity of the ^{31}P spectral data to that of the analogous nickel complex (δ 77.86 (t, $J = 22.7$ Hz), 73.64 (t, $J = 22.1$ Hz)).[8]



(5)

Importantly, reaction of $[(dippe)PtH]_2$ with **1** and **2** also afforded similar insertion adducts, which have been fully characterized, providing the first series of transition-metal insertion complexes of **1**, **2**, and **3** (eq 6). As seen in the nickel system, platinum metal insertion took place exclusively into the C−S bond distal to the methyl group of **2**. Surprisingly, X-ray data have revealed that there is no correlation of biphenyl twist with degree of alkylation on the dibenzothiophene unit for platinum, with angles of 36.0° and 44.1° for **8** and **9**, respectively. Qualitatively, the lack of any trend in this structural feature may be attributed to tradeoffs between steric interactions of the dibenzothiophene methyl groups with the dippe ligand and torsional freedoms imparted by the relatively long Pt−S, Pt−P, and Pt−C bond lengths. The availability of a series of dibenzothiophene insertion adducts now allows for structure/reactivity studies relevant to the problems of *deep* HDS to be undertaken, such as substrate lability, hydrogenolysis, and kinetics of desulfurization.



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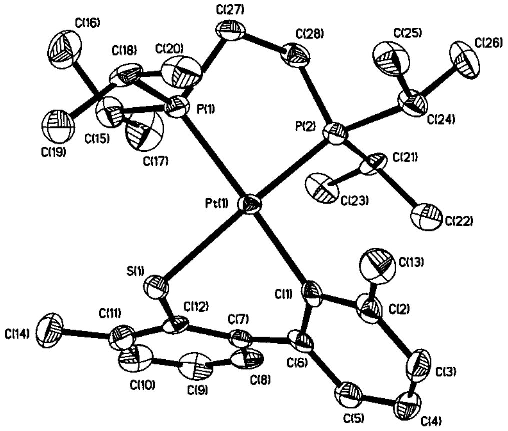

Figure 2. ORTEP drawing of **6**. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Pt(1)−C(1) 2.056(6), Pt(1)−S(1) 2.348(1), S(1)−C(12) 1.779(5), C(1)−C(6) 1.404(7), C(6)−C(7) 1.488(8), C(7)−C(12) 1.400(7). Selected bond angles (deg): P(2)−Pt(1)−P(1) 86.8(5), C(1)−Pt(1)−S(1) 83.1(1), P(2)−Pt(1)−C(1) 95.0(1), P(1)−Pt(1)−S(1) 95.2(5), C(12)−S(1)−Pt(1) 96.8(2).

Acknowledgment is made to the National Science Foundation (Grant No. CHE-9421727) for their support of this work.

Supporting Information Available: Tables of complete crystallographic data for **5**, **6**, **8**, and **9** and text describing experimental procedures (37 pages). Ordering information is given on any current masthead page.

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(13) For a related unsubstituted Pt complex, see: Garcia, J. J.; Arevalo, A.; Capella, S.; Chehata, A.; Hernandez, M.; Montiel, V.; Picazo, G.; Del Rio, F.; Toscano, R. A.; Adams, H.; Maitlis, P. M. *Polyhedron* **1997**, *16*, 3185−3195.