New hydrogenation and isomerization reactions involving thiaplatinacycles derived from benzothiophene

Alexei Iretskii,[a] Harry Adams,[a] Juventino J. Garcia,[b] Graciela Picazo[b] and Peter M. Maitlis[a]

[a] *Department of Chemistry, The University of Sheffield, Sheffield, UK S3 7HF*
[b] *Facultad de Química, Universidad Nacional Autónoma de México, 04510 México D.F.*

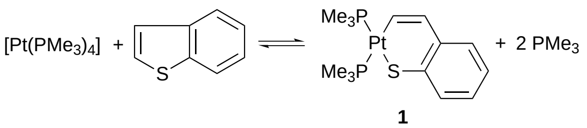
Hydrogenation of the thiaplatinacycle [Pt{*C,S*-(CH=CHC$_6$H$_4$S)}(dppe)] 2 (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) derived from benzothiophene, leads to [Pt{*C,S*-(CHMeC$_6$H$_4$S)}(dppe)] 3 in which 2H have added and a H-shift has occurred; the X-ray structures of 2 and 3 are reported.

Thiophenes (T), benzothiophenes (BT), dibenzothiophenes (DBT), and their alkyl derivatives pose particular problems for hydrodesulfurization (HDS) as they occur in substantial amounts, notably in the heavier crude oils, and are rather resistant to normal HDS catalysts such as Co–Mo–S on alumina.[1] Quite recently platinum has emerged as a viable catalyst for second stage industrial hydrotreating;[2] this has allowed the production of the so-called city diesel fuel, with a very low sulfur content ($\leqslant$30 ppm).

In our researches to model such HDS reactions we have found that the platinum(0) complex [Pt(PEt$_3$)$_3$] can reversibly oxidatively insert into the C–S bonds of T, BT or DBT, giving six-membered thiaplatinacycles.[3–5] These thiaplatinacycles extrude S and Pt on reaction with sources of hydride to give hydrocarbons, thus demonstrating a full HDS sequence mediated by platinum.

Related thiametallacycles are formed by the oxidative insertion of other metals (*e.g.* Rh and Ir[6]) into the thiophene; those derived from BT generally react with hydrogen to give 2-ethylthiophenol (or a salt thereof)[7] or 2,3-dihydrobenzothiophene,[8] though ethylbenzene can be obtained under forcing conditions.[9] We have now isolated and characterised a novel isomerisation product from partial hydrogenation of a thiaplatinacycle derived from BT, which indicates that the HDS cycle may be more complex than previously proposed.

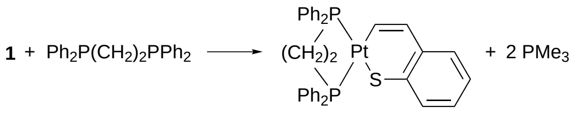
The trimethylphosphine complex **1**† was synthesised either from reaction of BT with pure [Pt(PMe$_3$)$_4$] in refluxing toluene [eqn. (1); 83%] or, more conveniently [eqn. (2); 69%] by a one-pot reaction of K$_2$PtCl$_4$, NaOH, and trimethylphosphine, forming [Pt(PMe$_3$)$_4$] *in situ*, to which BT was then added. Reaction of **1** with a small excess of dppe (Ph$_2$PCH$_2$CH$_2$PPh$_2$) gave complex **2** [eqn. (3); 89%].



1

(1)

$$\mathrm{K_2PtCl_4 + NaOH + PMe_3;\ BT} \longrightarrow \mathbf{1} \qquad (2)$$



2

(3)

The complexes were characterised by microanalysis, NMR spectra and an X-ray structure determination for **2**.‡ This showed the expected arrangement (Fig. 1) and was very similar to the structure already determined for [Pt{*C,S*-(CH=CHC$_6$H$_4$S)}(PEt$_3$)$_2$].[3] Complex **2** was hydrodesulfurised by reaction with LiAlH$_4$ in toluene–thf to give ethylbenzene (42%). Similar results but poorer yields were obtained for complex **1** and for [Pt{*C,S*-(CH=CHC$_6$H$_4$S)}(dppp)].

Complex **2** could also be hydrogenated (toluene solution, 120 °C, 20 atm H$_2$) directly to give a mixture of ethylbenzene (6%) and free BT (12%). The low yield of HDS product under these conditions is explained by the additional formation of a new platinum complex (in 74% yield). FABMS showed it to have a molecular ion at *m*/*z* 730 corresponding to [Pt(C$_8$H$_8$S(dppe)], indicating that 2 H have added to **2**. The new complex was identified as **3**§ by an X-ray determination which showed that the S-ligand did not have the expected saturated six-membered thiaplatinacycle structure; instead a ring contraction had occurred and the product had a methyl attached to CH in a five-membered thiaplatinacycle (Fig. 2).

