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Equilibria of the Thiametallacycles with Tris(triethylphosphine)platinum(0) and Dibenzothiophene, Benzothiophene, or Thiophene: The Hydrodesulfurization Reaction

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Abstract: The thiaplatinacycles, [$(PtSC_{12}H_8)(PEt_3)_2$], **1**, [$(PtSC_8H_6)(PEt_3)_2$], **2**, and [$(PtSC_4H_4)(PEt_3)_2$], **3**, in which $Pt(PEt_3)_2$ has inserted into one C−S bond of dibenzothiophene (DBT), benzothiophene (BT), and thiophene (T), respectively, are formed by the *reversible* reaction of tris(triethylphosphine)platinum(0) with the thiophene. The structure of complex [$(PtSC_8H_6)(PEt_3)_2$] (**2**) was confirmed by an X-ray determination that showed a square-planar Pt(II) bound to two *cis* PEt_3 ligands, and to the S and the CH=, in a six-membered Pt−S−C−C−C−C ring [Pt−S(1), 2.315(5) Å; Pt−C(4), 2.035(19) Å; Pt−P(1), 2.301(5) Å, *trans* to S(1); and Pt−P(2), 2.386(5) Å, *trans* to C(4); P(1)−Pt−P(2), 97.6(2)°; S(1)−Pt−P(2), 87.0(2)°; S(1)−Pt−C(4), 88.6(6)°; P(1)−Pt−C(4), 86.8(6)°]. The adducts **1** and **3**, derived from DBT and T, have been shown to have similar structures spectroscopically. The free thiophenes and $Pt(PEt_3)_3$ are regenerated on heating complexes **1**−**3** with Et_3P; [$(PtSC_aH_b)(PEt_3)_2$] + $Et_3P \rightleftharpoons$ [$Pt(Et_3P)_3$] + SC_aH_b. K_{eqm} = [$Pt(Et_3P)_3$][SC_aH_b]/[$PtSC_aH_b)(PEt_3)_2$][Et_3P] and is 10 for **1** (DBT) and **3** (T) and 1 for **2** (BT) at 100 °C. The complexes **1**−**3** undergo a variety of cleavage reactions; thus, the Pt−C bond in **1** is cleaved by HCl to give 2-phenylthiophenol and [$Pt(PEt_3)_2Cl_2$], and all three complexes are degraded by hydride reagents to give the completely desulfurized hydrocarbons: biphenyl from **1**, styrene and ethylbenzene from **2**, and butadiene and butenes from **3**. When the reactions are carried out with Et_3SiH as reducer, the complex [$Pt(SH)(H)(PEt_3)_2$] is identified among the products, together with [$Pt(Et_3Si)(H)(PEt_3)_2$]. The former is a coproduct of the desulfurization, while the latter arises from addition of Et_3SiH to [$Pt(PEt_3)_2$] (from reversal of the formation of [$(PtSC_aH_b)(PEt_3)_2$]) and is accompanied by the formation of the free thiophene. Under comparable conditions, the amount of desulfurization decreases in the order BT complex **2** (73%) > DBT complex **1** (50%) > T complex **3** (ca. 4%). These hydride reactions show the novel feature that the C−S bond is cleaved as well as the Pt−C bond; possible mechanisms for the platinum and for the known nickel- and hydride-promoted hydrodesulfurization (HDS) reactions are discussed.

Introduction

There is currently much interest in the reactions that occur in metal-promoted removal of sulfur (hydrodesulfurization, HDS) during the pretreatment of fossil fuels (e.g., crude oil) prior to refining. HDS removes undesirable impurities, such as sulfur-containing molecules. This prevents poisoning of the reforming catalysts, produces sulfur-free fuels, and is practiced on a vast scale using a sulfided metal catalyst (e.g., Co−Mo on alumina) at high temperature and pressure.[1,2] However, the highest HDS activity is shown by platinum metals.[3]

Heterocycles such as thiophenes (T), benzo[*b*]thiophenes (BT), and dibenzo[*b*,*d*]thiophenes (DBT) present problems as they occur in substantial amounts, particularly in heavier crudes, and are rather resistant to normal HDS techniques. Thus, there is considerable interest in developing new HDS methods to treat these compounds, and model studies are being carried out to establish mechanisms and to probe new possibilities. The thiophenes and benzothiophenes bind to metal centers by a variety of modes, including η^1-S, η^5- and η^4-T to the thiophene, and η^6 to the benzo rings.[4]

Two different approaches have been developed to give information on the HDS process. The first assumes that hydrogenation of the unsaturated heterocycle to a saturated (or partially saturated) species is followed by desulfurization, while the second postulates that desulfurization occurs first and that the product moieties are hydrogenated in subsequent steps. The first hypothesis has enjoyed considerable vogue, but attention is now increasingly turning to the second. Here, loss of S is presumed to occur via C−S cleavage processes involving the insertion of a metal into the C−S bond, followed by reaction with sources of H. Since this insertion can be considered as an oxidative addition, one may expect it to be promoted by electron rich metal centers.

Although a number of ring-opening oxidative additions have been reported (involving low-valent cobalt, rhodium, iridium, or ruthenium complexes), in many cases, the subsequent reactions do not lead to complete HDS but to isolated complexes that still retain one C−S bond, even after further reduction. By contrast, nickel compounds have also long been known to be active catalysts for HDS in organic synthesis and to lead to

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1995.

(1) Weisser, O.; Landa, S. *Sulphide Catalysts, Their Properties and Applications*; Pergamon: Oxford, 1973.

(2) Angelici, R. J. *Acc. Chem. Res.* **1988,** *21,* 387 and references therein.

(3) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981,** *67,* 430. Vissers, J. P. R.; Groot, C. K.; van Oers, E. M.; de Boer, V. H. J.; Prins, R. *Bull. Soc. Chim. Belg.* **1984,** *93,* 813.

(4) Reviews by: Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991,** *39,* 259. Angelici, R. J. *Coord. Chem. Rev.* **1990,** *105,* 61. Sanchez-Delgado, R. A. *J. Mol. Catal.* **1994,** *86,* 287. For a summary of bonding modes and the results of MO calculations, see: Harris, S. *Organometallics* **1994,** *13,* 2628.

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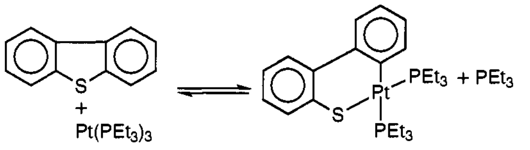
non-sulfur-containing organic products;[5] however, mechanistic details are sparse. We have focused on platinum because (a) it has a well-explored low-valent chemistry with readily accessible and easily tuned complexes and (b) it is the most kinetically inert element of the triad and hence can model catalytic reactions undergone by the lighter and more labile elements.

This approach is very versatile and capable of wide development since it uses readily accessible systems with simple ligands. In these first studies, we describe the use of platinum as the metal that oxidatively adds to the C−S bond and give details of the two-step hydrodesulfurization of dibenzothiophene into biphenyl, of benzothiophene into styrene, and of thiophene into C_4 hydrocarbons, in each case via a defined thiaplatinacycle derived from tris(triethylphosphine)platinum(0). The results also allow us to understand features of the reactions of other metals that have hitherto been obscure. One such feature is that the initial insertion of the platinum into the C−S bond giving the thiaplatinacycle is reversible, and further, that the equilibria are influenced by the nature of the thiophene, the metal, and the other co-ligands. This is likely to be true in general for all HDS systems, and we may anticipate that the position of the equilibrium will be important in determining the overall extent of HDS for a given molecule. In turn, this will allow predictions to be made for the rational design of HDS catalysts. The work we describe allows ready HDS under rather simple conditions, especially for the benzothiophenes, with the addition of hydrides. However, the use of acid in place of hydrides for the decomposition of the thiametallacycle gives the potential to allow the conversion of thiophenes into thiols. A preliminary communication on a part of the DBT work has appeared.[6]

