Synthesis and structure of 4,6-disubstituted dibenzothiophenes and their use in the preparation of binuclear platinum(II) complexes

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The reaction of two equivalents of [Pt(PEt$_3$)$_4$] with 4,6-dibromodibenzothiophene (DBT-Br$_2$) afforded *trans,trans*-[(μ-DBT-1κC^4:2κC^6){PtBr(PEt$_3$)$_2$}$_2$] (**5**), a unique example of double oxidative addition of a heteroaromatic substrate to Pt(0). The related bimetallic Pt(II) complex, *cis,cis*-[(μ-DBT-1κC^4:2κC^6){Pt-(η^4-cod)Cl}$_2$] (**6**), was isolated *via* a double transmetallation of 4,6-bis(trimethylstannyl)dibenzothiophene with [Pt(η^4-cod)Cl$_2$], where cod is 1,5-cyclooctadiene. The new complexes were characterised by spectroscopic techniques. The disubstituted dibenzothiophene compounds were prepared by dilithiation of dibenzothiophene, followed by quenching with chlorotrimethylsilane and chlorotrimethylstannane, to give 4,6-(SiMe$_3$)$_2$(SC$_{12}$H$_6$) (**2**) and 4,6-(SnMe$_3$)$_2$(SC$_{12}$H$_6$) (**4**), respectively. Treatment of 4,6-(SiMe$_3$)$_2$(SC$_{12}$H$_6$) with bromine produced 4,6-Br$_2$(SC$_{12}$H$_6$) (**3**). The X-ray crystal structures of **2** and **3** were determined. An improved method of synthesis of 2,8-dibromodibenzothiophene (**1**) was also developed.

Introduction

Many examples of σ-carbon-bonded complexes of the type *trans*-[MX(R′)(PR$_3$)$_2$], where M = Pd, Pt; X = halide and R′ = alkyl, aryl, alkenyl or acyl, have been isolated.[1,2] Oxidative addition or insertion into Si–X bonds by platinum(0) have also been reported and similar *trans*-type complexes can be obtained.[3] Only a few examples of insertion of zerovalent palladium and platinum into C–X bonds of heteroaromatic compounds are known.[4–6] The catalytic processes of C–C and C–heteroatom (nitrogen, sulfur and oxygen) coupling have been studied but much less attention has been given to the stoichiometric reactions that lead to the isolation of the metal(II) oxidation products of heteroaromatic substrates. Hor and co-workers[4,5] studied the oxidation addition reactions of [Pd-(PPh$_3$)$_4$] with bromothiophenes and the formation of *trans*-[PdBr(2-thienyl)(PPh$_3$)$_2$] complexes. Lin and co-workers[6] prepared heterobimetallic compounds from ferrocene-substituted halothiophenes, such as ferrocene end-capped Pd(II) and Pt(II) complexes with thiophene spacers. The authors claimed that this was the first reported case of the oxidative addition of [Pt(PPh$_3$)$_4$] to a heteroaromatic compound. In fact, Chia and McWhinnie[7] reported the isolation of *trans*-[PtBr(2-C$_4$H$_3$S)(PPh$_3$)$_2$] based on elemental analysis and ^{31}P NMR data. The $^1J_{\mathrm{Pt,P}}$ coupling was reported as 1870 Hz, which is an unusually small value for *trans*-Pt(PR$_3$)$_2$ systems of this type.

Binuclear complexes synthesised by a double oxidative addition to a dihalo aromatic compound are relatively rare and [bis(*trans*-M(PR$_3$)$_2$X)(R′)] complexes with M = Pd, Pt; R = Et, Ph; X = I, Br and R′ = 1,4-benzene, 4,4′-biphenyl, 4,4″-ter-*p*-phenyl, 4,4′-tolane or 4,4′-benzophenone are known.[8] Double oxidative addition reactions of this type have been found to occur with dihalo heteroaromatic compounds where the heteroaryl moiety is part of a metalloporphyrin macrocycle *viz.* dipalladioporphyrins, or mixed palladio-/platinioporphyrins.[9] Binuclear platinum(II) complexes incorporating heteroaryl ligands have previously been prepared by a double transmetallation with two equivalents of [Pt(η^4-cod)Cl$_2$] (cod = 1,5-cyclooctadiene) and 2,5-bis(trimethylstannyl)thiophene or 2,5′-bis(trimethylstannyl)-5-(2′-thienyl)thiophene.[10] We report, to the best of our knowledge, the first double oxidative addition reaction of platinum(0) to a heteroaromatic compound, namely 4,6-dibromodibenzothiophene, as well as the double transmetallation of 4,6-bis(trimethylstannyl)dibenzothiophene with [Pt(η^4-cod)Cl$_2$].

