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# Mechanistic Insights into the C−S Bond Breaking in Dibenzothiophene Sulfones

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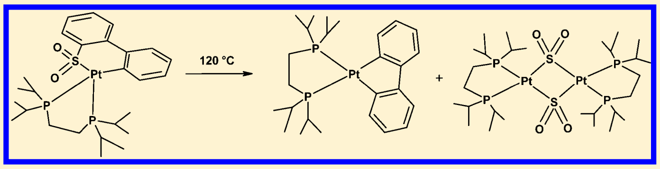
Supporting Information



**ABSTRACT:** The reactivity of Grignard reagents in the presence of nickel catalysts is known to be highly efficient in the deoxydesulfurization of dibenzothiophene sulfone ($DBTO_2$), 4-methyldibenzothiophene (4-$MeDBTO_2$), and 4,6-dimethyldibenzothiophene (4,6-$Me_2DBTO_2$), to yield sulfur-free biphenyls via cross-coupling reactions. However, the mechanistic details involved in the process remained unknown. In this report the reactivity of $[(\text{dippe})Pt(\mu\text{-}H)]_2$ with $DBTO_2$ turned out to be catalytically less efficient compared with $[(\text{dippe})Ni(\mu\text{-}H)]_2$, but the first allowed the isolation and full characterization of several reaction intermediates, such as $[(\text{dippe})Pt(\kappa^2\text{-}C,S\text{-}DBTO_2)]$. It was demonstrated that this is a key intermediate in all the deoxydesulfurization reactions of the above-mentioned aromatic sulfones ($DBTsO_2$).

## INTRODUCTION

The removal of sulfur from petroleum and other fossil feedstocks is a highly important activity in refineries worldwide, due to the increasingly tougher specifications for sulfur contents in fuels. In this context, acceptable sulfur contents in dispensed gasoline and diesels in the USA (<30 ppm, 2006),[1] Europe (<10 ppm, 2008), and Canada are diminishing.[2] Therefore it is necessary to lower the atmospheric contaminants caused by the emission of $SO_x$, as byproducts of the fuel combustion process contribute to acid rain production. Another important reason to eliminate sulfur contaminants from fuel is that there are several diseases related to prolonged exposure to $SO_x$ adsorbed particles in humans.[3] The most refractory compounds present in fossil fuels are methyl-substituted dibenzothiophenes, such as 4-methyldibenzothiophene (MeDBT) and 4,6-dimethyldibenzothiophene ($Me_2DBT$). These species typically exhibit low conversions in the industrial hydrodesulfurization process (HDS), which uses high temperatures (300−400 °C), high pressures of hydrogen (150−1000 psi), and heterogeneous catalysts based on Mo, Co, and W sulfides.

An alternative technology to eliminate methyl-substituted dibenzothiophenes without the use of hydrogen is oxidative desulfurization (ODS), which consists in the oxidation of the above-mentioned sulfur compounds to yield the corresponding sulfoxides and sulfones, all of them exhibiting high melting and boiling points and relative chemical inertness;[4] ODS uses peroxides as oxidant agents in basic ($Na_2CO_3$)[5] or acid conditions,[6] in a biphasic system of diesel−acetonitrile with polymolybdates,[7] and in the ultrasound-assisted use of ionic liquids.[8] ODS has been widely studied according to several patents on this topic.[9] However, the produced sulfoxides and sulfones are considered an industrial waste even when these compounds have great potential as raw materials in organic synthesis.

The activation of sulfones via the coordination of the oxygen atoms has been reported by using zirconium and titanium[10] and also for rhodium,[11] lithium,[12] and palladium.[13] However, the C−S bond cleavage of sulfoxides and sulfones has been scarcely studied. Some relevant examples have been reported for cobalt metallocenes such as $[CpCo(PPh_3)_2]$,[14] with ultrasonically dispersed potassium to activate unsaturated cyclic sulfones.[15] The elimination of the $SO_2$ moiety from the dibenzothiophene sulfone ($DBTO_2$) has also been less studied and has been achieved under severe conditions, either by using sodium metal and liquid ammonia[16] or with Nickel Containing Complex Reducing Agents (NiCRA's).[17] The use of other methodologies for the $SO_2$ Nickel Containing Complex Reducing Agents (extrusion) from aromatic and heterocyclic sulfones has been reported, for instance, the use of supercritical water[18] and radiolytic[19] or photochemically assisted processes.[20] Particularly, the latter is effective for the desulfurization of methyl-substituted dibenzothiophenes (DBT) sulfones in 2-propanol.