Results and Discussion

(i) Formation and Structures of Adducts with Dibenzothiophene, Benzothiophene, and Thiophene. Tris(triethylphosphine)platinum(0) reacted readily with dibenzothiophene (DBT) in toluene at 70 °C. One triethylphosphine was liberated, and the stable ivory-colored crystalline adduct, [$(PtSC_{12}H_8)(PEt_3)_2$] (**1**), was obtained in 92% yield. Microanalysis and NMR spectroscopy indicate that the adduct has the structure (eq 1) with a six-membered ring ("thiaplatinacycle") formed by the insertion of $Pt(PEt_3)_2$ into one C−S bond of the DBT.[7]



(1)

1

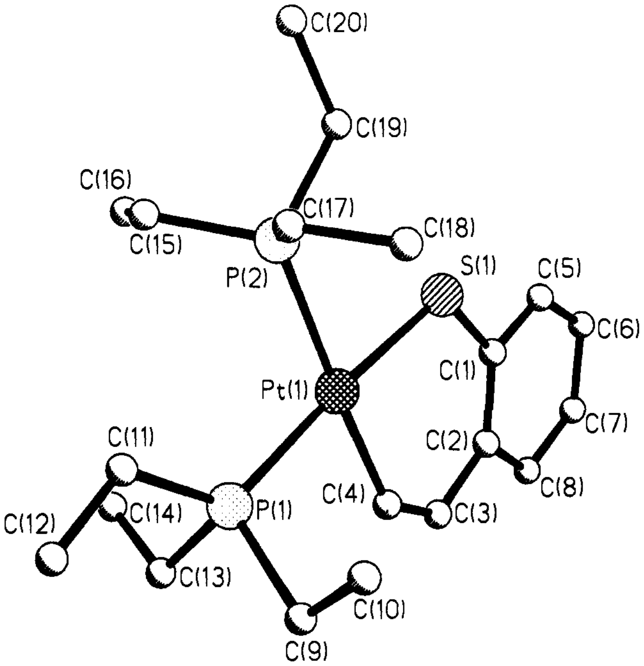
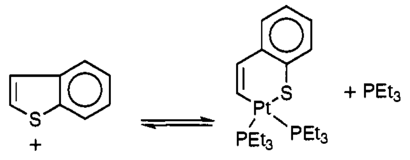


Figure 1. Representation of the X-ray structure determination of complex **2**, [$(PtSC_8H_6)(PEt_3)_2$]; hydrogens omitted.

Tris(triethylphosphine)platinum(0) also reacted with benzothiophene and with thiophene to form analogous thiaplatinacycles, **2** and **3**. For example, the vinylic *C*H resonance in the BT complex **2** at δ 131.1 shows both *cis* and *trans* two-bond couplings (^2J(P−C) = 9 and 98 Hz, respectively). The adduct **2** between $Pt(PEt_3)_2$ and benzothiophene (eq 2) gave better quality crystals, which permitted a good X-ray structure determination. This confirmed that a thiaplatinacycle had been formed and also showed that the Pt had entered into the S−C(2) bond of BT (i.e., between S and the vinylic CH=CH). None of the isomeric thiaplatinacycle, with the Pt between the S and the aromatic ring of BT, was detected.



(2)

2

The structure determination of **2** shows that the molecule is a *cis*-bis(triethylphosphine)platinum(II) complex of the bidentate 2-(2-thiolatophenyl)ethenyl ligand and adopts a fairly flat shape (Figure 1). The coordination geometry of the platinum is approximately square-planar, as expected (rms deviation of P_2SC plane, 0.031 Å; displacement of platinum, 0.023 Å): P(1)−Pt−P(2), 97.6(2)°; S(1)−Pt−P(2), 87.0(2)°; S(1)−Pt−C(4), 88.6(6)°; P(1)−Pt−C(4), 86.8(6)°. The angle P(1)−Pt−P(2) is substantially larger than 90°, presumably due to repulsion between the ethyl substituents on the phosphines, while the other three angles are correspondingly smaller. The metal coordination plane is inclined to the planar benzo ring (rms deviation, 0.015 Å; displacements of S(1) and ethenyl C(3), 0.024 and −0.061 Å, respectively) by 11.3° and to the alkene plane (rms deviation of PtC_3, 0.013 Å) by 8.6°. The alkene plane is inclined to the benzo plane by 7.8°, while the internal bond angles at C(3) and C(4) are 128 and 137°, respectively. Key bond lengths in complex **2** are Pt−S(1), 2.315(5) Å; Pt−C(4), 2.035(19) Å; Pt−P(1), which is *trans* to S(1), 2.301(5) Å; and Pt−P(2), which is *trans* to the vinylic carbon C(4), 2.386(5) Å. The last is a manifestation of the high *trans* influence of the σ-bonded carbon.

X-ray crystal structure determinations have been carried out for a dinuclear iron[8] and a mononuclear iridium[9] complex derived from benzothiophene. In each case, the insertion

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[5] See, for example: (a) Eisch, J. J.; Hallenbeck, L. E.; Han, K. I. *J. Org. Chem.* **1983**, *48*, 2963; *J. Am. Chem. Soc.* **1986**, *108*, 7763. (b) Luh, T.-Y.; Ni, Z.-J. *Synthesis* **1990**, 89. Becker, S.; Fort, Y.; Vanderesse, R.; Caubere, P. *J. Org. Chem.* **1989**, *54*, 4848. Back, T. G.; Baron, D. L.; Yang, K. *Ibid.* **1993**, *58*, 2407.

[6] Garcia, J. J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 12200.

[7] An X-ray diffraction study of the crystals was undertaken, but the data obtained did not allow complete refinement. Data of the structure determination (R = 0.075) show that **1** contains a racemic twin with two symmetry independent molecules, a total of 4, in space group $P2_1$. All four molecules are structurally identical and contain a puckered six-membered Pt−S−C−C−C−C ring, formed by the insertion of $Pt(PEt_3)_2$ into one C−S bond of DBT. We are grateful to Dr. K. M. A. Malik and Professor M. B. Hursthouse (SERC Crystallography Service, Cardiff) for the information.

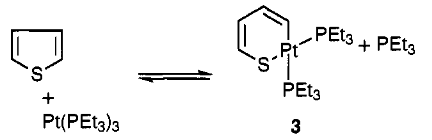
[8] Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171.

occurred in the same sense as in complex **2**, and none of the other isomer appears to have been produced. Choi and Angelici[10] also found that when BT is S-bonded to the metal, the S−C(vinyl) bond is lengthened relative to the uncomplexed heterocycle, but the S−C(aryl) bond length does not change on complexation. They argue that the former bond is thus activated toward cleavage, which indeed occurs in that sense, and that the other is not. Inspection shows that the S−C(vinyl) bond is also more open than the S−C(aryl) bond and hence may be expected to be more reactive to a large nucleophile such as $Pt(PEt_3)_2$ on steric grounds.

Evidence has been cited that suggests that the iridium complex, $[(triphos)(C_8H_6SIr)]^+$, derived from BT has a delocalized C_8H_6SIr π-bonding system,[9] and the situation in some related metallathiabenzenes has recently been analyzed.[11] While the C_8H_6SPt moiety in **2** is also largely planar, the bond lengths (within the constraints posed by the substantial estimated standard deviations for both complexes) suggest that M−C in **2** may be somewhat shorter and that the M−S and C−S distances are a little longer than in $[(triphos)(C_8H_6SIr)]^+$. It may also be noted that the DBT complex **1** has a distinctly nonplanar core. Thus, we conclude that delocalization, if important in these systems, is probably less in the Pt than in the Ir molecule. This may also correlate with the ease of degradation of the thiametallacycles; however, more data are needed concerning the structures of, and the bonding in, such complexes.

Glavee et al.[12] have reported a structure determination of the η^2-bonded platinum complex, $[Pt(PEt_3)_2(\eta^2\text{-S,C-}C_4H_7S)]^+$, obtained from reaction of $[HPt(Et_3P)_2(acetone)]^+$ with 2,3-dihydrothiophene. In this molecule, the Pt binds to S and the adjacent CH but the ring has not opened. Here the angle P(1)−Pt−P(2) is even larger than in **2** (101.8(2)°), but this is not surprising as the angle S−Pt−C opposite is only 46.7°. Bond lengths are similar to those found in **2**, [Pt−S, 2.328(6) Å; Pt−C, 2.12(1) Å; Pt−P, 2.242(5) Å (*trans* to S); 2.306(4) Å (*trans* to CH)].