The dibenzothiophene moiety is expected to act as a rigid spacer, giving rise to a binuclear complex in which the two platinum metal centres are set at a distance of *ca.* 6 Å apart. Many examples of bimetallic and heterobimetallic A-frame complexes containing the bridging ligands bis(diphenylphosphanyl)methane, dppm, and bis(diphenylphosphanyl)ethane, dppe, have been recorded.[11] Symmetrical and unsymmetrical diplatinum complexes bridged by two dppm molecules are also known.[12] These complexes can undergo oxidative addition reactions without disruption of the binuclear complex.[13,14] The Pt–Pt separation in dppm bridged complexes are typically of the order of 2.58 to 2.64 Å,[13,15] comparable to, but slightly shorter than in elemental platinum (2.77 Å). The binuclear complex presented here is constructed *via* a double oxidative addition reaction at the two C–Br bonds of 4,6-dibromodibenzothiophene. The alignment of the metal centres is brought about by the geometry and orientation of the planar condensed aromatic dibenzothiophene ring system and the position of attachment of the metal fragments to the ring. The inter-metal distance is too long for metal-metal bonding to occur, but through the electron-conjugated, aromatic ring system, the metals may still "communicate" in a cooperative way. Such a system would allow enough space for the possible activation of larger organic substrates such as butadiyne and allyls in the inter-metal region.

Results and discussion

Ligand synthesis

While the syntheses of 2,8-; 3,7- and 2,4-dibromodibenzothiophene (Scheme 1) are recorded in the literature,[16–18] no

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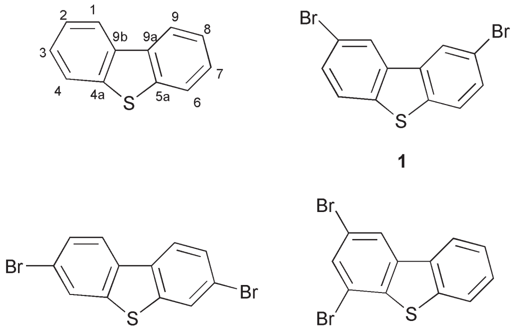
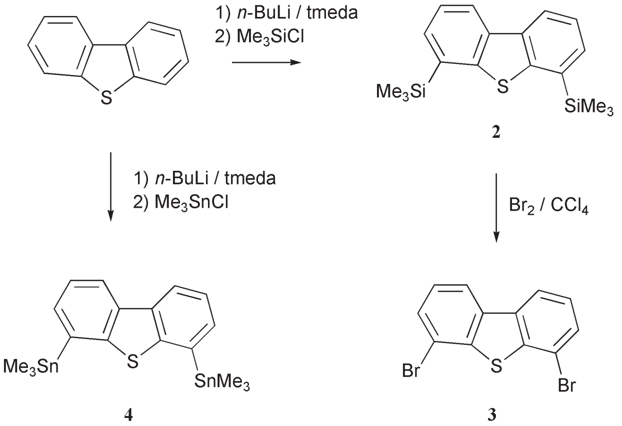


Scheme 1 Numbering system for dibenzothiophene and 2,8-; 3,7- and 2,4-dibromodibenzothiophene.