Our group has maintained interest in the C−S activation of DBTs.[21] Recently, we reported the activation and catalytic deoxydesulfurization of dibenzothiophene sulfones ($DBTO_2$, 4-$MeDBTO_2$, and 4,6-$Me_2DBTO_2$) in high yields to produce the sulfur-free substituted methyl-byphenyl derivatives, using a variety of nickel precursors in low oxidation states (see Scheme 1).[22]

A ring-opening mechanistic pathway via a sulfinametallacycle of the type $[(\text{dippe})Ni(\kappa^2\text{-}C,S\text{-}DBTO_2)]$ was suggested as a key intermediate in the mechanistic proposal over a pathway via the reduction of the corresponding sulfone to dibenzothiophene; the latter was initially ruled out considering the high oxidesulfurization yields that would not be expected if DBTs could be generated from $DBTsO_2$.[23] However, the corresponding nickel intermediates could not be isolated or detected in

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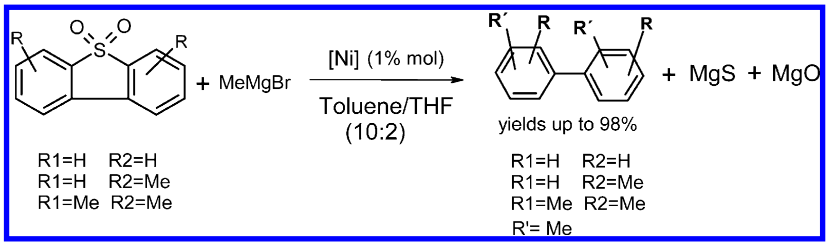
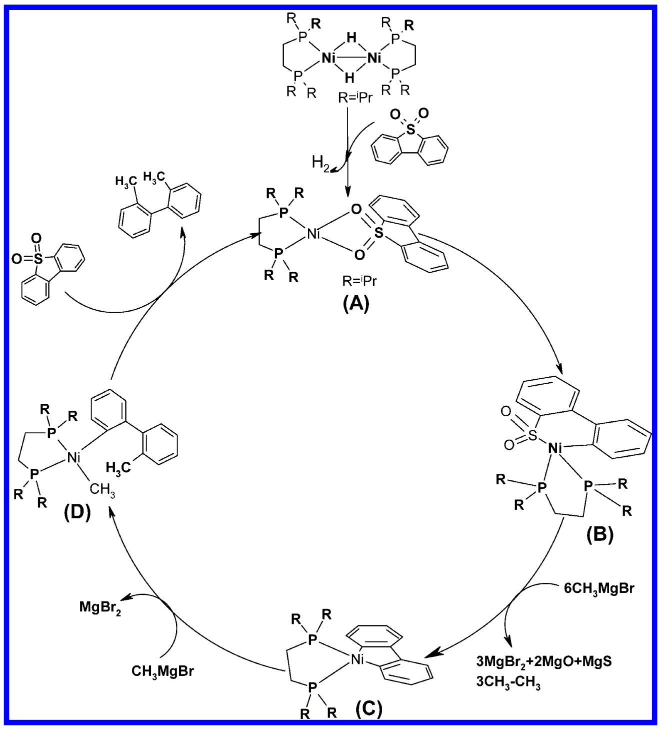
### Scheme 1. General Reactivity of Deoxydesulfurization with Nickel Catalysts



### Scheme 2. Mechanistic Proposal for the Catalytic Deoxydesulfurization of $DBTO_2$[22]

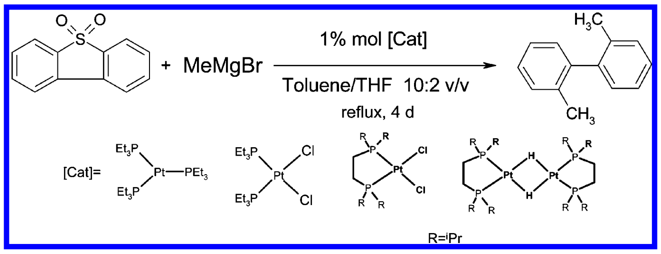


solution (Scheme 2). This encouraged us to isolate closely related intermediate species using platinum as metallic center, since Pt−C bonds are roughly 17 kcal/mol stronger than the corresponding Ni−C.[24,25] We disclose those findings herein.

## ■ RESULTS AND DISCUSSION

In order to make a direct comparison in reactivity with our previous findings with nickel, we prepared a variety of similar platinum catalytic precursors, including the complex $[(dippe)Pt(\mu\text{-}H)]_2$ (**1**); then we assessed the catalytic activity under the optimized reaction conditions found for nickel. A summary of the catalytic experiments and the corresponding results using platinum catalytic precursors is presented in Scheme 3 and Figure 1 respectively.

### Scheme 3. Catalytic Experiments with Platinum Precursors



As a general trend, the platinum catalytic precursors exhibit lower conversions compared to the corresponding nickel analogues; this is in agreement with the expected stability of the intermediates having a robust Pt−C bond. Noteworthy, despite the expected results, complex $[(dippe)PtCl_2]$ (**2**) showed high conversion (>90%) toward deoxydesulfurization of $DBTO_2$ and $4MeDBTO_2$, similar to the nickel analogue $[(dippe)NiCl_2]$. The last was highly active with all sulfones; in sharp contrast, complex **1** was completely ineffective in the catalytic process. The use of complex $[(PEt_3)_2PtCl_2]$ (**3**) yielded a modest conversion (∼30%) compared with the high activity of the nickel analogue $[(PEt_3)_2NiCl_2]$. Considering the above, in order to isolate the potential intermediates involved in catalysis, compound **1** was selected as a good candidate due to its poor catalytic performance, although highly similar to compounds **2** and **3**. Reactions of **1** with $DBTO_2$, $4\text{-}MeDBTO_2$, and $4,6\text{-}Me2DBTO_2$ were assessed as depicted in Scheme 4.