Thiophene forms a similar complex, **3**, $[Pt(PEt_3)_2(\eta^2\text{-S,C-}C_4H_5)]$, on reaction with tris(triethylphosphine)platinum(0) (eq 3). That this complex contains what may formally be described as a "1-platina-2-thiacyclohexa-3,5-diene" is clear from the analytical and spectroscopic data. The ^{13}C NMR spectrum shows four CH resonances, two of which show no coupling to P or Pt, while the third at δ 124.2 assigned to C(3) shows a ^2J(Pt−C) of 120 Hz. The fourth CH resonance, at δ 131.1, shows coupling to both phosphorus nuclei (^2J(P−C), 10 Hz (*cis*) and 98 Hz (*trans*)) and is assigned to C(4); the chemical shift and the coupling to phosphorus establish that a Pt−CH σ-bond is present. The related $[(triphos)(C_6H_4SIr)]^+$ has been described as a "thiametallabenzene" since both the ^{13}C and the ^1H NMR C_4H_4 resonances appear at lower fields.[11a]



(3)

(ii) Equilibria between Thiophenes and Thiaplatinacycles. We observed that the further reactions of complex **1** frequently led to the reformation of some DBT in addition to degradation products. In our search for the origin of this DBT, we discovered that the thiaplatinacycle product regenerates DBT and $[Pt(Et_3P)_3]$ if it is heated with excess Et_3P. This led to a recognition that DBT and $[Pt(Et_3P)_3]$ on the one hand, and complex **1** on the other, were in equilibrium (eq 1). The same situation was also found for complex **2** and BT (eq 2) and for complex **3** and T (eq 3). We have therefore measured the equilibrium constants for the three processes, by heating the complex (**1**, **2**, or **3**) with 1.5 equiv of PEt_3 in toluene-d_8 at 100 °C and determining the amounts of $[(PtSC_aH_b)(PEt_3)_2]$, $[Pt(Et_3P)_3]$, and C_aH_bS at 100 °C by ^1H and ^{31}P NMR spectroscopy.

The values of the equilibrium constants, $K_{eqm} = [Pt(Et_3P)_3][SC_aH_b]/[(PtSC_aH_b)(PEt_3)_2][Et_3P]$, are 10 for **1** (DBT) and **3** (T) and 1 for **2** (BT). Thus, the thiaplatinacycle from BT, **2**, is the most stable, while those derived from DBT and T are less stable and similar to each other. The situation is complicated by the fact that while the equilibria involving the BT and T adducts are established fast ($\leq$1 h at 100 °C), that with DBT is established more slowly and requires more than 4 h at 100 °C to reach equilibrium.[13] Prolonged heating of the complexes with Et_3P leads to decomposition and the formation of insoluble solids.

The reason for the lower reactivity of **1** is almost certainly the steric constraint between the incoming Et_3P and the two benzo substituents in **1** that hinder the approach to the metal along an axial direction, the likely site of attack. That the metal center in **1** is very crowded, leading to a puckered, nonplanar molecule, is also evident from the ^1H NMR spectrum, which shows the inequivalence of the triethylphosphine CH_2 protons. We estimate a lower limit of ca. 70 kJ/mol for inversion of the nonplanar thiaplatinacycle moiety in **1**,[14] a barrier that we suggest arises from the interaction of the C_6H_4Pt with the *cis*-Et_3P.

While there is precedent for the oxidative addition or reductive elimination in C−S ring opening being facilitated by redox processes[15] or acids and bases,[16] this appears to be the first observation of a reversible thermal process. This reversibility has considerable significance in relation to HDS (see below).

The only other comparative data available relate to the relative stabilities of a series of S-bonded thiophene−ruthenium complexes. For the reaction $[CpRu(CO)_2(T')]^+ + T'' \rightleftharpoons [CpRu(CO)_2(T'')]^+ + T$, K_{eqm} was found to increase when the thiophenes were more heavily substituted by methyls (Me_4T (887) > BT (48) > 2,5-Me_2T (21) > 3-MeT (5) > 2-MeT (3) > T (1)) and T itself was the poorest ligand. A similar series of measurements for $[CpRu(CO)(PPh_3)(T')]^+ + T'' \rightleftharpoons [CpRu(CO)(PPh_3)(T'')]^+ + T'$ showed that DBT bound most strongly and T least strongly to the Ru center (K_{eqm}, DBT (74) > BT (30) > T (1)).[17]

We find that BT and T react faster with $Pt(PEt_3)_3$ than DBT. Assuming that these reactions also go via η^1-S-bonded complexes $[Pt(SC_aH_b)(PEt_3)_n]$ and that the equilibrium constants for Pt(0) vary in the same sense as for Ru(II), this suggests that the rate-determining step is not likely to be formation of the

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[9] Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7505. Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Moneti, S.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1994**, *116*, 4370.

[10] Choi. M.-G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328.

[11] (a) Bianchini, C.; Meli, A.; Peruzini, M.; Vizza, F.; Fredioni, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731. (b) Buys, I. E.; Field, L. D.; Hambley, T. W.; McQueen, A. E. D. *J. Chem. Soc., Chem. Commun.* **1994**, 557.

[12] Glavee, G. N.; Daniels, L. M.; Angelici, R. J. *Organometallics* **1989**, *8*, 1856.

[13] In our earlier paper, we quoted a value for K_{eqm} of 3 for complex **1** (DBT); however, this number only represents the situation after ca. 1 h.

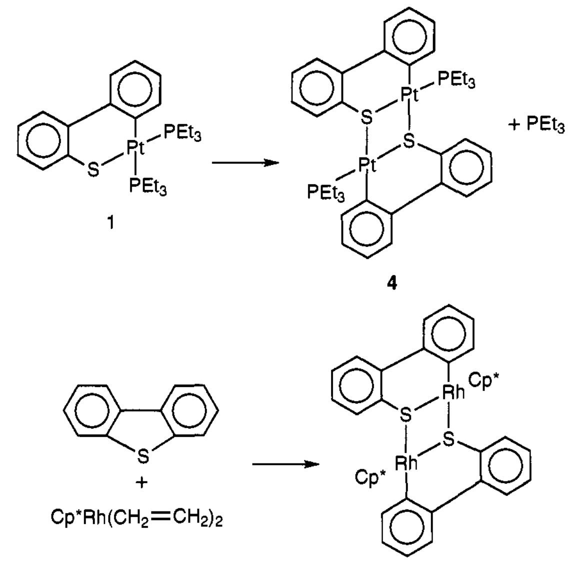
[14] The CH_2 signals of the coordinated Et_3P at 293 K were very sharp, $\Delta\nu$ < 0.5 Hz. From the relationship $k = \pi\Delta\nu$, we can estimate that $\Delta G^{\ddagger}_{293}$ > 70 kJ mol^{-1}.

[15] Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.

[16] Krautscheid, H.; Feng, Q.; Rauchfuss, T. B. *Organometallics* **1993**, *12*, 3273.

[17] Benson, J. W.; Angelici, R. J. *Organometallics* **1993**, *12*, 680.

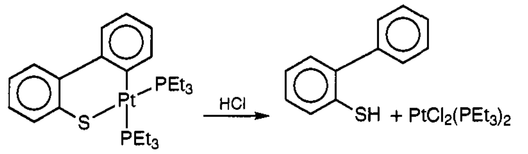
Scheme 1



intermediate S-bonded complex but rather the oxidative addition of the thiophene to the Pt center within the intermediate.