The structure for **3** indicates that a hydrogen shift has occurred in addition to the hydrogenation so that the benzylic carbon is now attached to the metal. This also has structural consequences: the benzothiaplatinacycle in complex **2** is very nearly planar with a dihedral angle of only 3.2° between the plane C(1)–Pt–S and the best plane through S–C(8)···C(2)–C(1). By contrast, and as a consequence of the presence of the sp^3 carbon at C(1) the thiaplatinacycle in complex **3** is much more bent, with a dihedral angle of 27.8° between the planes C(1)–Pt–S and C(1)–C(2)–C(3).

The difference in the structures is also manifested in their reactions with HCl. Complex **3** was degraded to give

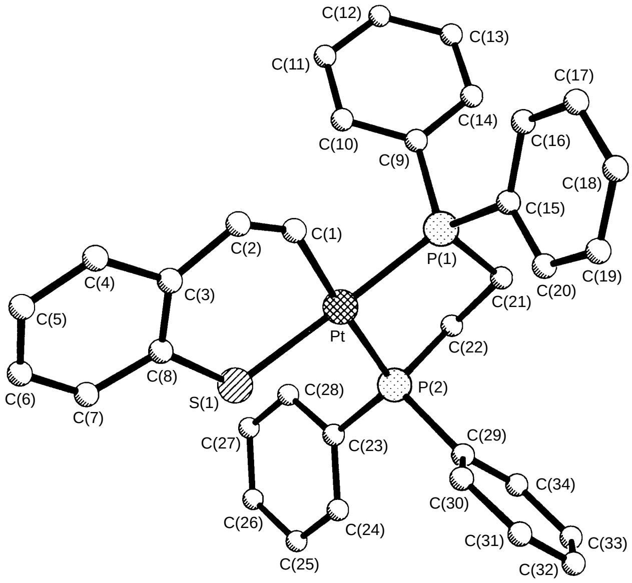


Fig. 1 The molecular structure determined for **2**. Bond lengths (Å) and angles (°): Pt–P(1) 2.2474(13), Pt–P(2) 2.2969(14), Pt–S 2.260(2), Pt–C(1) 2.054(4); C(1)–Pt–P(1) 93.1(2), P(1)–Pt–P(2) 85.20(5), C(1)–Pt–S 88.4(2), P(2)–Pt–S 93.40(5)°.

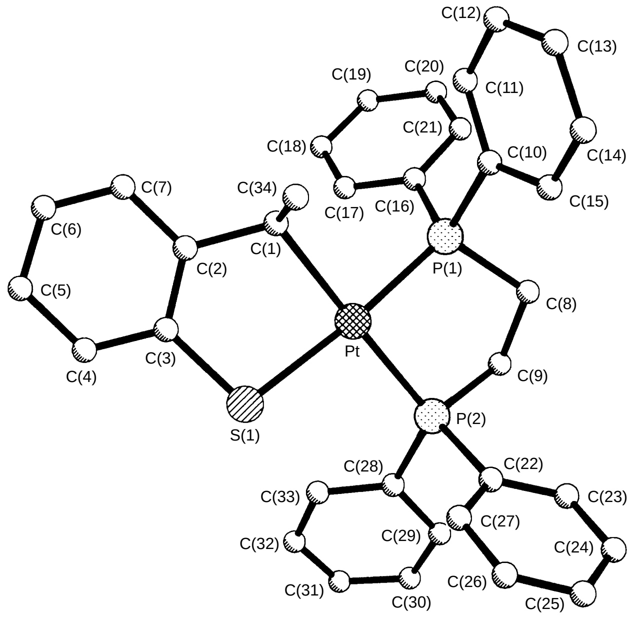
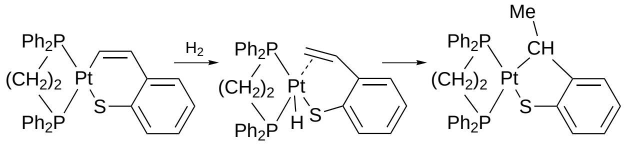


Fig. 2 The molecular structure determined for **3**. Bond lengths (Å) and angles (°): Pt–P(1) 2.232(4), Pt–P(2) 2.313(4), Pt–S 2.328(4), Pt–C(1) 2.202(14), Pt–C(34) 3.05 Å; C(1)–Pt–P(1) 93.3(4), P(1)–Pt–P(2) 85.49(13), C(1)–Pt–S, 82.7(4), P(2)–Pt–S 98.60(13)°.