Compounds derived from the sulfone ring-opening (**4**−**6**) were detected; particularly, complex $[(dippe)Pt(\kappa^2\text{-}C,S\text{-}DBTO_2)]$ (**4**) displays resonances in the $^{31}P\{^1H\}$ NMR spectrum at $\delta$ 71.48 (s, $^1J_{Pt-P}$ = 1941 Hz) and 55.29 (s, $^1J_{Pt-P}$ = 2374 Hz), just as seen in closely related thiaplatinacycles derived from dibenzothiophenes.[26] Table 1 contains the $^{31}P\{^1H\}$ NMR details for the sulfinaplatinacycles derived from $DBTsO_2$. In addition, FT-IR spectra showed bands for this compounds at 1269 (m), 1079 (s), and 1022 (s) $cm^{-1}$, assigned to the symmetric and asymmetric vibrational modes, respectively, of the $SO_2$ moiety,[27−29] showing a shift to lower energy compared with the free $DBTO_2$ (1287(s) and 1162 (s) $cm^{-1}$) upon coordination.

Suitable crystals for X-ray diffraction were obtained on cooling a benzene solution of complex **4** at −20 °C overnight, allowing full structural characterization of that compound. The corresponding ORTEP representation is depicted in Figure 2, and a summary of crystallographic data for **4** can be found in Table 2. The geometry is slightly distorted square planar around platinum, the metal center is situated 0.0951(5) Å above the P1/P2/C13/S1 plane with a rms deviation of fitted atoms of 0.0812, and the sum of the angles P(1)−Pt(1)−P(2) 86.29(2)°, S(1)−Pt(1)−P(2) 98.48(2)°, C(13)−Pt(1)−S(1) 83.51(6)°, and C(13)−Pt(1)−P(1) 91.32(5)° is 359.6°, confirming such geometry around the metal center. Also, the structure displays a characteristic biphenyl twist of 36.85(1)°, and a comparison with closely reported compounds such as other thiaplatinacycles with a chelating dippe is of interest. For instance, the complex $[(dippe)Pt(\kappa^2\text{-}C,S\text{-}C_{12}H_8S)]$ reported by Vicic and Jones[26c] displays a more regular square -planar geometry compared with complex **4** due to the presence in the last of the oxygen over the sulfur atom, causing an increment in the angle S(1)−Pt(1)−P(2), 98.48(2)°, compared with the same angle in the thiaplatinacycle, S−Pt−P 95.2(5)°, and consequently a decrease in the opposite angle, C(13)−Pt(1)−P(1)

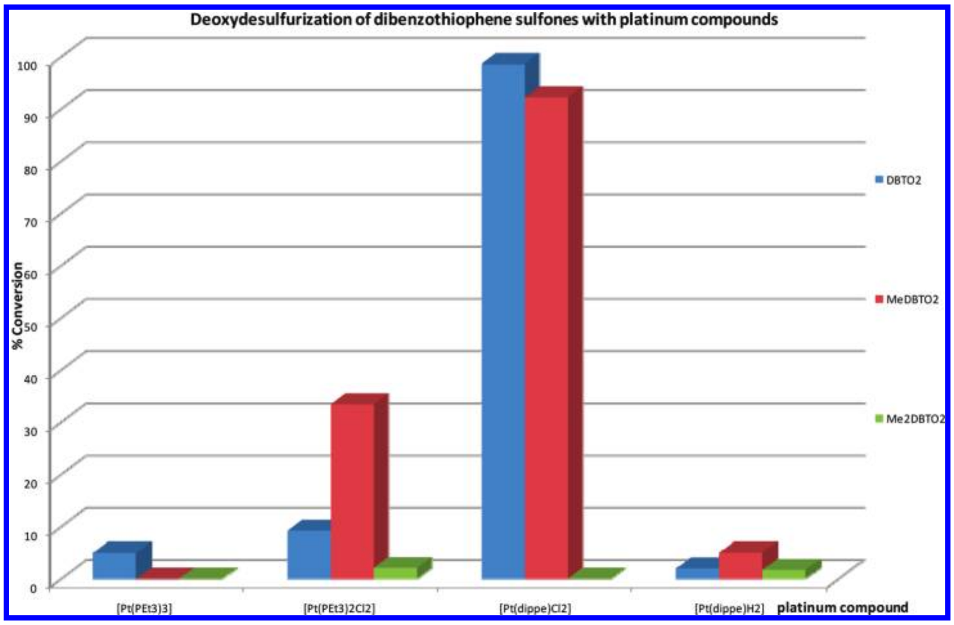
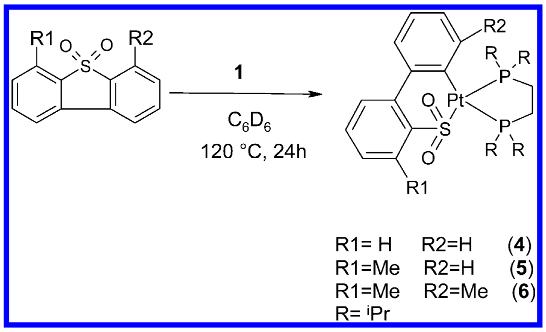


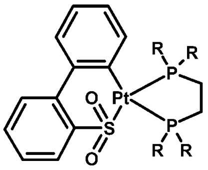
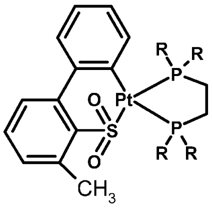
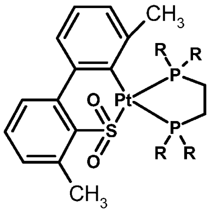
**Figure 1.** Platinum-catalyzed deoxydesulfurization of dibenzothiophene sulfones with MeMgBr.