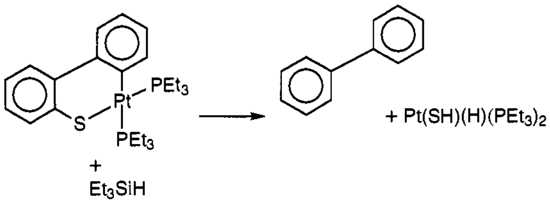
(iii) Thermal Reactions and Attempted Hydrogenation of Complex 1. No reaction occurred between the thiaplatinacycle **1** with hydrogen below 70 °C at 1 atm, but after 12 h at 70 °C, a white complex, **4**, was isolated. The ^{1}H NMR spectrum showed no signals due to hydrogenation products or hydrides, and the same product was obtained when the reaction was carried out under argon. Spectroscopic data showed the presence of one triethylphosphine and one DBT residue in the molecule, and analytical and molecular weight data were consistent with the dimeric formulation, $[\{Pt(Et_3P)(DBT)\}_2]$. The structure shown in Scheme 1 is proposed on the basis of the closely related complex $[\{(Cp^*)Rh(C_{12}H_8S)\}_2]$, a dinuclear species containing dibenzorhodiathiacycles linked by S$-$Rh bridges, which is formed when $[(Cp^*)Rh(C_2H_4)_2]$ reacts with DBT.[18]

(iv) Reaction of Complex 1 with Acid: 2-Phenylthiophenol from DBT. The reaction of complex **1** with protonic acids led to Pt$-$C bond cleavage. Thus, **1** reacted with an excess of HCl gas in $CDCl_3$ under ambient conditions to give *cis-* and *trans-*$[PtCl_2(PEt_3)_2]$[19] (**5a**, 90% and **5b**, 10% yield) and free 2-phenylthiophenol (95%, eq 4). Overall, therefore, this procedure represents a highly efficient and unusual two-step transformation of DBT into 2-phenylthiophenol. In the first step, the thiaplatinacycle is formed by insertion of Pt into the C$-$S bond, while in the second step, two protons derived from HCl cleave the thiaplatinacycle Pt$-$C and Pt$-$S bonds.



(4)

(v) Hydrodesulfurization Reactions of the Thiaplatinacycles 1, 2, and 3. The reactions with hydrides caused cleavage of both the Pt$-$C and the C$-$S bond in the DBT complex **1**. Different hydride reagents showed slightly different reactivities and slightly different metal complex products, but biphenyl was the common organic cleavage product; the data are summarized in Table 1. Thus, reaction of complex **1** with excess triethylsilane in toluene (reflux, 3 h) gave biphenyl (56%), DBT (32%), *trans*-$[Pt(SH)(H)(PEt_3)_2]$[20] (**6**, 50%), and *cis*-$[PtH(SiEt_3)(PEt_3)_2]$[21] (**7**, 31%). We propose that the biphenyl and **6** arise from HDS (eq 5), while DBT and **7** (eq 6) arise via reversal of reaction 1. In support of this proposal, we find that Et_3SiH reacts immediately with $Pt(PEt_3)_3$ in toluene to give *cis*-$[PtH(SiEt_3)(PEt_3)_2]$, **7**, within the time required for mixing.



(5)

$$\underset{\mathbf{1}}{[Pt(SC_{12}H_8)(PEt_3)_2]} + Et_3SiH \rightarrow DBT + \underset{\mathbf{7}}{[Pt(SiEt_3)(H)(PEt_3)_2]} \quad (6)$$

$$\underset{\mathbf{6}}{\textit{trans}\text{-}[Pt(SH)(H)(PEt_3)_2]} + HCl \rightarrow H_2S + \underset{\mathbf{8}}{[Pt(Cl)(H)(PEt_3)_2]} + \underset{\mathbf{5}}{[PtCl_2(PEt_3)_2]} \quad (7)$$

Addition of a saturated solution of HCl gas in $CDCl_3$ released H_2S (47%) from **6** and converted the complexes into a mixture of $[Pt(Cl)(H)(PEt_3)_2]$[22] (**8**, 10%) and **5a** + **5b** (90%; *cis-*:*trans-*, 9:1), eq 7.

Complex **1** was also degraded to biphenyl (50% after 72 h), DBT (16%), *cis*-**5a** and *trans*-**5b** (3%), *trans*-$[Pt(SH)(H)(PEt_3)_2]$ (**6**, 53%), and *trans*-$[PtHCl(PEt_3)_2]$[23] (**8**, 7% by NMR in $CDCl_3$) when it was reacted with $NaBH_4$ (in THF/2-propanol). However, this reaction was quite slow, and only 6% biphenyl was formed after 8 h at ambient temperature.

By contrast, the reaction of **1** with Red-Al ($Na[AlH_2(OCH_2CH_2OMe)_2]$) (Aldrich) in toluene was very exothermic (with evolution of gas), even at 0 °C, and was complete after a few minutes at 20 °C. After workup, the organic products were analyzed to be biphenyl (60%) and DBT (40%) by HPLC and the complexes were identified as *cis*-**5a** and *trans*-**5b** (34%), **6** (35%), **8** (30%),[23] and free PEt_3 by ^{31}P NMR spectroscopy in $CDCl_3$.

The reaction of **1** with $LiAlH_4$ (in THF) was similarly energetic to that with Red-Al; the products were biphenyl (38%), DBT (15%), *trans*-**5b** (20%), **6** (5%), **8** (75%),[23] and free PEt_3.

Similar degradation reactions were also carried out on the complex **2** derived from BT. Thus, **2** reacted with triethylsilane (toluene, 3 h reflux) to give the desulfurized products styrene (61%) and ethylbenzene (12%); in addition, BT (26%) was found. The complexes identified (NMR in toluene-d_8) were the HS and the Et_3Si hydrides **6** (70%) and **7** (30%). These data again provide good evidence for the coexistence of two reaction paths, one (eq 8, ca. 70%) leading to desulfurization and the formation of the HS complex **6**, the other (eq 9, ca.

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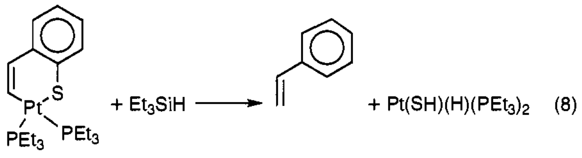
[23] The NMR spectra of the crude complexes from the reactions with $NaBH_4$, $Na[AlH_2(OCH_2CH_2OMe)_2]$, or $LiAlH_4$ (in toluene or THF) were broad and poorly resolved. Thus, in each case, the quantification was accomplished by measuring the ^{31}P NMR spectra in $CDCl_3$, which gave much sharper spectra; however, as the solvent contained small amounts of HCl, *cis-* and *trans*-$[PtCl_2(PEt_3)_2]$ and *trans*-$[PtHCl(PEt_3)_2]$ were formed.

Table 1. Products from the Reactions of Complexes **1**, **2**, and **3** (P = PEt_3) with Hydrides

complex + reagent	organic, desulfurized (%)	recovered DBT/BT/T (%)	$HSPtH(P)_2$ **6** (%)	$Et_3SiPtH(P)_2$ **7** (%)	$HPtCl(P)_2$ **8** (%)	recovered **1**, **2**, or **3** (%)
1 + Et_3SiH	Ph_2 (56)	DBT (32)	50	31		
1 + $NaBH_4$	Ph_2 (50)	DBT (16)	53	–	7	**1** (37)
1 + Red-Al	Ph_2 (60)	DBT (40)	*a*	–	*a*	
1 + $LiAlH_4$	Ph_2 (38)	DBT (15)	*b*	–	*b*	
2 + Et_3SiH	$PhCH{=}CH_2$ (61) + PhEt (12)	BT (26)	70	30		
2 + $NaBH_4$	$PhCH{=}CH_2$ (22) + PhEt (23)	BT (29)	38	–	10	**2** (26)
2 + Red-Al	$PhCH{=}CH_2$ (24) + PhEt (15)	BT (21)		–		
2 + $LiAlH_4$	$PhCH{=}CH_2$ (48) + PhEt (16)	BT (30)		–		
3 + Et_3SiH	$C_4H_6 + C_4H_8$ (ca. 4)	T (80)	*c*		*c*	

[a] Not quantified, ratio 6:8 = 7:6. [b] Not quantified, ratio 6:8 = 1:15. [c] Not quantified, ratio 6:8 = 1:1.

30%) leading to the loss of BT and the formation of the silyl hydride complex **7**.



2

(8)

$$\underset{\mathbf{2}}{[Pt(SC_8H_6)(PEt_3)_2]} + Et_3SiH \rightarrow BT + \underset{\mathbf{7}}{[Pt(SiEt_3)(H)(PEt_3)_2]} \quad (9)$$

Confirmation is given by the close match between the amounts of the organic products, styrene and ethylbenzene (total 72%), and the amount of **6** (70%), on the one hand, and the amount of BT released (26%) and the formation of complex **7** (30%), on the other. We propose that the styrene is the initial product of the desulfurization and that it is subsequently reduced to ethylbenzene by a platinum–hydride system.