2 **A** **3**

Scheme 1

2-ethylthiophenol, while the six-membered thiaplatinacycles [Pt{*C*,*S*-(CH=CHC$_6$H$_4$S)}(PEt$_3$)$_2$] and **2** gave 2-vinylthiophenol.[4]

One attractive mechanism by which the reaction **2** → **3** can occur is *via* a σ-*S* bonded π-alkene (η^3) intermediate (**A**), as shown in Scheme 1. Such species have been previously invoked in the reactions of various thiophenes with metal hydrides; a related iridium complex derived from thiophene itself has been isolated and characterised as [(triphos)Ir(η^3-S(Me)CH=CHCH=CH$_2$)]$^+$ [triphos = MeC(CH$_2$PPh$_2$)$_3$], and this shows equivalent bonding of the iridium to both the CH [2.19(3) Å] and to the CH$_2$ [2.12(3) Å].[10] That complex **3** does not have a type **A** structure is shown by the Pt···Me distance [Pt···C(34)] of 3.05 Å, which is well outside bonding; by contrast the distance Pt–C(1) is 2.202(14) Å.

Complex **3** can be hydrodesulfurised to ethylbenzene (*ca.* 80%) with LiAlH$_4$ (thf, 20 °C); this demonstrates a new HDS pathway, BT → **2** → **3** → PhEt.

We thank the EPSRC, the Royal Society, EERO, the European Community (Contract CL1*CT94-0062) and CONACYT for support and Professor W. Clegg for collecting the data for complex **2**.

Footnotes and References

* E-mail: P.Maitlis@Sheffield.ac.uk

† [Pt(*C*,*S*-SC$_8$H$_6$)(PMe$_3$)$_2$] **1**. Anal. Calc. for C$_{14}$H$_{24}$P$_2$PtS: C, 34.9; H, 5.0; S, 6.65. Found: C, 35.0; H, 4.95; S, 6.7%. NMR (CDCl$_3$): ^{1}H: δ 1.2–2.0 (m, 18 H, CH$_3$), 7.0–7.1 (m, 1 H, CH), 7.1–7.2 (m, 1 H, CH), 7.2–7.4 (m, 2 H, CH), 7.4–7.6 (m, 1 H, CH), 7.9 (m, 1 H, CH). ^{31}P: δ −22.6 [d, ^1J(PPt) 3065 Hz], −29.3 [d, ^1J(PPt) 1708 Hz]. ^{13}C{^{1}H}: δ 138.6 [t, CH, ^2J(PtC) 85 Hz], 131.4 (s, 2CH), 129.8 (s, C), 129.8 (s, CH), 129.7 [dd, CH, ^2J(*trans*-PC) 100.6, ^2J(*cis*-PC) 8.6 Hz], 125.3 (s, C), 121.7 (s, CH).

‡ [Pt(*C*,*S*-SC$_8$H$_6$)(dppe)] **2**. Anal. Calc. for C$_{34}$H$_{30}$P$_2$PtS·CH$_2$Cl$_2$: C, 51.7; H, 4.0. Found: C, 52.2; H, 3.8%. NMR (CDCl$_3$), ^{1}H δ 2.25–2.6 (m, CH$_2$, 4 H), 7.0–8.0 (m, CH + Ar, 26 H). ^{31}P: δ 41.5 [d, ^1J(PtP) 1743 Hz, ^2J(PP) 6 Hz], 46.3 [d, ^1J(PtP) 3122 Hz]. FABMS: *m/z* 728.

Crystal data for C$_{35}$H$_{32}$Cl$_2$P$_2$PtS: *M* = 812.60, crystallised from CH$_2$Cl$_2$–hexane as yellow blocks and containing one molecule of CH$_2$Cl$_2$; crystal dimensions 0.48 × 0.38 × 0.27 mm. Monoclinic, space group $P2_1/n$ (a non-standard setting of $P2_1/c$,C^5_{2h}, no. 14), a = 9.5594(7), b = 19.5003(14), c = 17.4993(12) Å, β = 91.683(2), U = 3260.7(4) Å^3, Z = 4, D_c = 1.655 Mg m^{-3}, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 4.653 mm^{-1}, F(000) = 1600.

Refinement converged at a final R = 0.0318 (wR_2 = 0.0863, for all 5728 unique data, 372 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −1.087 and 1.308 e A^{-3}.

§ [Pt(*C*,*S*-SC$_8$H$_8$)(dppe)], **3**. Anal. Calc. for C$_{34}$H$_{32}$P$_2$PtS·0.5CHCl$_3$: C, 52.5; H, 4.2; Found: C, 53.1; H, 4.4%. NMR spectra in CDCl$_3$, ^{1}H: δ 1.1–1.4 (m, 3 H, CH$_3$), 1.9–2.7 (m, 4 H, CH$_2$), 3.1–3.5 (m, 1 H, CH), 6.7 (t, 1 H, Ar), 6.8 (t, 1 H, Ar), 6.9 (d, 1 H, Ar), 7.4–8.0 (m, 21 H, Ar). ^{31}P: δ 43.0 [^1J(PtP) 1594, ^2J(PP) 4 Hz], 45.9 [^1J(PtP) 3190 Hz]. FABMS: *m/z* 730.