**Scheme 4. Ring-Opening for DBT Sulfones with Platinum**



91.32(6)°, compared with the same angle, C−Pt−P 95.0(1)°, in the thiaplatinacycle. Also of interest is the observed shorter distance of S(1)−Pt(1) (2.2986(6) Å) in complex **4** compared with the same one in the thiaplatinacycle, S−Pt 2.348(1) Å, perhaps due to an increment in the electron density provided by the $SO_2$ moiety to the S−Pt bond. Regarding this, a further look into the geometry and distances around the sulfur atom in **4** shows a distorted tetrahedral geometry with an angle O(1)−S(1)−O(2) of 113.71(10)°, smaller than in the free sulfone, O−S−O 120°,[30] and a S═O distance in complex **4** of 1.465 Å (av), slightly shorter than the same distance in the free sulfone, 1.49 Å. To note, the S−C distance in **4** is longer (1.814 Å)

**Table 1.** $^{31}P\{^1H\}$ **NMR Data for Complexes of the Type [(dippe)Pt(κ²-*C*,*S*-sulfone)]**

| Complex | $^{31}P\{^1H\}$ |
|---|---|
|  **(4)** | 55.29 ppm, $^1J_{Pt\text{-}P}$=2473 Hz<br>71.48 ppm, $^1J_{Pt\text{-}P}$=1941 Hz |
|  **(5)** | 54.54 ppm, $^1J_{Pt\text{-}P}$=2426 Hz<br>69.73 ppm, $^1J_{Pt\text{-}P}$=1932 Hz |
|  **(6)** | 51.13 ppm, $^1J_{Pt\text{-}P}$=2219 Hz<br>69.27 ppm, $^1J_{Pt\text{-}P}$=2097 Hz |

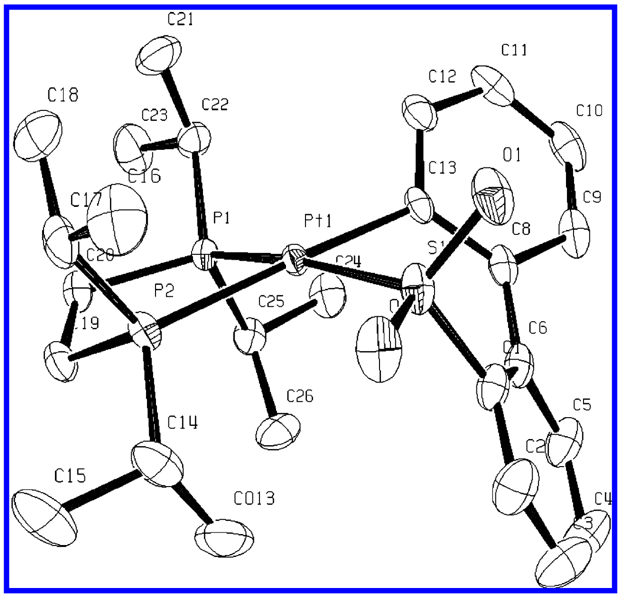


**Figure 2.** ORTEP drawing for **4**·$C_6H_6$. Ellipsoids are shown at the 50% probability level; hydrogen atoms and benzene are omitted for clarity. Selected bond lengths (Å): C(13)–Pt(1) 2.072(2), S(1)–Pt(1) 2.2986(6), P(1)–Pt(1) 2.2892(6), P(2)–Pt(1) 2.3199(6), C(1)–S(1) 1.814(2), O(1)–S(1) 1.4635(18), O(2)–S(1) 1.4659(17). Bond angles (deg): P(1)–Pt(1)–S(1) 169.157(19), C(13)–Pt(1)–P(2) 176.78(6), P(1)–Pt(1)–P(2) 86.29(2), S(1)–Pt(1)–P(2) 98.48(2), C(13)–Pt(1)–S(1) 83.51(6), C(13)–Pt(1)–P(1) 91.32(6), C(1)–S(1)–Pt(1) 96.74(8), O(1)–S(1)–Pt(1) 115.97(8), O(2)–S(1)–Pt(1) 116.29(7), O(1)–S(1)–O(2) 113.71(10).

compared with that in the thiaplatinacycle (1.779 Å) and with the free $DBTO_2$ (1.74 Å), thus suggesting that the Pt–S bond is strengthened by the C–S bond weakening.

Noteworthy, even when sulfinate species are well known, they are derived from the $SO_2$ insertion reaction into the M–C bond of alkyl,[31] unsaturated rings,[32,33] and terminal phenyl derivatives,[34] but none of them from the ring-opening and metal insertion into the C–S bond of sulfones.

In order to assess the stability of the new compounds, the thermolysis in solution of complex **4** was studied by heating a sample up to 120 °C for a period of 10 d, monitored by $^{31}P\{^1H\}$NMR. The results are shown in Scheme 5.