These reactions also proceeded with the other hydrides used above for HDS of complex **1**; the organic products were again styrene and ethylbenzene (see Table 1).

The thiaplatinacycle **3** derived from thiophene was also reacted with triethylsilane; however, the amounts of products were rather small, complexes **6** and **8**[23] (ratio 1:1) were identified spectroscopically, together with small amounts of C_4 hydrocarbons (butadiene, ca. 2%; *cis*- and *trans*-2-butenes, <1%) identified by GC–MS. The major product was free thiophene (80%).

Thus, the HDS reaction also proceeds for complex **3** (eq 10), but to a very much smaller extent than for **1** and **2**. The major pathway here must be reversal of reaction 3. This is not surprising given the fact that the reversal of formation of **3** proceeds to a greater extent and much faster than the corresponding reactions for the complexes derived from BT and DBT.

$$\underset{\mathbf{3}}{[Pt(SC_4H_4)(PEt_3)_2]} + Et_3SiH \rightarrow CH_2{=}CHCH{=}CH_2 + [Pt(SH)(H)(PEt_3)_2] \quad (10)$$

(vi) Mechanistic Considerations. The above data allow us to characterize the platinum-mediated HDS reaction of thiophenes as proceeding in two stages: first, the formation of a six-membered thiaplatinacycle by oxidative addition of a Pt(0) species to the thiophene and second, the cleavage of the Pt–C, Pt–S, and C–S bonds in the thiaplatinacycle. The first stage requires a very electron rich metal center; thus, we find that the triphenylphosphine analog, $Pt(PPh_3)_3$, did not react with the thiophenes under conditions where reaction with $Pt(PEt_3)_3$ proceeded readily.

The thiaplatinacycles are in equilibrium with the thiophene and $Pt(PEt_3)_3$. The position depends on the thiophene; thus, the thiaplatinacycle derived from BT is significantly more stable toward reversion than those derived from DBT and T. In the HDS reactions using Et_3SiH, the yields of hydrocarbon decrease in the order BT complex **2** (73%) > DBT complex **1** (50%) > T complex **3** (ca. 4%). However, 32% DBT was recovered from reaction with the DBT complex **1**, making an effective conversion of over 82%. Similarly, the effective percentage of HDS for the reaction of the BT complex **2** with triethylsilane was over 97%, allowing for recovered BT. The only case where HDS was poor was for the thiophene complex **3**, where 80% of thiophene was found after reaction. This is entirely consistent with our equilibrium measurements and the data that indicate that the back-reaction, regenerating T, is very efficient.

The order of efficiency of HDS, BT > DBT ≫ T, can thus be understood (i) since the thiaplatinacycle **2** from BT shows the least tendency for dissociation and reversion to the free thiophene and (ii) because the rate of regeneration of DBT from **1** is substantially slower than for the other two. This leads to an effective relative activity for regeneration of the free heterocycle of T > DBT > BT. Since it is the complex and not the free heterocycle that is undergoing the HDS, it is not surprising that the order for HDS found is the reverse, BT > DBT > T. Thus, an important general point that emerges from this work is that the effectiveness of an HDS reaction toward a thiophene will depend on the position and rate of attainment of the equilibrium with the thiametallacycle.

Although many interesting reactions have been reported for thiametallacycles obtained by the oxidative addition of various metal complexes (of iron,[24] ruthenium,[25] rhodium,[26] cobalt,[27] or iridium[9,28]) into C–S bonds of heterocycles such as DBT and BT, rather few of them have actually led to clean

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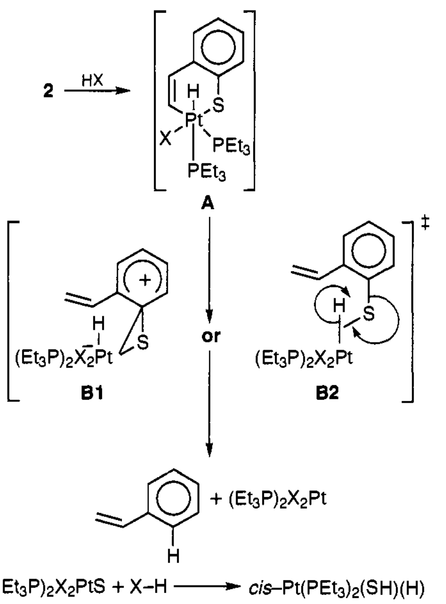
Scheme 2[a]



[a] (X = Et_3Si, etc.).

dsulfurizations, giving a metal sulfide and the hydrocarbon, in the manner that has been demonstrated here.

The HDS reactions of the thiaplatinacycles can be regarded as occurring in two steps: (i) hydride-promoted cleavage of the Pt−C bond and (ii) hydride-promoted cleavage of the remaining C−S bond. It is likely that the first step proceeds via intermediate platinum(IV) hydrides, by X−H oxidative addition. This is illustrated for the BT complex **2** in Scheme 2 where intermediate **A** (proposed tò be formed during the reduction of **2** by hydrides such as Et_3SiH = X−H) transfers H in reductive elimination steps from the metal. Since there is substantial evidence that the M−C bonds in the thiametallacycles are cleaved first,[4] we suggest that in the reaction of **2**, the platinum−alkenyl σ-bond is hydrogenolyzed first to give **B**; the process is then completed, to give styrene and $Pt(Et_3P)_2(SH)(H)$, by the transfer of further hydrides.

The most novel aspect of these reactions is the demonstration that with hydrides, the Pt−S−C linkage is cleaved at the C−S bond to give the hydrocarbon plus a Pt−SH complex. There are several ways this could occur; one is that the platinum complex promotes the release of H atoms, which attack directly at the carbon bearing the sulfur. This is certainly conceivable for the reactions on the thiophene complex **3** itself, since that gives a low yield of a mix of hydrocarbons, as might be anticipated from a radical reaction, but seems less likely for the reactions of **1** and **2**, which are rather clean. Alternative pathways are via a triangular intermediate, **B1**, or by H-transfer in a four-center transition state **B2** (Scheme 2). The type of interaction in **B1** may be analogous to that which has been found in $[Pt(PEt_3)_2(\eta^2\text{-}S,C\text{-}C_4H_7S)]^+$, obtained from reaction of $[HPt(Et_3P)_2(acetone)]^+$ with 2,3-dihydrothiophene,[12] where the metal is interacting strongly with the S and an adjacent CH (Pt−S, 2.328(6) Å; Pt−C, 2.12(1) Å) in a three-membered thiaplatinacyclopropane. At present, we have no way of differentiating between the situations represented by **B1** and **B2**. In either case, the metal complex product would be a platinum(IV) sulfide, which could give the observed *cis*-$Pt(PEt_3)_2(SH)(H)$ by further reaction with X−H.

The reactions described here can be regarded as models for the nickel-catalyzed HDS.[5] Thus, Eisch and co-workers have described the nickel complex Ni(bipy)(cod), two molecules of which were used to desulfurize DBT, giving biphenyl in 45% yield. A donor such as bipy was required to activate the nickel, and comparison with several others showed that bipy was the best of some nine amines that were tried. Other recent studies have suggested that two metal atoms are needed for complete desulfurization where two C−S bonds are broken,[29] since a single metal atom will only cleave one C−S bond. The same effect may be manifest in the nickel desulfurizations, but it is not clear whether the two cleavages are sequential or whether a small nickel cluster is formed which cleaves both. Deuteration studies carried out by Eisch were interpreted in terms of the intermediacy of nickel complexes such as 2-nickelabiphenyl and dibenzonickelole. These workers also noted that the nickel complex in the presence of $LiAlH_4$ increased the amount of HDS of DBT to 93% biphenyl.

The latter data are very close to our results, where we find very good HDS yields from the platinum complexes when treated with hydridic agents. In this case, the phosphines act (in the same way as the amines for nickel) to increase the nucleophilicity of the metal. The efficacy of the various hydrides we tried varied considerably; triethylsilane was consistently good, while the complex boro- and aluminohydrides proved more variable.

Eisch interprets the first step in the interaction of the zero-valent nickel compound and DBT as involving a stepwise electron transfer rather than a nucleophilic attack and suggests the intermediacy of radical anions. We have shown that at least for platinum, there is a clear sequence of steps that leads to the formation of a metal-inserted product, not just a radical anion.

