Hydrodesulfurization of Dibenzothiophene into Biphenyl by Tris(triethylphosphine)platinum(0)

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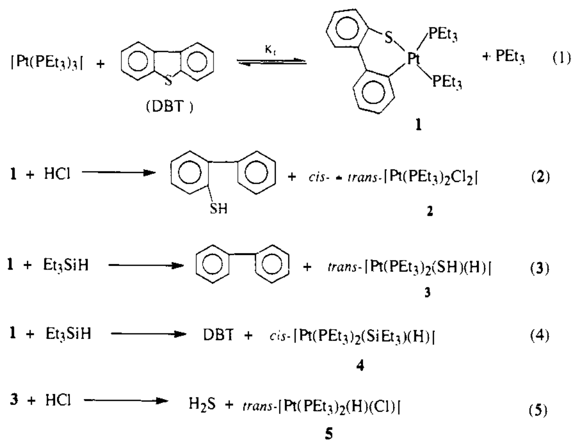
The need to utilize oil and coal deposits with high sulfur levels has sharply focused interest on the metal-promoted processes which lead to hydrodesulfurization (HDS). Although commercial operations use cobalt–molybdenum sulfide catalysts, the highest activity is shown by platinum metals, especially Rh and Ir, but also Ru, Os, Pd, and Pt.[1] Several homogeneous model systems (based on Fe, Co, Ru, Rh, and Ir) for the extrusion of sulfur from heterocycles (which are most resistant to HDS) have recently been discussed.[2] There is also an extensive literature on the use of transition metal (especially nickel) complex hydride systems for HDS in organic synthesis.[3] Nevertheless, many mechanistic details, in particular the mode of cleavage of the C–S bond, are still unclear.[2f]

We here report that platinum(0) inserts (reversibly) into the C–S bond of dibenzothiophene (DBT, which is particularly difficult to degrade) to give a metallacycle containing a Pt–S–C linkage. This S–C bond is readily cleaved by hydridic reducing agents to give biphenyl and a Pt–SH complex, allowing the definition of this key step.

$[Pt(PEt_3)_3]$[4] reacted with an excess of DBT (toluene, 70 °C) to yield $[Pt(SC_{12}H_8)(PEt_3)_2]$, **1** (92%).[5] The reaction (1) leading to **1** was reversed with excess PEt_3 (at 100 °C), and an equilibrium constant, $K_1 = 3$, was evaluated (toluene-d_8; 100 °C). Complex **1**, which contains a $\overline{\text{PtSCCCC}}$ six-membered ring (Scheme I, eq 1), was characterized by NMR spectroscopy[6] and confirmed by an X-ray crystal structure determination.[7]

Scheme I



The bonds to sulfur in complex **1** were cleaved by both protonic and hydridic reagents. The reaction with acid led to Pt–C but not to C–S bond cleavage; thus, with an excess of HCl gas in $CDCl_3$, **1** reacted quantitatively to give *cis*- and *trans*-$[PtCl_2(PEt_3)_2]$[8] (**2**, 90% and 10% yield, respectively) and free 2-phenylthiophenol (eq 2).[9]

Reaction of complex **1** with excess triethylsilane in toluene (reflux, 3 h) gave biphenyl (56%; where both the C–Pt and the C–S bonds have been cleaved), DBT (32%),[10] *trans*-$[Pt(SH)(H)(PEt_3)_2]$[11] (**3**, 50%), and *cis*-$[PtH(SiEt_3)(PEt_3)_2]$[12] (**4**, 31%). We propose that the biphenyl and **3** arise from HDS (eq 3), while DBT and **4** (eq 4) arise via reversal of reaction 1. Addition of a saturated solution of HCl gas in $CDCl_3$ released H_2S (47%)[13] from **4** and converted the complexes into a mixture of $[Pt(Cl)(H)(PEt_3)_2]$[14] (**5**, 10%) and **2** (90%; *cis*:*trans*, 9:1).