The thermal decomposition of complex **4** yielded a mixture of compounds. To note, complex **7** clearly represents evidence for the reaction sequence postulated in Scheme 2 (compounds **B** and **C**), i.e., the extrusion of $SO_2$ from the sulfinaplatinacycles derived from $DBTO_2$. Since no Grignard reagents were used in the current case, the extruded $SO_2$ moiety forms a binuclear platinum compound, **9**, along with **8** and free $DBTO_2$. A recrystallized sample of **9** was independently reacted with an excess of MeMgBr, to yield MgO, MgS, and $MgBr_2$, confirming the above reaction in Scheme 2. Compounds **7** and **8** were characterized by comparing them with authentic samples prepared independently (*vide infra*). The new compound **9** crystallized with two molecules of $DBTO_2$ on cooling a reaction mixture at −20 °C. Suitable crystals for X-ray diffraction studies were obtained, allowing full characterization of complex **9**. The corresponding ORTEP representation is depicted in Figure 3.

Complex **9** displays an arrangement of two platinum centers in a square-planar geometry with bridging $SO_2$. The average P–Pt–P angle is 86.25(2)°, typical of a diphosphine. The Pt–Pt distance is 3.605(10) Å, approximately 0.145 Å longer than the sum of their van der Waals radii, indicative of the absence of a metal–metal interaction. The average Pt–S distance is typical of a single-bond interaction at 2.338 Å in closely related compounds. Noteworthy, the symmetric unit exhibits an interaction of the $SO_2$ bridging moiety with the aromatic hydrogens of a cocrystallized $DBTO_2$, since several short O–H and S–H contacts, which probably stabilize **9** in the solid state, are observed, for instance, C(5)–H(5)···O(3) 2.524 (1), C(8)–H(8)···O(3) 2.330(2), C(3)–H(3)···O(4) 3.051(2), C(2)–H(2)···O(4) 2.689(3) Å, and C(8)–H(8)···S(3) 3.0810(1) Å. Additionally, there is a C(3)–H(3)···Pt(1) interaction with a distance of 3.080(1) Å.

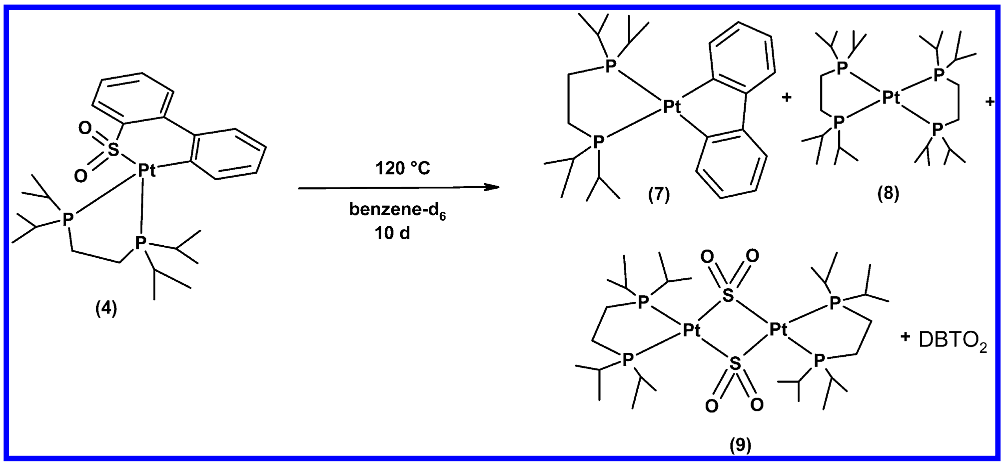
We envisaged an alternative synthesis for complex **4** via the independent preparation of complex **7**, according to the reaction depicted in Scheme 6. The formation of platinacycle **7** was confirmed by multinuclear NMR (see Experimental Section). However, the insertion reaction of $SO_2$ gas into **7** to yield **4** was unsuccessful using a variety of reaction conditions, probably due to the high stability of the chelating biphenyl moiety.[35]