Scheme 2 Ligand synthesis of 4,6-disubstituted dibenzothiophenes.

reference to the 4,6-dibromo isomer could be found. While investigating a method for the preparation of 4,6-dibromodibenzothiophene, an improved method for the synthesis of 2,8-dibromodibenzothiophene, **1**, was developed. Isomer **1** had previously been prepared by direct bromination of dibenzothiophene with bromine.[16] Under reflux in carbon disulfide, this method resulted in variable yields.[19–21] Very low yields of **1** were obtained when using dichloromethane as solvent,[22] but the reaction of 5-methyldibenzo[*b,d*]thiophenium tetrafluoroborate with bromine gave satisfactory yields.[22,23] An improved method of synthesis utilises the free radical brominating agent *N*-bromosuccinimide, NBS, under mild conditions with chloroform as solvent. NBS has recently become more commonly used in bromination reactions of heteroaromatic compounds.[24]

The approach used to prepare 4,6-dibromodibenzothiophene involved the dilithiation of dibenzothiophene. Derivatisation at positions 4 and 6 of dibenzothiophene *via* metallation is inherently problematic. Attempts at dilithiation by different research groups have in the past led to mixtures of monolithiated (major) and dilithiated (minor) products that were difficult to separate.[25,26] Caubère and co-workers[27] found that the activation of *n*-butyllithium with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, tmeda, only becomes effective at 60 °C in hexane. By employing 3 equiv. of *n*-butyllithium and 3 equiv. of tmeda for 2 h at 60 °C, they were able to obtain 4,6-disubstituted dibenzothiophene in yields of 50–60%, depending on the electrophile used. Recently, 4,6-dibenzothiophenedicarboxylic acid has been prepared in 88% yield by dicarboxylation of dilithiodibenzothiophene with dry ice.[28] Following the dilithiation of dibenzothiophene using the method of Caubère, subsequent reaction of 4,6-dilithiodibenzothiophene with bromine could be expected to give the desired 4,6-dibromosubstituted compound. However, it was found that the bromination of 4,6-dilithiodibenzothiophene with 2 equiv. of bromine afforded a mixture of brominated dibenzothiophene products. It was not possible to separate these products by column chromatography on silica gel. To overcome this problem, the 4,6-dilithiodibenzothiophene intermediate was treated with chlorotrimethylsilane, which led to the isolation of 4,6-bis-(trimethylsilyl)dibenzothiophene, **2**. When **2** was reacted with bromine in carbon tetrachloride, pure 4,6-dibromodibenzothiophene, **3**, was obtained in a quantitative yield (Scheme 2). The stannyl analogue of **2**, namely 4,6-bis-(trimethylstannyl)-dibenzothiophene, **4**, was prepared in a similar way by quenching 4,6-dilithiodibenzothiophene with chlorotrimethylstannane.

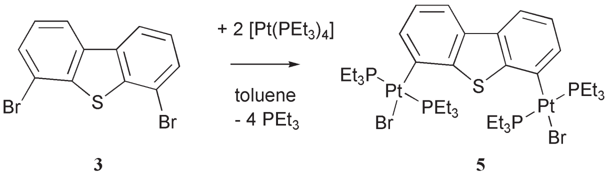
Platinum(II) complexes

Compound **3** reacted with 2 equiv. of tetrakis(triethylphosphane)platinum(0) in refluxing toluene after 1 h to give μ-dibenzothienyl-1κC^4:2κC^6-bis[*trans*-bromobis(triethylphosphane)platinum(II)], **5** (Scheme 3). Each platinum centre in this binuclear complex has a square planar geometry. The ^{31}P{^{1}H} NMR spectrum of **5** displayed a single resonance at 12.47 ppm with accompanying ^{195}Pt satellite peaks ($^1J_{\mathrm{Pt,P}} = 2694$ Hz), indicating the presence of 2 equivalent phosphorus atoms. These data compare favourably with that of other *trans*-"PtX(PR$_3$)$_2$" type compounds, where X = I or Br and R = Et or Ph[3,6,8] with $^1J_{\mathrm{Pt,P}}$ values ranging from 2780 to 3100 Hz. Similarly, [PtXY(PR$_3$)$_2$] complexes (X = halide, Y = carbon-donor anionic ligand) occur predominantly as *trans* isomers.[29]

A rare example of a *cis*-[PtXY(PR$_3$)$_2$] type complex is that of [Pt{CH(NHCOPh)(CO$_2$Me)}Br(PPh$_3$)$_2$], which displays two separate singlet resonances,[30] attributed to two nonequivalent phosphorus atoms, in its ^{31}P NMR spectrum: δ = 17.90 ppm [$^2J_{\mathrm{P,P}}$ 16.5 Hz, $^1J_{\mathrm{Pt,P}(trans)}$ 1903 Hz] and 20.45 ppm [$^2J_{\mathrm{P,P}}$ 16.5 Hz, $^1J_{\mathrm{Pt,P}(cis)}$ 4482 Hz].

