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A key intermediate in the platinum-mediated hydrodesulfurization of dibenzothiophene

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The thiaplatinacycles, $[PtL_2(C,S–C_{12}H_8S)]$ and $[PtL_2(C,S–C_{13}H_{10}S)]$ ($L = PEt_3$, PMe_3; $L_2 = Ph_2PCH_2CH_2PPh_2$), obtained from oxidative insertion of $[Pt^0L_n]$ into dibenzothiophene and 4-methyldibenzothiophene are hydrodesulfurized by reaction with hydrogen (toluene, 20 atm, 100 °C) to biphenyl and 3-methylbiphenyl, respectively; addition of acidic alumina improves the reaction. These observations link the model systems and the latest generation of commercial second-stage HDS catalysts.

Keywords: hydrodesulfurization, dibenzothiophene, platinum

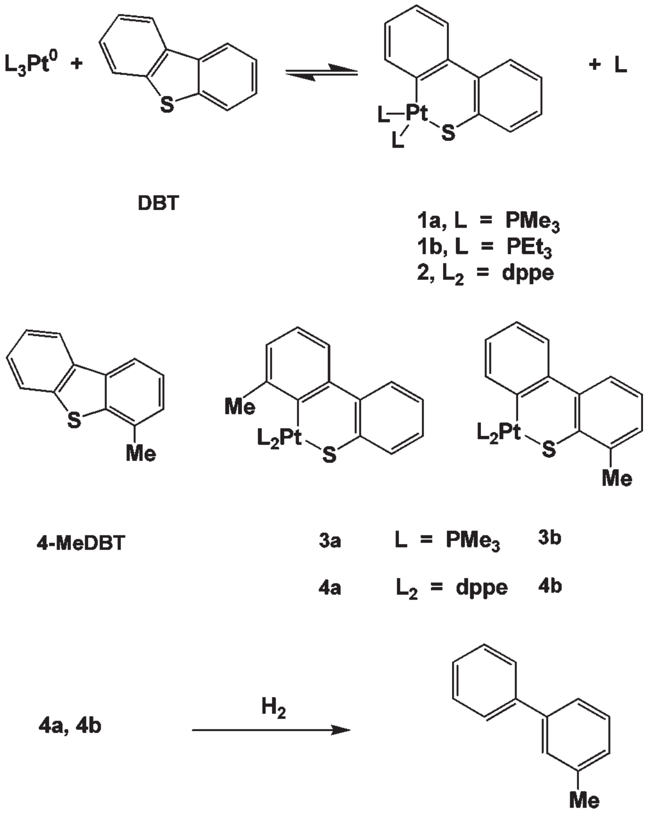
1. Introduction

Although the mainstay of the hydrodesulfurization (HDS) processes remains hydrogenation over the familiar Co–Mo–S catalyst [1], the new environmental requirements to reach very low sulfur levels have prompted the development of new deep HDS catalyst systems. These catalyst systems can take the sulfur levels down to meet the new legislation in the USA and Europe; for example, the Swedish Urban Diesel I specification sets a maximum sulfur content of 0.001 wt% [2].

One very interesting development has been the introduction of Pt–Pd catalysts on a variety of supports, including alumina and USY zeolite. These were originally put forward as catalysts for the hydrogenation of aromatics in diesel feedstocks [3]. However, the published data show that they are extremely good HDS catalysts and, indeed, that they reduce sulfur levels proportionately more than aromatics [2a,3,4]. As a consequence, a number of workers have investigated these noble metal catalyst systems for the HDS of refractory sulfur-containing compounds in feedstocks, the various annelated thiophenes such as dibenzothiophene (DBT) and their alkylated derivatives, which are most resistant towards the conventional Co–Mo–S catalysts [5]. Studies have indicated that the key-role is played by the platinum, but that acidic sites on the supports (e.g., USY zeolite) are also required. We here present preliminary results concerning the mechanism for the platinum-promoted HDS reaction.