**Table 2. Summary of Crystallographic Data for 4 and 9**

| | 4 | 9 |
|---|---|---|
| empirical formula | $C_{29}H_{43}O_2P_2PtS$ | $C_{58}H_{86}O_8P_4Pt_2S_4$ |
| fw | 712.72 | 1553.57 |
| temperature (K) | 193(2) | 193(2) |
| wavelength (Å) | 0.71073 | 0.71073 |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ |
| unit cell dimens | $a$ = 12.30300(10) Å | $a$ = 11.10870(10) Å |
| | $b$ = 17.4680(2) Å | $b$ = 16.7375(2) Å |
| | $c$ = 13.8190(2) Å | $c$ = 17.0714(2) Å |
| | $\alpha$ = 90° | $\alpha$ = 90° |
| | $\beta$ = 98.4850(10)° | $\beta$ = 93.1390(10)° |
| | $\gamma$ = 90° | $\gamma$ = 90° |
| volume (Å$^3$) | 2937.32(6) | 3169.36(6) |
| $Z$ | 4 | 2 |
| density(calcd) (g cm$^{-3}$) | 1.612 | 1.628 |
| $\mu$ (mm$^{-1}$) | 4.981 | 4.692 |
| $F$(000) | 1428 | 1556 |
| cryst color | colorless | yellow |
| cryst size (mm) | 0.2 × 0.15 × 0.1 | 0.3 × 0.25 × 0.15 |
| $\theta$ range (deg) | 3.12 to 25.35 | 3.05 to 26.05 |
| no. reflns collected | 20 592 | 21 700 |
| no. independent reflns | 5371 [$R$(int) = 0.0251] | 6251 [$R$(int) = 0.0247] |
| obsed reflns | 4648 | 5394 |
| absorp corr | analytical | analytical |
| max. and min. transmn | 0.6105 and 0.4258 | 0.891 and 0.779 |
| refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| data/restraints/params | 5371/0/324 | 6251/0/343 |
| GOF on $F^2$ | 1.004 | 0.999 |
| final $R$ indices [$I > 2\sigma(I)$] | R1 = 0.0151, wR2 = 0.0340 | R1 = 0.0180, wR2 = 0.0369 |
| $R$ indices (all data) | R1 = 0.0206, wR2 = 0.0347 | R1 = 0.0249, wR2 = 0.0378 |

## ■ CONCLUSIONS

The current results confirm the occurrence of a ring-opening reaction during the catalytic oxidesulfurization of dibenzothiophene sulfones. The key intermediary is a sulfinametallacycle, Scheme 5. Thermolysis Reaction of [(dippe)Pt($\kappa^2$-*C*,*S*-DBTO$_2$)] (4)



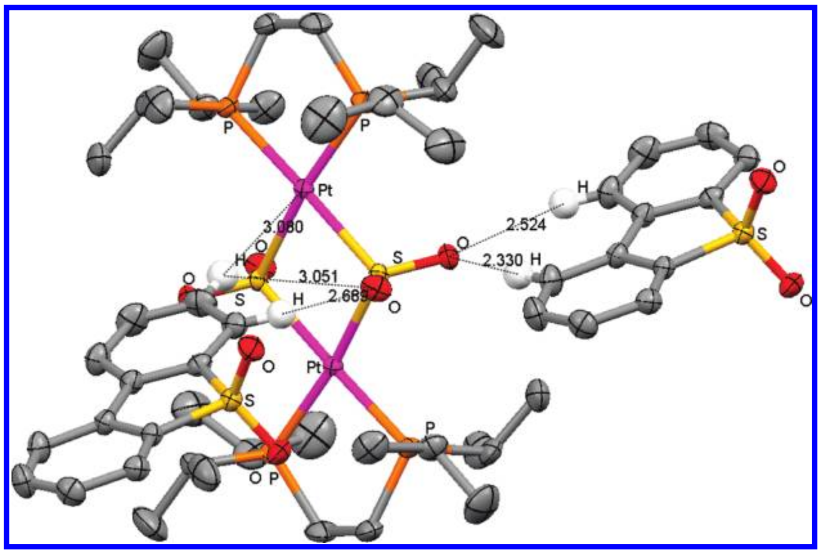
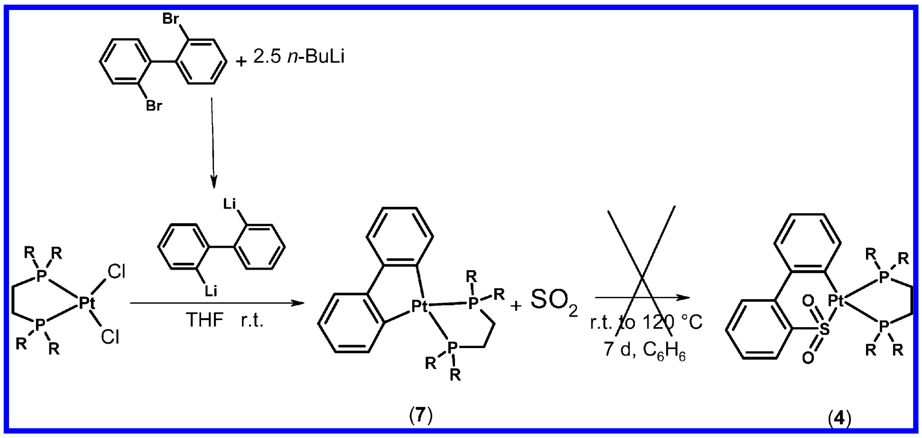


**Figure 3.** ORTEP drawing for **9**·2DBTO$_2$. Ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P(1)–Pt(1) 2.3082(6), P(2)–Pt(1) 2.3040(6), Pt(1)–S(3) 2.3321(6), O(4)–S(3) 1.4807(17), O(3)–S(3) 1.4858(15). Bond angles (deg): P(2)–Pt(1)–P(1) 86.25(2), P(2)–Pt(1)–S(3) 96.21(2), O(2)–S(2)–O(1) 117.18(10), P(1)–Pt(1)–S(3) 177.18(2), P(2)–Pt(1)–S(3) #2 171.29(2). Short contact interactions (Å): O(3)···H(5) 2.524(1), O(3)···H(8) 2.330(2), S(3)···H(8) 3.083, O(4)···H(3) 3.051, O(4)···H(2) 2.689 (3), S(3)···H(8) 3.0810(1), Pt(1)···H(3) 3.080(1).