Related reactions occurred when **1** was reacted with (i) $NaBH_4$ (in THF/2-propanol), to give biphenyl (50% after 72 h), DBT (16%), *cis*- and *trans*-**2** (3%), *trans*-$[Pt(SH)(H)(PEt_3)_2]$ (**3**, 53%), *trans*-$[PtHCl(PEt_3)_2]$ (**5**, 7%); (ii) Red-Al (in toluene; very exothermic with evolution of gas), giving biphenyl (60%), DBT (40%), and complexes *cis*- and *trans*-**2** (34%), **3** (35%), **5**, (30%), and free PEt_3; or (iii) $LiAlH_4$ (in THF) to give biphenyl (38%), DBT (15%), *trans*-**2** (20%), **3** (5%), **5** (75%), and free PEt_3.[15,16]

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[3] 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. *J. Org. Chem.* **1993**, *58*, 2407.

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[5] $[Pt(PEt_3)_3]$ (1.0 g, 1.81 mmol) and DBT (1.0 g, 5.43 mmol) were reacted in toluene (25 mL) under argon; after heating (70 °C) in vacuo to remove volatiles, a yellow-brown solid was obtained, which was crystallized from toluene/hexane, giving complex **1** (1.03 g; 92%). The ring-opening was reversed by heating **1** with PEt_3 (at 100 °C); this equilibrium accounts for the occurrence of DBT in the products of further reactions.

[6] NMR spectra of **1** in $CDCl_3$: ^{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(Pt–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).

[7] Preliminary data of the structure determination ($R = 0.075$) shows that **1** contains a racemic twin with two symmetry independent molecules, total of 4, in space group $P2_1$. All the four molecules are structurally identical, with bond lengths and angles about Pt: Pt–S, 2.367 Å, Pt–P(1), 2.287 Å; Pt–P(2) (*trans* to C), 2.341 Å; Pt–C 2.039 Å; S–Pt–P(2), 86.3°; S–Pt–C, 83.6°; P(1)–Pt–P(2), 99.3°; C–Pt–P(1), 92.6°. We are grateful to Dr. K. M. A. Malik and Professor M. B. Hursthouse (SERC Crystallography Service, Cardiff) for the information.

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[9] 2-Phenylthiophenol was isolated, essentially quantitatively, and identified by its mass spectrum ($z/e = 186$) and NMR spectrum: ^1H ($CDCl_3$) δ 3.3 (s, 1H, SH), 7.05–7.2 (m, 3H, CH), 7.3–7.45 (m, 6H, CH).

[10] Quantified by HPLC.

[11] Blacklaws, I. M.; Ebsworth, E. A. V.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton. Trans.* **1978**, 753.

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[15] The metal complexes produced were identified and estimated by ^{31}P NMR spectroscopy in $CDCl_3$. Since the solvent contained small amounts of H(D)Cl, significant quantities of *cis*- and *trans*-$[PtCl_2(PEt_3)_2]$ were formed from the complexes sensitive to acid; thus the amounts of **3**, **4**, and **5** found represent lower limits.

[16] No HDS of **1** occurred with hydrogen gas (1 atm) below 100 °C.

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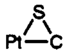
Perhaps the most significant aspect of these reactions is the demonstration that with hydrides the ***Pt–S–C linkage is cleaved at the C–S bond***, giving a Pt–SH complex, possibly via a triangular transition state:



The mechanism of this unusual reaction is under investigation.

Preliminary data indicate that similar reactions occur with benzothiophene (BT) and thiophene. For example, complex [Pt(SC$_8$H$_6$)(PEt$_3$)$_2$] (**6**, 85%), obtained from reaction of [Pt(PEt$_3$)$_3$] with BT (toluene, 80 °C, 2 h), reacted with triethylsilane to give styrene (61%), ethylbenzene (12%), and the Pt–SH complex **3**.

Thus, in summary, the platinum(0) complex Pt(PEt$_3$)$_3$ inserts readily into the C–S bonds of thiophene heterocycles; hydrides cause cleavage of both the S–C and the Pt–C bond in the ring-opened adduct, yielding the hydrocarbon and a Pt–SH complex. This parallels the HDS activity of Pt metal. These reactions also offer an interesting comparison to the nickel-promoted desulfurization of DBT which has been proposed to proceed via an initial single electron transfer step.[3a]

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Supplementary Material Available: Experimental details and NMR spectral data (2 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.