A concerted effort was made to obtain crystals of **5** in order to determine the exact Pt–Pt non-bonding distance by X-ray crystallography. Colourless prisms were grown from a cold saturated solution of **5** in toluene–hexane. However, the crystals readily become opaque when handled and were thus unsuitable for crystallographic studies.

The oxidative addition reactions of [Pt(PEt$_3$)$_4$] with 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene were also investigated. Although the xanthene molecule is not fully conjugated and is non-aromatic, a double oxidative addition at positions 4 and 5 would bring about an inter-metal distance in the range of 4 Å as a result of the folding-in of the two benzenoid rings in the xanthene molecule.[31] However, oxidative addition was found to be extremely sluggish. A single oxidation addition product was observed by NMR spectroscopy under similar reaction conditions as for the preparation of **5**.[32] The ^{31}P NMR data, δ = 10.96 ppm and $^1J_{\mathrm{Pt,P}} = 2739$ Hz, indicated once again a *trans* bisphosphane geometry at the platinum(II) centre. When the reaction mixture was allowed to reflux for 24 h, the mono-oxidation product was once again detected by NMR spectroscopy. However, a second phosphane resonance was detected in the ^{31}P NMR spectrum (δ = 13.06 ppm, $^1J_{\mathrm{P,P}} = 2752$ Hz) due to the presence of a small amount of the corresponding binuclear platinum(II) complex. Increasing the reaction time to 1 week still yielded a mixture of mono- and binuclear products (4 : 1 based on ^{31}P NMR peak intensities).



Scheme 3 Double oxidative addition reaction.

The related binuclear platinum(II) complex μ-dibenzothienyl-1κC^4:2κC^6-bis[*cis*-chloro(η^4-1,5-cyclooctadiene)platinum(II)], **6**, was prepared by a double transmetallation of **4** with the *cis*-directing precursor [Pt(η^4-cod)Cl$_2$] (Scheme 4).

[PtXR(η^4-cod)] type complexes (where X = Br or Cl and R = aryl) are commonly prepared by a halide exchange reaction between [Pt(η^4-cod)X$_2$] and organolithium substrates.[33] This methodology is not applicable to dibenzothiophene because of the difficulty involved in the dilithiation of dibenzothiophene. The cod ligand can readily be replaced by chelating phosphanes or amines to give *cis* complexes,[10] which would render the bimetallic complex more susceptible to oxidative addition to platinum(IV). The NMR chemical shifts of **6** correspond well with that obtained for related monoplatinum-substituted dibenzothiophene compounds.[34]

Crystal structures

Crystals of **2** and **3** were grown from refrigerated hexane solutions and their respective structures were confirmed by single crystal X-ray crystallography (Table 1). Selected bond lengths and angles for **2** and **3** are given in Tables 2 and 3, while ball-and-stick molecular representations of **2** and **3** are shown in Figs. 1 and 2, respectively.