2. Results and discussion

We suggest that the route by which these dibenzothiophenes undergo HDS to the appropriate biphenyls is via the thiaplatinacycle. An example is complex **1b** (scheme 1, $L = PEt_3$), formed by oxidative insertion of “PtL_2” into the thiophene. We have previously shown by synthetic studies of such reactions and by full characterisations (spectroscopic and X-ray single crystal) of the thiaplatinacycles how such products are formed. These studies have been reported in detail [6]. We have also prepared and characterised new thiaplatinacycles **1a** ($L = PMe_3$)



Scheme 1.

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Table 1
Desulfurization of the thiaplatinacycles **1a**, **2** and **4**.

Substrate	Reagent	Conditions	Products
1a, L $=$ $\mathrm{PMe_3}$	$\mathrm{Et_3SiH}$	toluene/3 h/110 °C	$\mathrm{Ph_2}$ 31% + DBT 62%
2, $\mathrm{L_2}$ $=$ dppe	$\mathrm{LiAlH_4}$	toluene/1 h/20 °C	$\mathrm{Ph_2}$ 92% + DBT 6%
4, $\mathrm{L_2}$ $=$ dppe	$\mathrm{LiAlH_4}$	toluene/1 h/20 °C	3-Me-bph 34% + 4-MeDBT 62%
1b, L $=$ $\mathrm{PEt_3}$	$\mathrm{H_2}$/20 atm	toluene/24 h/100 °C	$\mathrm{Ph_2}$ 9% + DBT 89%
1a, L $=$ $\mathrm{PMe_3}$	$\mathrm{H_2}$/20 atm	toluene/24 h/100 °C	$\mathrm{Ph_2}$ 37% + DBT 58%
1a, L $=$ $\mathrm{PMe_3}$	$\mathrm{H_2}$/20 atm + $\mathrm{Al_2O_3}$	toluene/24 h/100 °C	$\mathrm{Ph_2}$ 56% + DBT 28%
2, $\mathrm{L_2}$ $=$ dppe	$\mathrm{H_2}$/20 atm	toluene/24 h/100 °C	$\mathrm{Ph_2}$ 22% + DBT 34%
2, $\mathrm{L_2}$ $=$ dppe	$\mathrm{H_2}$/20 atm + $\mathrm{Al_2O_3}$	toluene/24 h/100 °C	$\mathrm{Ph_2}$ 74% + DBT 16%
DBT	$\mathrm{H_2}$/20 atm + $\mathrm{Al_2O_3}$	toluene/24 h/100 °C	$\mathrm{Ph_2}$ 4% + DBT 96%
DBT	$\mathrm{H_2}$/20 atm + $\mathrm{Pt/Al_2O_3}$	toluene/24 h/100 °C	$\mathrm{Ph_2}$ 4% + DBT 96%
4, $\mathrm{L_2}$ $=$ dppe	$\mathrm{H_2}$/20 atm	toluene/24 h/100 °C	3-Me-bph 17% + 4-MeDBT 43%
4, $\mathrm{L_2}$ $=$ dppe	$\mathrm{H_2}$/20 atm + $\mathrm{Al_2O_3}$	toluene/24 h/100 °C	3-Me-bph 58% + 4-MeDBT 30%

[a] Acid-washed alumina (Aldrich, 300 mg) and DBT (25 mg); no metal complex.

[b] Platinum on acid-washed alumina (Aldrich, 300 mg; a solution of $\mathrm{Pt(norbornene)_3}$ (65 mg) in diethyl ether was absorbed on the alumina which was then dried and heated/100 °C in vacuo to remove the organic ligand) and DBT (25 mg).

made from $[\mathrm{Pt(PMe_3)_4}]$ [7], equation (1), and **2** ($\mathrm{L_2} = \mathrm{Ph_2PCH_2CH_2PPh_2}$, dppe) made from **1a** (L $=$ $\mathrm{PMe_3}$) by a phosphine exchange, equation (2).