Scheme 6. Alternative Synthesis of Complex 4



which in the case of nickel is a rather elusive compound to be isolated or detected in solution, while in the case of platinum and DBTO$_2$, the complex could be structurally characterized as complex **4**. Sulfones 4-MeDBTO$_2$ and 4,6-Me$_2$DBTO$_2$ also form sulfinaplatinacycles in solution, which allowed high oxidesulfurization yields.

Thermolysis of complex **4** confirms the production of a sulfur-free biphenyl moiety (complex **7**) and the extrusion of sulfur as $SO_2$ (complex **9**). The release of $SO_2$ turned out to be an irreversible process under the explored reaction conditions.

## ■ EXPERIMENTAL SECTION

**General Considerations.** All procedures were carried out using standard Schlenk and glovebox techniques, using an MBraun glovebox (<1 ppm $H_2O$, $O_2$) under high-purity argon (Praxair, 99.998%). THF (J.T. Baker) was dried using an MBraun MB-SPS solvent purification system. Toluene (J.T. Baker) was dried over sodium and distilled under an inert atmosphere. Superhydride $Li(BEt_3)H$ (1.0 M, THF solution), n-BuLi (2.5 M, hexanes solution), and $SO_2$ (gas, 99.9%) were supplied by Aldrich. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves in the glovebox, for at least 24 h prior to use. DBT, MeDBT, and $Me_2DBT$ were purchased from Aldrich and were used as received to prepare the corresponding sulfones: $DBTO_2$, $MeDBTO_2$, and $Me_2DBTO_2$, which were dried *in vacuo* prior to their use.[36] The chelating bisphosphine ligand, dippe, was prepared from 1,2-bis(dichlorophosphino)ethane (Aldrich) and the corresponding isopropylmagnesium chloride solution (2.0 M, in THF solution, Aldrich).[37] $[(dippe)Pt(\mu\text{-}H)]_2$ was prepared as reported[38] from $[(dippe)PtCl_2]$ using a Na/Hg amalgam in 1 atm of $H_2$ in a THF solution at room temperature. Neutral alumina and silica were heated at 200 °C under vacuum for 2 d and stored in the glovebox. All other chemicals and filter aids were reagent grade and were used as received. Isolated complexes were purified by crystallization or column chromatography. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were determined at room temperature in benzene-$d_6$. $^1H$ chemical shifts ($\delta$, ppm) are reported relative to the residual proton resonances in the corresponding deuterated solvent. $^{31}P\{^1H\}$ NMR spectra were recorded relative to external 85% $H_3PO_4$. All spectra were carried out using thin-wall (0.38 cm) WILDMAD NMR tubes with J. Young valves. Catalytic experiments were carried out in a 100 mL Parr, T315SS stainless steel reactor. Elemental analyses (EAs) were also performed by USAI-UNAM using a Perkin-Elmer 2400 microanalyzer. Unless otherwise stated, EAs of pure compounds showed variable inconsistencies due to their high oxygen sensitivity and were not reported; however, most of them displayed satisfactory MS-EI$^+$. Mass spectrometry determinations (MS-EI$^+$) of pure compounds were performed by USAI-UNAM using a Thermo-Electron DFS.

**Catalytic Deoxydesulfurization of Sulfones of Dibenzothiophene.** A typical experiment was performed as follows: in the glovebox, a 50 mL Schlenk flask was charged with $[Pt(dippe)H]_2$ (0.002 g, 0.0031 mmol) and $DBTO_2$ (0.067 g, 0.31 mmol), added in a 10:2 v/v mixture of toluene (10 mL) and THF (2 mL). The resulting solution was stirred for 30 min at room temperature, venting all the released gases in the drybox. After this time, a 3.0 M solution of MeMgBr (0.62 mL, 1.86 mmol) was added to the mixture, a color change being observed from red to orange. The reaction mixture was then heated to reflux for 4 days under argon in a Schlenk line. A blend of precipitates (beige to brown) was observed to form gradually. After that time, the reaction mixture was then acid-hydrolyzed at room temperature. A strong effervescence was observed upon addition of mineral acid (HCl, 10 mL, 10% vol), due to the release of $H_2S$ (***caution poisonous gas!***), which was bubbled into a trap with a $Pb(CH_3COO)_2$ solution, thereby precipitating PbS as a black solid. After venting all gases, the remaining mixture was extracted with $CH_2Cl_2$ (3 × 7 mL), and the organic layers were separated, dried, and analyzed by GC-MS. To note, if a characterization of the solid was required, acid hydrolysis was avoided and the reaction mixture was centrifuged and washed with hexanes and acetone. The solid was dried for 4 h under high vacuum and analyzed by powder-XRD, confirming the presence of MgO, $MgBr_2$, and MgS.