From our data, it would appear that one metal plus a source of hydrides is needed for HDS. The latter can be another transition metal hydride, or it can be a main group hydride such as SiH, BH, or AlH.

Conclusion

We have shown that dibenzothiophene, benzothiophene, and thiophene all react with the nucleophilic platinum(0) complex, $Pt(PEt_3)_3$, to give the appropriate thiaplatinacycles **1**, **2**, and **3** in *reversible* reactions, with equilibrium constants $K_{\mathrm{eqm}} = [Pt(Et_3P)_3][SC_aH_b]/[(PtSC_aH_b)(PEt_3)_2][Et_3P]$ 10 for **1** (DBT) and **3** (T), and 1 for **2** (BT) at 100 °C. The thiaplatinacycles **1** and **2** are very efficiently hydrodesulfurized on reaction with hydrides (for example, Et_3SiH) to give biphenyl and styrene, respectively, and a platinum−thiol complex, $Pt(Et_3P)(H)(SH)$; **2** also gives some ethylbenzene. The relative yields of HDS products reflect the stability of the complexes to reversion; thus **1**, which reverts most readily to thiophene, gives the lowest yields of HDS products. The most novel feature of the reactions is that the C−S bond is cleaved as well as the Pt−C bond. These reactions bear a close analogy to the nickel- and hydride-promoted HDS reactions reported earlier by Eisch et al.

In addition, a novel and efficient two-step process for the conversion of DBT to 2-phenylthiophenyl is reported, via acid cleavage of the Pt−C and the Pt−S bond of the DBT thiaplatinacycle **1**.

Experimental Section

All reactions were carried out using standard Schlenk techniques under argon. Solvents were dried and distilled prior to use. Deuterated solvents for NMR experiments were purchased from CEN SACLAY

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(France) and dried over molecular sieves. Dibenzothiophene, benzothiophene, and thiophene (Aldrich) and potassium tetrachloroplatinate (Johnson Matthey) were used as received. All other chemicals were reagent grade. The synthesis of $[Pt(PEt_3)_3]$ was carried out using a previously reported procedure.[30] ^1H, ^{31}P, and $^{13}C\{^1H\}$ NMR spectra were obtained using Bruker AM-250, AMX-400, and WH-400 NMR spectrometers, chemical shifts (δ) with reference to the deuterated solvent. IR spectra (Nujol mulls) were recorded on a Perkin-Elmer PE-1710 FT spectrometer; fast-atom bombardment mass spectra were recorded in *p*-nitrobenzyl alcohol matrices on a Kratos MS80RF mass spectrometer. GC analyses were performed on a Perkin-Elmer 8700 gas chromatograph equipped with a flame ionization detector, while GC–MS analyses were performed on Hewlett-Packard HP5890 series II equipment. Elemental analyses were carried out by the University of Sheffield Microanalytical Service.

Preparation of $[Pt(SC_{12}H_8)(PEt_3)_2]$ (1). Complex **1** was prepared from $[Pt(PEt_3)_3]$ (1.0 g, 1.81 mmol) and DBT (1.0 g, 5.43 mmol) in toluene (25 mL) under argon. The solution was then heated to 70 °C (0.2 mmHg), at which point the toluene and excess phosphine distilled out and the color changed from red-orange to yellow-brown. At this point, the heating was stopped and the mixture was evaporated to dryness with increasing vacuum (0.01 mmHg) and cooling to room temperature. Hexane (50 mL) was added with stirring to yield a yellow-brown precipitate. This was washed several times with hexane to afford an ivory residue, which was crystallized from toluene/hexane, giving 1.03 g (92%) of complex **1**. Anal. Calcd for $C_{24}H_{38}P_2PtS$: C, 46.8; H, 6.2; S, 5.2. Found: C, 46.0; H, 6.0; S, 5.5. NMR spectra in $CDCl_3$, ^1H: δ 0.6–1.05 (m, 18H, CH_3), 1.15–2.05 (m, 12H, CH_2), 6.9–7.05 and 7.25–7.5 (m, 8H, DBT). ^{13}C: δ 7.6–8.7 (m, CH_3), 15.3–17.6 (m, CH_2), 123.1 (s, CH), 123.5 (s, CH), 125.9 (s, br, CH), 127.0 (s, CH, ^2J(Pt–C) = 45 Hz), 130.4 (s, CH, ^3J(Pt–C) = 26 Hz), 135.5 (s, CH), 135.6 (s, CH), 140.0 (d, C, ^2J(Pt–C) = 41 Hz, ^3J(P–C) = 3 Hz), 143.5 (s, C), 149.3 (s, C), 158.0 (dd, C, ^2J(*trans*-P–C) = 114 Hz, ^2J(*cis*-P–C) = 9 Hz, ^1J(Pt–C) not observed). ^{31}P: δ 7.5 (d, ^1J(Pt–P) = 1777 Hz, ^2J(P–P) = 14 Hz), 11.6 (d, ^1J(Pt–P) = 3272 Hz).

Preparation of $[Pt(SC_8H_6)(PEt_3)_2]$ (2). Complex **2** was prepared in 85% yield from $[Pt(PEt_3)_3]$ (0.20 g, 0.36 mmol) and benzothiophene (0.19 g, 1.45 mmol) in toluene (80 °C for 2 h) using a procedure similar to that described above for **1**. Anal. Calcd for $C_{20}H_{36}P_2PtS$: C, 42.5; H, 6.4; S, 5.7. Found: C, 42.2; H, 6.6; S, 5.9. NMR spectra in $CDCl_3$, ^1H: δ 1.1 (m, CH_3, 18H), 2.0 (m, CH_2, 12H), 7.0–7.2 (m, CH, 3H), 7.8 (d, CH, 1H). ^{31}P: δ 1.0 (d, ^1J(Pt–P) = 1733 Hz, ^2J(P–P) = 23 Hz), 11.1 (d, ^1J(Pt–P) = 3124 Hz). ^{13}C: δ 8.1–8.8 (m, CH_3), 15.5–17.0 (m, CH_2), 121.5 (s, CH), 125.1 (s, CH, ^4J(Pt–C) = 18 Hz), 128.6 (s, CH), 130.0 (d, C, ^2J(Pt–C) = 56 Hz, ^3J(P–C) = 10 Hz), 131.1 (dd, CH, ^2J(P–*trans*-C) = 98 Hz, ^2J(P–*cis*-C) = 9 Hz, ^1J(Pt–C) not observed), 131.2 (s, CH), 138.4 (s, C), 139.1 (s, C).

Preparation of $[Pt(SC_4H_4)(PEt_3)_2]$ (3). Complex **3** was obtained (89% yield) by reaction of $[Pt(PEt_3)_3]$ (0.20 g, 0.36 mmol) with thiophene (120 μL, 1.44 mmol) in toluene (80 °C for 2 h) by a procedure similar to that used to make **1**. Anal. Calcd for $C_{16}H_{34}P_2PtS$: C, 37.3; H, 6.6; S, 6.2. Found: C, 36.9; H, 6.8; S, 6.4. NMR spectra in $CDCl_3$, ^1H: δ 1.0 (m, CH_3, 18H), 1.9 (m, CH_2, 12H), 6.7–6.85 (m, CH, 1H), 6.9–7.15 (m, CH, 2H), 7.35–7.6 (m, CH, 1H). ^{31}P: δ 0.0 (d, ^1J(Pt–P) = 1684 Hz, ^2J(P–P) = 23 Hz), 10.7 (d, ^1J(Pt–P) = 3112 Hz). ^{13}C: δ 8.0–8.7 (m, CH_3), 15.8–17.3 (m, CH_2), 117.2 (s, br, CH), 121.0 (s, CH), 124.2 (s, CH, ^2J(Pt–C) = 120 Hz), 131.5 (dd, CH, ^2J(Pt–*trans*-C) = 98 Hz, ^2J(P–*cis*-C) = 10 Hz, ^1J(Pt–C) not observed).