Crystal data for **3**: C$_{34}$H$_{32}$P$_2$PtS; *M* = 729.69, crystallised from CH$_2$Cl$_2$–hexane as yellow blocks; crystal dimensions 0.43 × 0.26 × 0.12 mm. Monoclinic, space group $P2_1/c$ (C^5_{2h}, No. 14), a = 9.266(4), b = 15.142(7), c = 21.303(9) Å, β = 98.51(3), U = 2956(2) Å^3, Z = 4, D_c = 1.640 Mg m^{-3}, Mo-Kα radiation (λ = 0.710 73 Å), μ(Mo-Kα) = 4.948 mm^{-1}, F(000) = 1440.

Refinement converged at a final R = 0.0665 (wR_2 = 0.1506, for all 5188 unique data 344 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.892 and 1.150 e A^{-3}. CCDC 182/670.

1 H. Topsoe, B. S. Clausen and F. Massoth, *Hydrotreating Catalysis*, Springer, Berlin, p. 114; A. N. Startsev, *Catal. Rev. Sci. Eng.*, 1995, **37**, 353; B. C. Weygand and C. Friend, *Chem. Rev.*, 1992, **92**, 491; C. M. Friend and D. A. Chen, *Polyhedron*, 1997, **16**, 3165; B. Delmon, *Catal. Lett.*, 1993, **1–2**, 1; O. Weisser and S. Landa, *Sulphide Catalysts, their Properties and Applications*, Pergamon, Oxford, 1973.

2 J. P. van den Berg, J. P. Lucien, G. Germaine and G. L. B. Thielemans, *Fuel Process. Technol.*, 1993, **35**, 119; B. H. Cooper, A. Stanislaus and P. N. Hannerup, *Hydrocarbon Process.*, 1993, 83; I. E. Maxwell, J. E. Naber and K. P. de Jong, *Appl. Catal., A: Gen.*, 1994, **113**, 153; S. Mignard, N. Marchal and S. Kasztelan, *Bull. Soc. Chim. Belg.*, 1995, **104**, 259; M. Sugioka, F. Sado, Y. Matsumoto and N. Maesaki, *Catal. Today*, 1996, **29**, 255.

3 J. J. Garcia, B. E. Mann, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Am. Chem. Soc.*, 1995, **117**, 2179; see also: J. J. Garcia and P. M. Maitlis, *J. Am. Chem. Soc.*, 1993, **115**, 12 200.

4 J. J. Garcia, A. Arevalo, V. Montiel, F. Del Rio, B. Quiroz, H. Adams and P. M. Maitlis, *Organometallics*, 1997, **16**, 3216.

5 J. J. Garcia, A. Arevalo, S. Capella, A. Chehata, M. Hernandez, V. Montiel, G. Picazo, F. Del Rio, R. Toscano, H. Adams and P. M. Maitlis, *Polyhedron*, 1997, **16**, 3185.

6 R. J. Angelici, *Polyhedron*, 1997, **16**, 3073 and following articles in *Polyhedron Symposium in Print on Hydrotreating*; see also: C. Bianchini and A. Meli, *J. Chem. Soc., Dalton Trans.*, 1996, 801.

7 C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, P. Frediani, V. Herrera and R. A. Sanchez-Delgado, *J. Am. Chem. Soc.*, 1993, **115**, 7505; C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, S. Moneti, V. Herrera and R. A. Sanchez-Delgado, *J. Am. Chem. Soc.*, 1994, **116**, 4370; C. Bianchini, A. Meli, V. Patinec, V. Sernau and F. Vizza, *J. Am. Chem. Soc.*, 1997, **119**, 4945.

8 V. Herrera, A. Fuentes, M. Rosales, R. A. Sanchez-Delgado, C. Bianchini, A. Meli and F. Vizza, *Organometallics*, 1997, **16**, 2465.

9 D. A. Vicic and W. D. Jones, *Organometallics*, 1997, **16**, 1912.

10 C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, P. Frediani, V. Herrera and R. A. Sanchez-Delgado, *J. Am. Chem. Soc.*, 1993, **115**, 2731.

11 G. M. Sheldrick, SHELXL93, An integrated system for solving and refining crystal structures from diffraction data, University of Gottingen, Germany 1993.

Received in Cambridge, UK, 15th September 1997; 7/06707K