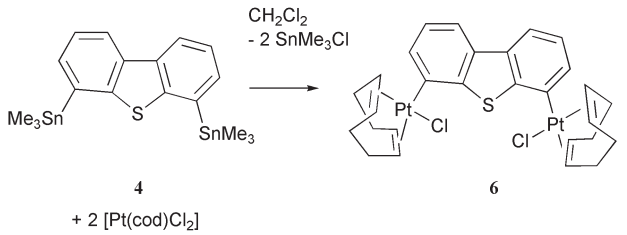
The non-bonding separation between the two silicon atoms in **2** was found to be 6.77 Å, while the distance between the two bromine atoms in **3** is shorter at 6.51 Å. Both these distances, however, are longer than the P–P non-bonding distance of 6.38 Å in 4,6-bis(diphenylphosphanyl)dibenzothiophene.[35] Bond lengths of the dibenzothiophene ring in **2** and **3** fall within the range of typical values reported in the Cambridge Structural Database.[36] Bond angles also compare favourably with the exception of C(3)–C(4)–C(4a) and C(7)–C(6)–C(5a) in **2** at 114.5(2)° and 114.7(2)°, respectively. These angles are smaller than the values typically reported (mean bond angle approximately 118° with a range of approximately 6° based on 71 structures in the Cambridge Structural Database[36]). The corresponding angles in free dibenzothiophene are 117.8°;[37] thus, dibenzothiophene compounds substituted at positions 4 and 6 contain smaller C(3)–C(4)–C(4a) and C(7)–C(6)–C(5a) bond angles than when substituted at other positions of the heterocycle. Examples include 116.13(7)° in 4,6-bis(diphenylphosphanyl)dibenzothiophene[35] and 117.6(4)° in 4,6-dimethyldibenzothiophene.[26] In contrast, the C(3)–C(4)–C(4a) and C(7)–C(6)–C(5a) angles in **3** are, at 120.5(4)° and 120.6(4)°, respectively, larger than in free dibenzothiophene. Consequently, the external C(4a)–C(4)–Br(1) and C(3)–C(4)–Br(1) angles in **3** are larger than the corresponding angles about silicon in **2**. The internal angle at sulfur is smaller in **3** than in **2** (90.6° *vs.* 91.5°) and C(9)–C(9a) is longer while C(4a)–C(9b) is shorter. The Br(1)–C(4) bond distance in **3** is almost identical to the Si(3)–C(4) separation in **2**: 1.894(5) and 1.890(2) Å, respectively.

Table 1 Crystallographic data for **2** and **3**

Empirical formula	$C_{18}H_{24}SSi_2$ (**2**)	$C_{12}H_6Br_2S$ (**3**)
Formula mass	328.61	342.05
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	15.169(2)	10.4977(17)
b/Å	8.4610(13)	8.5629(14)
c/Å	15.288(2)	12.947(2)
α/°	90	90
β/°	94.228(3)	106.813(3)
γ/°	90	90
U/Å^3	1956.8(5)	1114.03(3)
T/K	294(2)	293(2)
Z	4	4
μ/mm^{-1}	0.281	7.423
Total reflect.	13 152	7581
Independent reflect.	4839	2766
R_{int}	0.0162	0.0462
Obs. reflect. ($I > 2\sigma$)	3566	1860
λ (Mo-K_α)/Å	0.71073	0.71073
R_1 (obs)	0.0394	0.0514
wR_2 (obs)	0.1026	0.1319
R_1 (all)	0.0588	0.0779
wR_2 (all)	0.1152	0.1470

Conclusion

The 4,6-disubstituted dibenzothiophene ligands **2**, **3** and **4** reported here are novel and methods for their synthesis were designed. The oxidative addition substrate **3** had to be prepared indirectly by the bromination of **2**. The double oxidative addition of two Pt(PEt$_3$)$_2$ moieties onto the two C–Br bonds of **3** proceeded relatively facilely. In contrast, 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene did not react in the same way and even under prolonged reflux a mixture of mono- and binuclear platinum(II) species was obtained. The crystal structures of **2** and **3** showed that the non-bonding distance between the heteroatoms connected at C(4) and C(6) are in the region of 6.5–6.8 Å. The Pt–Pt inter-metal distance in **5** is expected to fall in the same region. A double transmetallation reaction gave the binuclear platinum(II) complex **6**.



Scheme 4 Double transmetallation reaction.