$$[\mathrm{PtL}_{3/4}] + \mathrm{DBT} \rightleftharpoons \big[\mathrm{PtL_2(C,S{-}C_{12}H_8S)}\big] + \mathrm{L} \qquad (1)$$

$$(\mathbf{1a},\ \mathrm{L} = \mathrm{PMe_3};\ \ \mathbf{1b},\ \mathrm{L} = \mathrm{PEt_3})$$

$$\underset{\mathbf{1}}{\big[\mathrm{PtL_2(C,S{-}C_{12}H_8S)}\big]} + \mathrm{dppe} \longrightarrow \underset{\mathbf{2}}{\big[\mathrm{Pt(dppe)(C,S{-}C_{12}H_8S)}\big]} + 2\mathrm{L} \qquad (2)$$

It was previously reported that the complex **1b** is readily hydrodesulfurized by various hydrides including $\mathrm{Et_3SiH}$ and $\mathrm{LiAlH_4}$, to biphenyl (equation (3), table 1); in each case some of the parent DBT heterocycle is again formed, due to the reversal of the equilibrium, equation (1). Very similar reactions occur between these hydrides and the new complexes **1a** (L $=$ $\mathrm{PMe_3}$) and **2** ($\mathrm{L_2}$ $=$ dppe).

$$\mathbf{1} + \mathrm{Et_3SiH} \rightarrow \mathrm{Ph_2} + \mathrm{DBT} + \big[\mathrm{PtL_2(SH)(H)}\big] + \big[\mathrm{PtL_2(SiEt_3)(H)}\big] \qquad (3)$$

$$(\mathrm{L} = \mathrm{PMe_3}\ \text{or}\ \mathrm{PEt_3})$$

However, the complexes **1a** and **2** also undergo HDS with hydrogen alone (scheme 1) under relatively mild conditions (20 atm, toluene, 100 °C; table 1); there is even some hydrodesulfurization of **1b** under these conditions, but to a significantly smaller extent.

4-methyldibenzothiophene (4-MeDBT) forms a 1 : 1 mixture of isomers $[\mathrm{Pt(PMe_3)_2(C,S{-}C_{13}H_{10}S)}]$, **3a**, **3b**, when reacted with $[\mathrm{Pt(PMe_3)_4}]$ (equation (4)); the trimethylphosphines were again exchanged for dppe to give the mixture of isomers $[\mathrm{Pt(dppe)(C,S{-}C_{13}H_{10}S)}]$, **4a**, **4b** (equation (5) and scheme 1). The thiaplatinacycles **4a**, **4b** also undergo HDS with $\mathrm{LiAlH_4}$ to give mixtures of 3-methylbiphenyl (3-Me-bph) and 4-MeDBT.

$$\big[\mathrm{Pt(PMe_3)_4}\big] + \text{4-MeDBT} \rightleftharpoons \underset{\mathbf{3a},\,\mathbf{3b}}{\big[\mathrm{Pt(PMe_3)_2(C,S{-}C_{13}H_{10}S)}\big]} + 2\mathrm{PMe_3} \qquad (4)$$

$$\big[\mathrm{Pt(PMe_3)_2(C,S{-}C_{13}H_{10}S)}\big] + \mathrm{dppe} \longrightarrow \underset{\mathbf{4a},\,\mathbf{4b}}{\big[\mathrm{Pt(dppe)(C,S{-}C_{13}H_{10}S)}\big]} + 2\mathrm{PMe_3} \qquad (5)$$

$$\mathbf{4} + \mathrm{LiAlH_4} \rightarrow \text{3-Me-bph} + \text{4-MeDBT} \qquad (6)$$

$$\mathbf{4} + \mathrm{H_2} \rightarrow \text{3-Me-bph} + \text{4-MeDBT} \qquad (7)$$

We also find that the HDS of complexes **1a** and **2** is significantly promoted by acid alumina; for example, in its presence, the yield of biphenyl from **2** rises from 22 to 74% (table 1). The mixture of complexes **4a**, **4b** from 4-MeDBT also undergoes HDS with hydrogen under the same conditions to give 3-methylbiphenyl (3-phenyltoluene); again, in the presence of alumina, the yield is enhanced from 17 to 58%.