Attempted Reaction of 1 with Hydrogen Gas. Complex **1** was heated under hydrogen (1 atm, 70 °C) in toluene; after 12 h of reaction, a white complex **4** precipitated, which was isolated by filtration and which showed no hydride signal in the NMR. The ^1H NMR spectrum of the reaction solution showed the presence of triethylphosphine and dibenzothiophene in a 1:1 ratio, together with signals due to **4**. Complex **4** was also isolated when the reaction was carried out under argon (12 h at 70 °C in toluene) instead of hydrogen, showing that the product was formed thermally; analytical and spectroscopic evidence indicate a dinuclear formula, $[Pt_2(C_{12}H_8S)_2(PEt_3)_2]$ (**4**). Anal. Calcd for $C_{36}H_{46}P_2Pt_2S_2$: C, 43.5; H, 4.6; S, 6.4; MW = 995. Found: C, 42.9; H, 4.6; S, 6.7; MW = 995 (osmometry in $CHCl_3$). NMR spectra in $CDCl_3$, ^1H: δ 0.95 (m, 18H, CH_3), 1.5 (m, 6H, CH_2), 1.8 (m, 6H, CH_2), 7.0 (m, 4H, CH), 7.15 (m, 4H, CH), 7.2 (m, 4H, CH), 7.45 (m, 2H, CH), 8.45 (d, 2H, CH). ^{31}P: δ 13.2 (^1J(Pt–P) = 3585 Hz).

Reaction of 1 with HCl. When complex **1** (0.25 g, 0.4 mmol) was reacted with an excess of gaseous HCl in $CDCl_3$, *cis*- and *trans*-$[PtCl_2(PEt_3)_2]$, **5a** and **5b**, respectively, were isolated (90 and 10% yield, respectively). Complex **5a** precipitated and was filtered off; complex **5b** and the organic product, 2-phenylthiophenol, were separated by column chromatography over silica gel, eluting with hexane and hexane/CH_2Cl_2. 2-Phenylthiophenol (0.07 g, 0.38 mmol, 95%) was identified by its mass spectrum (m/z = 186) and ^1H NMR spectrum [($CDCl_3$) δ 3.3 (s, 1H, SH), 7.05–7.2 (m, 3H, CH), 7.3–7.45 (m, 6H, CH)].

Reaction of 1 with Et_3SiH. Complex **1** (0.250 g, 0.4 mmol) and triethylsilane (450 μL, 2.8 mmol) were refluxed in toluene-d_8 (3 mL). After 3 h, all the initial complex had been consumed and new signals were observed in the ^{31}P and ^1H NMR spectra (toluene-d_8) of the reaction mixture, which are assigned to complexes **6** and **7**, respectively. They are assigned by direct comparison with literature values; they were also separated by flash column chromatography on silica gel, eluting with CH_2Cl_2/acetone, increasing polarity until 1:1 (v/v) in both solvents. *cis*-$[PtH(SiEt_3)(PEt_3)_2]$ (**7**).[19] Yield: 31%. ^{31}P NMR (C_7D_8): δ 20.7 (d, ^1J(Pt–P) = 2409 Hz, ^2J(P–P) = 15 Hz), 24.2 (d, ^1J(Pt–P) = 1409 Hz). ^1H NMR (C_7D_8): δ −2.40 (dd, ^1J(Pt–H) = 948 Hz, ^2J(P–H) = *trans*-155 Hz, ^2J(P–H) *cis* = 24 Hz). *trans*-$[Pt(SH)(H)(PEt_3)_2]$ (**6**).[18] Yield: 50%. ^{31}P NMR (C_7D_8): δ 19.9 (^1J(Pt–P) = 2721 Hz). ^{31}P NMR ($CDCl_3$): δ 19.2 (^1J(Pt–P) = 2685 Hz). ^1H NMR ($CDCl_3$): δ −1.2 (m, ^2J(Pt–H) = 43 Hz, ^3J(P–H) = 11 Hz, ^3J(H–H) = 3 Hz), −11.1 (t, ^1J(Pt–H) = 1045 Hz).

The toluene spectra were rather broad, indicating exchange; thus, the toluene was removed and replaced by $CDCl_3$, which gave sharp spectra but caused some decomposition with the formation of new species. When the crude reaction mixture was dissolved in $CDCl_3$, H_2S was released and three new complexes, **8**, *cis*-**5a**, and *trans*-**5b**, were formed in solution. This process was strongly promoted on adding HCl dissolved in $CDCl_3$, at which point **8**, *cis*-**5a**, and *trans*-**5b** were formed with relative abundances 1:8:1. *trans*-$[PtHCl(PEt_3)_2]$ (**8**):[20] ^{31}P NMR ($CDCl_3$) δ 23.3 (d, ^1J(Pt–P) = 2711 Hz); ^1H NMR ($CDCl_3$) δ −17.9 (t, ^1J(Pt–H) = 1321 Hz, ^2J(P–H) = 14 Hz). *cis*-$[PtCl_2(PEt_3)_2]$ (**5a**): ^{31}P NMR ($CDCl_3$) δ 9.6 (d, ^1J(Pt–P) = 3503 Hz). *trans*-$[PtCl_2(PEt_3)_2]$ (**5b**):[16] ^{31}P NMR ($CDCl_3$) δ 13.1 (d, ^1J(Pt–P) = 2490 Hz).

The mixture obtained after reaction of complex **1** (100 mg, 0.16 mmol) with triethylsilane (180 μL, 1.13 mmol) in refluxing toluene (3 mL, 3 h) was concentrated to dryness; 10 mL of $CDCl_3$ saturated with HCl(g) was added by syringe, and the H_2S released was quantified. This was done by absorption of the hydrogen sulfide in an ammoniacal solution of zinc sulfate with the formation of zinc sulfide and titration in an acid solution with a standard solution of iodine (iodate/iodide solution); starch was used to indicate the end point.[31] A triplicate determination gave 47% of the total amount expected, if all the sulfur present in the original insertion complex was converted to H_2S.

The organic products were identified as starting material, dibenzothiophene (yield 32%), and the product of hydrodesulfurization, biphenyl (yield 56%). They were quantified by HPLC in a Spherisorb ODS column, with a solvent gradient from 50%/50% (v/v) acetonitrile/water to 100% acetonitrile; the retention time was 9.8 min for biphenyl and 11.6 min for DBT. Both were also isolated from the reaction mixture using a Techsphere ODS semipreparative column (250 × 20 mm; solvent gradient from 100% water to 100% acetonitrile over 30 min with a 10 cm^3 flow rate).

Reaction of 1 with Sodium Borohydride. Complex **1** (0.250 g, 0.4 mmol) was treated with $NaBH_4$ (60 mg, 1.6 mmol) in THF (2 mL) and 2-propanol (3 mL) at 20 °C. After 72 h, the volatiles were removed in vacuo and the products analyzed by proton NMR spectroscopy in $CDCl_3$. This showed the presence of *trans*-$[Pt(SH)(H)(PEt_3)_2]$ (**6**, 53%), *trans*-$[PtHCl(PEt_3)_2]$ (**8**, 7%), *cis*- and *trans*-$[PtCl_2(PEt_3)_2]$ (**5a** + **5b**, 3%), and complex **1** (37%). Some of the original starting material was still present, probably because it and $NaBH_4$ are poorly soluble in the solvents used. Biphenyl (50%) and dibenzothiophene (16%) were also produced and analyzed by HPLC.

Reaction of 1 with Red-Al. The reaction of **1** (0.250 g, 0.4 mmol) with Red-Al (82 mg, 0.4 mmol) in toluene was very exothermic and evolved gas. The color changed from very pale yellow to brown (5

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min); after 1 h, the mixture was concentrated to dryness, and the residue was dissolved in $CDCl_3$ and filtered through Celite. The ^{31}P NMR spectrum in toluene was broad but showed the presence of *trans*-$[Pt(SH)(H)(PEt_3)_2]$ (**6**, 35%). To obtain better spectra, the toluene was removed and replaced by $CDCl_3$; the NMR spectra then showed the presence of *trans*-$[PtHCl(PEt_3)_2]$ (**8**) and *cis*- and *trans*-$[PtCl_2(PEt_3)_2]$ (**5a** and **5b**) in a ratio of 1:3:3; in addition, resonances were also seen at δ 12.6 and 13.6 in the ^{31}P NMR spectrum arising from two further bis(triethylphosphine)platinum(II) complexes, so far uncharacterized, in low amounts (relative ratios, 0.3 and 0.2). In addition, the spectra showed the presence of free PEt_3 in solution.