Experimental

General remarks

All solvents were dried and distilled according to established methods. All reagents were purchased from commercial sources and tmeda was distilled prior to use. [Pt(η^4-cod)Cl$_2$] and [Pt(PEt$_3$)$_4$] was prepared from K$_2$[PtCl$_4$] according to the procedures described in the literature.[38,39] Air-sensitive compounds were handled using standard Schlenk and vacuum line techniques under an atmosphere of dry nitrogen or argon. NMR spectra were recorded on a Bruker ARX-300 (7.0 T) instrument operating at 300.136 MHz for ^{1}H, 121.496 MHz for ^{13}C and 75.469 MHz for ^{31}P. Spectra were calibrated

Table 2 Selected bond lengths (Å) and angles (°) for **2** with e.s.d.'s in parentheses

Si(3)–C(4)	1.890(2)	C(4a)–S(1)–C(5a)	92.24(8)
S(1)–C(4a)	1.756(2)	C(9b)–C(4a)–S(1)	111.1(1)
C(9a)–C(9b)	1.448(2)	C(4a)–C(9b)–C(9a)	112.8(2)
C(1)–C(2)	1.370(3)	C(9b)–C(4a)–C(4)	123.8(2)
C(2)–C(3)	1.390(3)	C(1)–C(9b)–C(4a)	118.5(2)
C(3)–C(4)	1.396(3)	C(2)–C(1)–C(9b)	119.4(2)
C(4)–C(4a)	1.406(2)	C(1)–C(2)–C(3)	120.6(2)
C(4a)–C(9b)	1.401(2)	C(2)–C(3)–C(4)	123.1(2)
C(1)–C(9b)	1.398(2)	C(3)–C(4)–C(4a)	114.5(2)
Si(3)–C(10)	1.854(2)	C(3)–C(4)–Si(3)	121.6(1)
Si(3)–C(11)	1.861(3)	C(4a)–C(4)–Si(3)	123.9(1)
Si(3)–C(12)	1.859(3)	C(4)–C(4a)–S(1)	125.0(1)
		C(1)–C(9b)–C(9a)	128.8(2)

Table 3 Selected bond lengths (Å) and angles (°) for **3** with e.s.d.'s in parentheses

Br(2)–C(2)	1.894(5)	C(1)–S–C(12)	90.6(2)
S–C(12)	1.753(4)	C(6)–C(1)–S	112.8(3)
C(6)–C(7)	1.446(6)	C(1)–C(6)–C(7)	111.9(4)
C(4)–C(5)	1.374(7)	C(6)–C(1)–C(2)	120.9(4)
C(3)–C(4)	1.402(7)	C(5)–C(6)–C(1)	118.3(4)
C(2)–C(3)	1.379(6)	C(4)–C(5)–C(6)	119.9(4)
C(1)–C(2)	1.379(6)	C(5)–C(4)–C(3)	121.4(4)
C(1)–C(6)	1.416(6)	C(4)–C(3)–C(2)	119.1(5)
C(5)–C(6)	1.407(6)	C(3)–C(2)–C(1)	120.5(4)
		C(3)–C(2)–Br(2)	120.7(4)
		C(1)–C(2)–Br(2)	118.9(3)
		C(2)–C(1)–S	126.3(3)
		C(5)–C(6)–C(7)	129.8(4)

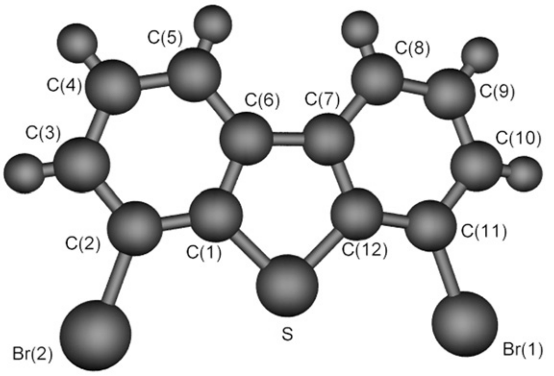


Fig. 2 Molecular structure of **3**.

using the deuterated solvent signal as the internal reference (7.2400 ppm for ^{1}H and 77.000 ppm for ^{13}C). ^{31}P NMR spectra were referenced to the deuterated lock solvent, which had been previously referenced to 85% H_3PO_4. Electon impact mass spectra (EI-MS) were recorded on a Finnigan Mat 8200 mass spectrometer operating at approximately 70 eV (1.12×10^{-17} J). IR spectra were recorded on a 113 V FT-IR Bruker instrument. Melting points were determined using a Kofler hot stage microscope and are uncorrected.