Under these mild conditions ($\mathrm{H_2}$, 20 atm, 100 °C, 20 h, toluene), the HDS reaction is stoichiometric and the sulfur which is lost from the DBT or MeDBT ends up as a platinum complex, currently under investigation. At that temperature, dibenzothiophene itself is also essentially unreacted in the presence of either added acid alumina or platinum on acid alumina. This indicates that a hydrodesulfurization path via the thiaplatinacycle is significantly easier than others, for example, via initial hydrogenation of the aromatic benz-rings.

Thus, although the conditions for modelling a complete HDS cycle for DBT have not yet been achieved, these observations do indicate the importance in the reaction of the thiaplatinacycle intermediates. Common factors such as the promotion offered by alumina also offer an intriguing link between the chemistry of such model platinum complexes and the new generation of commercial heterogeneous platinum catalysts for removal of the more intractable sulfur heterocycle compounds from diesel fuel. It is also noteworthy that although the thiaplatinacycle from 4-MeDBT is a little harder to hydrodesulfurize than that from DBT, the difference is small. The small effect of an adjacent methyl may well contribute to the success of the Pt/alumina HDS catalysts.

In summary, the thiaplatinacycles derived from DBT and from 4-MeDBT are hydrodesulfurized to biphenyl or 3-methylbiphenyl, by hydrogen under rather mild conditions and in the absence of a second metal reagent. Further work is in progress to explain the role of the alumina support in the reaction.

3. Experimental

3.1. Syntheses and characterisation of starting materials

[Pt(PEt_3)$_2$(C,S–$C_{12}H_8S$)] **1b**, L = PEt_3 was synthesised by the literature preparation [6].

[Pt(PMe_3)$_2$(C,S–$C_{12}H_8S$)] **1a**, L = PMe_3 was prepared in 68% yield from [Pt(PMe_3)$_4$] [6] by the method used for **1b**. Anal. Calcd for $C_{18}H_{26}P_2PtS$: C, 40.7; H, 4.9; S, 6.0%. Found: C, 40.7; H, 4.9; S, 6.0%. NMR spectra in $CDCl_3$, ^{1}H: δ 1.2–1.8 (m, CH_3, 18H), 6.8–7.15 and 7.35–8.2 (m, 8H, DBT); ^{31}P: δ -24.6 (d, ^1J(Pt–P) = 1709 Hz, ^2J(P–P) = 16 Hz), -22.6 (d, ^1J(Pt–P) = 3219 Hz).

[Pt(dppe)(C,S–$C_{12}H_8S$)] **2**, L_2 = dppe was prepared from [Pt(PMe_3)$_2$(η^2-C,S–$SC_{12}H_8$)] (500 mg, 0.94 mmol) and dppe (380 mg, 0.95 mmol) in toluene (reflux; 1 h). The light-yellow precipitate was filtered off, washed with hexane and dried (yield 670 mg, 0.87 mmol, 94%). Anal. Calcd for $C_{38}H_{32}P_2PtS$: C, 58.7; H, 4.1%. Found: C, 58.2; H, 3.9%. NMR spectra in $CDCl_3$, ^{1}H: δ 2.1–2.6 (m, CH_2, 4H), 6.5–7.6 (m, Ar, 28H); ^{31}P: δ 41.7 (^1J(Pt–P) = 1736 Hz), 45.3 (^1J(Pt–P) = 3201 Hz).