The organic components, analyzed by HPLC, were composed of biphenyl (60%) and dibenzothiophene (40%); similar reactions occurred, with similar yields, when the reaction was carried out at 0 °C, but fewer dark decomposition products were formed.

Reaction of 1 with $LiAlH_4$. The reaction between **1** (0.25 g, 0.4 mmol) and $LiAlH_4$ (15.4 mg, 0.4 mmol) in THF was very energetic, and the solution quickly turned red with the evolution of gas. After 1 h, the volatiles were evaporated, and the residue was redissolved in $CDCl_3$; the ^{31}P NMR spectra showed the presence of *trans*-$[Pt(SH)(H)(PEt_3)_2]$ (**6**), *trans*-$[PtHCl(PEt_3)_2]$ (**8**), and *trans*-$[PtCl_2(PEt_3)_2]$ (**5b**) in a ratio of 1:15:4, together with one other bis(triethylphosphine)platinum(II) complex (^{31}P NMR δ 10.6), so far uncharacterized (ratio, 0.1), and free PEt_3. The organic components, analyzed by HPLC, were biphenyl (38%) and dibenzothiophene (15%).

Reaction of 2 with Et_3SiH. Following the procedure used for **1**, complex **2** (0.11 g, 0.19 mmol) was reacted with Et_3SiH (217 μL, 1.33 mmol) in refluxing toluene (3 h). Two complexes were present and were identified by ^{31}P NMR spectroscopy (in the toluene solution): *cis*-$[PtH(SiEt_3)(PEt_3)_2]$ (7, 30%) and *trans*-$[Pt(SH)(H)(PEt_3)_2]$ (**6**, 70%). The organic products of desulfurization, styrene (61%) and ethylbenzene (12%), plus some of the original benzothiophene (26%), were identified and quantified by GC.

Reaction of 2 with Sodium Borohydride. Complex **2** (0.1 g, 0.17 mmol) was reacted with $NaBH_4$ (0.027 g, 0.71 mmol) as described above. HPLC analysis showed that the organic products comprised styrene (22%), ethyl benzene (23%, giving a total HDS yield of 45%), and free benzothiophene (29%). Some of the original complex **2** (26%) remains at the end of the reaction.

Reaction of 2 with Red-Al. Complex **2** (0.1 g, 0.17 mmol) was reacted with Red-Al (71 mg, 0.35 mmol) was described for **1**. HPLC analysis showed the organic products to be styrene (24%) and ethylbenzene (15%, giving a total HDS yield of 39%), together with free benzothiophene (21%).

Reaction of 2 with $LiAlH_4$. Complex **2** (0.1 g, 0.17 mmol) was reacted with $LiAlH_4$ (12 mg, 0.31 mmol), as described for **1**. The organics, found by HPLC, were styrene (48%), ethylbenzene (16%, giving a total HDS yield of 64%), and free benzothiophene (30%).

Reaction of 3 with Et_3SiH. Complex **3** (0.11 g, 0.21 mmol) was reacted with Et_3SiH (243 μL, 1.52 mmol) as described above. After 3 h of reflux, the following complexes were detected (NMR, toluene solution): *cis*-$[PtH(SiEt_3)(PEt_3)_2]$ (7) and *trans*-$[Pt(SH)(H)(PEt_3)_2]$ (**6**), ratio 1:1. The organic HDS products were identified by GC−MS as butadiene (2%), *trans*-2-butene (<1%), *cis*-2-butene (<1%), and free thiophene (80%).

Determination of Equilibrium Constants. The complexes **1**, **2**, and **3** were reacted with 1.5 equiv of PEt_3 to achieve reversibility. The reaction was monitored using ^1H and ^{31}P NMR as follows: The ^1H NMR spectra were measured (Bruker WH400 or AMX400) using a 10 s relaxation delay and a $\pi/4$ pulse. The $^{31}P\{^1H\}$ NMR spectra were recorded using a 10 s relaxation delay with ^1H decoupling off and a $\pi/4$ pulse. The 5 mm NMR tubes, containing $[(PtSC_aH_b)(PEt_3)_2]$ (complex **1**, **2**, or **3**; approximately 50 mg) and PEt_3 (1.5 molar equiv) in toluene-d_8 as solvent, were sealed under vacuum. The initial spectrum showed only the presence of $[(PtSC_aH_b)(PEt_3)_2]$ and PEt_3; this was unchanged after 15 h at 20 °C. Reaction occurred on heating the NMR tubes in a water bath at 100 °C. After 1 and 4 h, the tubes were cooled to room temperature and the NMR spectra were immediately recorded. The ratio of the thiaplatinacycles to the free thiophenes at different times was determined by integrating signals of the aromatic protons of **1** against those of free DBT, H^2 of **2** against H^7 of BT, and H^1, H^2, and H^4 of **3** against $H^{2,5}$ and $H^{3,4}$ of T.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**, $[(PtSC_8H_6)(PEt_3)_2]$

Pt(1)−S(1)	2.315(5)	Pt(1)−P(1)	2.301(5)
Pt(1)−P(2)	2.386(5)	Pt(1)−C(4)	2.035(19)
S(1)−C(1)	1.756(18)	C(1)−C(2)	1.403(25)
C(2)−C(3)	1.483(29)	C(3)−C(4)	1.301(27)
C(8)−C(2)	1.455(26)	C(8)−C(7)	1.402(39)
C(7)−C(6)	1.391(38)	C(6)−C(5)	1.372(33)
C(1)−C(5)	1.430(29)		
S(1)−Pt(1)−P(1)	175.4(2)	S(1)−Pt(I)−P(2)	87.0(2)
P(1)−Pt(1)−P(2)	97.6(2)	S(1)−Pt(1)−C(4)	88.6(6)
P(1)−Pt(1)−C(4)	86.8(6)	P(2)−Pt(1)−C(4)	174.8(6)
Pt(1)−S(1)−C(1)	114.2(6)	Pt(1)−C(4)−C(3)	137.3(16)
S(1)−C(1)−C(2)	128.7(15)	C(1)−C(2)−C(3)	121.5(16)
C(2)−C(3)−C(4)	128.4(18)	S(1)−C(1)−C(5)	115.9(14)

The equilibrium constants (K) for each complex found were K = 2.2 and 10 (**1**); K = 1.0 and 1.0 (**2**); and K = 10 and 11 (**3**) after 1 and 4 h, respectively. On further heating, the complexes **1** and **3** slowly decomposed and deposited dark solids.

X-ray Structure Determination of $[Pt(SC_8H_6)(PEt_3)_2]$ (2). Crystal data for $C_{20}H_{36}P_2PtS$: MW = 565.61; crystallizes from toluene/hexane as yellow needles; crystal dimensions 0.55 × 0.20 × 0.175 mm; orthorhombic, $a = 9.930(8)$, $b = 13.069(7)$, and $c = 19.124(10)$ Å, $U = 2482(3)$ Å^3; $Z = 4$; $D_c = 1.514$ g cm^{-3}; space group $P2_12_12_1$ (D^4_2, No. 19); Mo Kα radiation (λ = 0.710 69 Å) μ(Mo Kα) = 59.21 cm^{-1}; $F(000) = 1119.74$.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Nicolet R3 diffractometer by the ω scan method. The 2481 independent reflections (of 3685 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarization effects and for absorption by analysis of seven azimuthal scans (minimum and maximum transmission coefficients, 0.009 and 0.027, respectively). The structure was solved by direct methods and refined by block cascade least-squares methods. Hydrogen atoms were included in calculated positions and refined in riding mode. The correct enantiomeric form of the crystal was confirmed by the lower R (by 0.0148) of the reported model. Refinement converged at a final R = 0.0555 (R_w = 0.0510; 217 parameters; mean and maximum δ/σ, 0.001 and 0.003, respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron densities were −1.45 and 1.18 e Å^{-3}, respectively. A weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,53(F)^2$ was used in the latter stages of refinement. Complex scattering factors were taken from reference[32] and from the program package SHELXTL[33] as implemented on the Data General DG30 computer. Selected bond lengths and angles for **2** are listed in Table 2.

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Supplementary Material Available: Tables of the anisotropic thermal vibration parameters, atomic position parameters (with estimated standard deviations) and observed structure amplitudes (4 pages); a table of observed and calculated structure factors (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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