**Preparation of [Pt(dippe)($\eta^2$-(*C*,*S*-DBTO$_2$)] (4).** A representative experiment was carried out as follows: in a drybox a Schlenk tube with a Teflon valve was charged with $[(dippe)PtH]_2$ (0.04 g, 0.0436 mmol) dissolved in 1 mL of benzene and $DBTO_2$ (0.018 g, 0.0872 mmol) suspended in the same solvent (3 mL). The mixture was sealed and warmed at 120 °C in a silicone oil bath. After 24 h, the heating was stopped and the solution was filtered through a 2 cm column of alumina, yielding a yellow solution. After solvent evaporation a yellow solid was obtained, which was vacuum-dried for 6 h. $^1H$ NMR: $\delta$ 8.5−8.45 (m, 1H), 7.443−7.180 (m, 2H), 7.05−6.95 (m,1H), 6.9−6.85(m, 1H), 6.75−6.7(m,2H), 2.5−1.5 (br m, 4H), 1.5−1.2 (m 4H), (m, 24 H). $^{31}P\{^1H\}$ ($C_6D_6$, 121.32 MHz): $\delta$ 71.597 ($^1J_{Pt-P}$ = 1941 Hz), 55.29 ($^1J_{Pt-P}$ = 2473 Hz). IR [cm$^{-1}$]: 1269m, 1079s, 1022s. [FAB$^+$]: *m*/*z* 675. Mp: 141−142 °C; dec above 180 °C. Anal. Calcd: C 49.35, H 6.9. Found: C 49.13, H 6.80. Yield: 80%.

Compounds **5** (yield 76%) and **6** (yield 43%) were prepared and monitored in a completely similar way. Key $^{31}P\{^1H\}$ signals in $C_6D_6$ (121.32 MHz): $\delta$ 54.54, $^1J_{Pt-P}$ = 2426 Hz, 69.73, $^1J_{Pt-P}$ = 1932 Hz, for **5**; 54.54, $^1J_{Pt-P}$ = 2426 Hz, 69.73, $^1J_{Pt-P}$ = 1932 Hz, for **6**.

**Thermolysis Reaction for Complex 4.** A NMR tube with a J. Young valve was loaded with 0.04 g of complex **4** and 0.75 mL of benzene-$d_6$, monitored every 4 h for 10 d, heating from room temperature to 120 °C. The relative yields of **7** (60%), **8** (10%), and **9** (30%) were obtained by integration of the characteristic signals by $^{31}P\{^1H\}$ NMR. An authentic sample of **7** was prepared as described (*vide infra*). Crystals for **9** were obtained on cooling the reaction mixture at −20 °C in the freezer within the drybox.

**Preparation of [Pt(dippe)($\eta^2$-(*C*,*C*-C$_{12}$H$_8$)] (7).** A stirred solution of 2,2′-dibromobiphenyl (0.05 g, 0.16 mmol) in 10 mL of THF was reacted by dropwise addition of *n*-buthyllithium (0.147 mL of a 2.5 M solution of THF) in an ice/acetone bath. Then the mixture was warmed to room temperature and stirred for 1 h. A suspension of $[(dippe)PtCl_2]$ (0.84 g, 0.16 mmol) in THF (3 mL) was then added, and the resulting solution was stirred at room temperature for 2 h and the solvent was then removed under vacuum. The resulting residue was extracted with toluene and filtered. Toluene was then evaporated under vacuum, and the residue yielded a yellow powder. Yield: 87%. $^{31}P\{^1H\}$ NMR ($C_6D_6$, 121.32 MHz): $\delta$ 63.32 ($^1J_{Pt-P}$ = 1676 Hz).

**Reactivity of Complex 7 with SO$_2$.** A benzene-$d_6$ solution of **7** (0.039 g, 0.06.8 mmol) was bubbled with $SO_2$ (***caution, poisonous gas!***) at −70 °C for 10 min. Then the system was sealed and gently heated from room temperature to 120 °C during 10 days without any changes in the reaction mixture, monitored by $^{31}P\{^1H\}$ NMR ($C_6D_6$, 121.32 MHz): $\delta$ 63.32 ($^1J_{Pt-P}$ = 1676 Hz).

**X-ray Structure Determination.** The crystals for compounds **4** and **9** were first cryoprotected using Paratone-N and mounted on glass fibers; immediately, the crystals were cooled at 193(2) K using a Cryojet cryostream (Oxford Cryosystems device). Diffraction data were collected on an Oxford Diffraction Gemini diffractometer with a CCD-Atlas area detector using a graphite-monochromated radiation source, $\lambda_{Mo\ K\alpha}$ = 0.71073 Å. CrysAlisPro and CrysAlis RED software packages[39a] were used for data collection and data integration. All data sets consisted of frames of intensity data collected with a frame width of 1° in $\omega$, a counting time of 27 to 30 s/frame, and a crystal-to-detector distance of 55.00 mm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans. Final cell constants were determined by a global refinement; collected data were corrected for absorbance by using analytical numeric absorption correction[39b] using a multifaceted crystal model based on expressions of the Laue symmetry using equivalent reflections.

Structure solution and refinement were carried out with the programs SHELXS97 and SHELXL97; for molecular graphics, ORTEP-3 for Windows was used.[39d] The software used to prepare material for publication was WinGX.[39e]

Full-matrix least-squares refinement was carried out by minimizing $(F_o^2 - F_c^2)^2$. All non-hydrogen atoms were refined anisotropically. H atoms attached to C atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C−H = 0.95−1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for aromatic, methylene, methyne, and methyl groups. Crystal data and experimental details of the structure determination are listed in the Supporting Information.

## ■ ASSOCIATED CONTENT

### Supporting Information

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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