[Pt(dppe)(C,S–$C_{13}H_{10}S$)], **4a** + **4b** (mixture of isomers) was prepared from the isomeric mixture of **3a** and **3b** obtained from reaction of 4-MeDBT with [Pt(PMe_3)$_4$] by a reaction similar to that used to make **2** above. Anal. Calcd for $C_{39}H_{34}P_2PtS$: C, 59.2; H, 4.3%. Found: C, 59.4; H, 4.2%. NMR spectra in $CDCl_3$, ^{1}H: δ 2.10 (s, 3H, Me); δ 2.20 (s, 3H, Me); ^{31}P: isomer **4a**, δ 46.6 and 42.8, $^1J_{\text{Pt–P}}$ = 3209 and 1744 Hz; isomer **4b**, δ 45.3 and 41.8, $^1J_{\text{Pt–P}}$ = 3200 and 1736 Hz. The two C–S bonds in 4-MeDBT are different and give mixtures of the thiaplatinacycle isomers (approximately 1 : 1) **4a** and **4b**; however, the HDS product, 3-methylbiphenyl, is the same from both.

3.2. Hydrogenation reactions

Hydrogenation reactions were carried out as follows: the complex (**1a**, etc., 75 mg) in degassed toluene (5 cm^3) in a glass-lined Fisher–Porter tube (20 cm^3) was heated under hydrogen (20 atm, 100 °C, 24 h) (and in the presence of alumina (1.0 g, Aldrich, acid-washed) as appropriate). At the end of the reaction, the toluene was removed and the organic products extracted with acetonitrile and analysed by HPLC (Techsphere 5 ODS column: 30% water and 70% acetonitrile as mobile phase). The results are summarised in table 1.

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References

[1] R.R. Chianell, M. Daage and M.J. Ledoux, Adv. Catal. 40 (1994) 177;
P.T. Vasudevan and J.L.G. Fierro, Catal. Rev. Sci. Eng. 38 (1966) 161;
T. Topsøe, B.S. Clausen and F.E. Massoth, *Hydrotreating Catalysis* (Springer, Berlin, 1996).

[2] (a) J.P. van den Berg, J.P. Lucien, G. Germaine and G.L.B. Thielemans, Fuel Proces. Technol. 35 (1993) 119;
(b) I.E. Maxwell, J.E. Naber and K.P. de Jong, Appl. Catal. A 113 (1994) 153;
(c) P.N. Hannerup and B. Cooper, Oil Gas Eur. Magaz. 1 (1995) 25.

[3] B.H. Cooper and B.B.L. Donnis, Appl. Catal. A 137 (1996) 203.

[4] S.M. Kovach and G.D. Wilson (Ashland Oil), US Patent 3,943,053 (filed 4/10/74; appn. 9/3/76).

[5] R. Navarro, B. Pawelec, J.L.G. Fierro, P.T. Vasudevan, J.F. Cambra and P.L. Arias, Appl. Catal. A 137 (1996) 269;
M. Sugioka, C. Tochiyama, Y. Matsumoto and F. Sado, in: *Catalysis by Microporous Materials,* Stud. Surf. Sci. Catal. 94 (1995) 544;
M. Sugioka, F. Sado, Y. Matsumoto and N. Maesaki, Catal. Today 29 (1996) 255;
H.R. Reinhoudt, R. Troost, S. van Schalkwik, A.D. van Langenveld, S.T. Sie, H. Schulz, D. Chadwick, J. Cambra, V.H.J. de Beer, J.A.R. van Veen and J.A. Moulijn, Stud. Surf. Sci. Catal. 106 (1997) 237;
see also, B.C. Gates and H. Topsøe, Polyhedron (Symposium in Print on Hydrotreating) 16 (1997) 3213.

[6] J.J. Garcia and P.M. Maitlis, J. Am. Chem. Soc. 115 (1993) 12200;
J.J. Garcia, B.E. Mann, H. Adams, N.A. Bailey and P.M. Maitlis, J. Am. Chem. Soc. 117 (1995) 2179;
J.J. Garcia, A. Arevalo, S. Capella, A. Chehata, M. Hernandez, V. Montiel, G. Picazo, F. Del Rio, R.A. Toscano, H. Adams and P.M. Maitlis, Polyhedron (Symposium in Print on Hydrotreating) 16 (1997) 3185.

[7] T. Yoshida, T. Matsuda and S. Otsuka, Inorg. Synth. 28 (1990) 122;
B.E. Mann and A. Musco, J. Chem. Soc. Dalton Trans. (1980) 776.