Syntheses

2,8-Dibromodibenzothiophene (1). A mixture of dibenzothiophene (9.95 g, 54 mmol) and NBS (20.3 g, 114 mmol) was stirred in chloroform (500 mL) at ambient temperature for 24 h. The reaction mixture was hydrolysed and the organic phase separated off and dried over anhydrous sodium sulfate. The volume of the solution was reduced by rotary vaporisation and a pure crystalline white solid precipitated upon cooling the solution to −25 °C. Yield: 13.8 g (75%). $C_{12}H_6Br_2S$ (342.05). ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.55$ [dd, $^3J_{H,H} = 8.53$, $^4J_{H,H} = 2.05$ Hz, 2 H, C(3)–H, C(7)–H], 7.68 [d, $^3J_{H,H} = 8.52$ Hz, 2 H, C(4)–H, C(6)–H], 8.20 [d, $^4J_{H,H} = 1.80$ Hz, 2 H, C(1)–H, C(9)–H]. ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 118.58$ [C(2), C(8)], 124.16 [C(4), C(6)], 124.68 [C(1), C(9)], 130.26 [C(3), C(7)], 136.12 [C(9a), C(9b)], 138.67 [C(4a), C(5a)]. EI-MS: m/z 342 (M^+, 28%), 182 ($M^+ - 2Br$, 31%), 149 ($M^+ - 2Br - SH$, 21%).

4,6-Bis(trimethylsilyl)dibenzothiophene (2). A 250 mL round-bottomed flask was charged with tmeda (11.9 mL, 78.8 mmol) and dry hexane (40 mL) under nitrogen. With the aid of a dropping funnel, a 1.6 M solution of *n*-butyllithium in hexane (49.6 mL, 79 mmol) was added to the tmeda solution at 0 °C. The mixture was stirred at 0 °C for 30 min and for a further 30 min at room temperature. The mixture was then diluted by the addition of hexane (60 mL) and dibenzothiophene (4.83 g, 26.2 mmol) was introduced *via* a powder funnel. After heating the mixture at 60 °C for 2 h, it was cooled to −70 °C and chlorotrimethylsilane (10.0 mL, 78.8 mmol) was added dropwise. The mixture was stirred for 20 min at −65 °C after which the cold bath was removed and the mixture stirred for an additional 40 min. The reaction was quenched upon pouring the mixture into a separating funnel containing water (60 mL). The organic layer was separated, the aqueous layer extracted with hexane, the hexane fractions combined, dried over anhydrous sodium sulfate and concentrated under reduced pressure. White crystals were obtained upon cooling the resulting yellow solution at −20 °C. The product was purified by column chromatography on silica gel using *n*-pentane as eluent. Crystals suitable for X-ray analysis were collected from a refrigerated hexane solution. Yield: 2.64 g (30%). $C_{18}H_{24}SSi_2$ (328.62): anal. calcd. C 65.79, H 7.36; found C 65.51, H 7.33. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 0.516$ (s, 18 H, $SiMe_3$), 7.455 [t, $^3J_{H,H} = 7.41$, 2 H, C(2)–H, C(8)–H], 7.610 [dd, $^3J_{H,H} = 7.05$, $^4J_{H,H} = 1.29$ Hz, 2 H, C(3)–H, C(7)–H], 8.173 [dd, $^3J_{H,H} = 7.82$, $^4J_{H,H} = 1.14$ Hz, 2 H, C(1)–H, C(9)–H]. ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = -1.182$ ($SiMe_3$), 122.29 [C(1), C(9)], 123.74 [C(2), C(8)], 132.39 [C(3), C(7)], 133.76 [C(4), C(6)], 134.45 [C(9a), C(9b)], 145.03 [C(4a), C(5a)]. EI-MS: m/z 328 (M^+, 65%), 313 ($M^+ - Me$, 100%), 298 ($M^+ - 3Me$, 2%), 256 ($M^+ - 3Me - Si$, 10%), 241 ($M^+ - 4Me - Si$, 22%), 73 ($SiMe_3{}^+$, 28%). Mp: 97–98 °C.

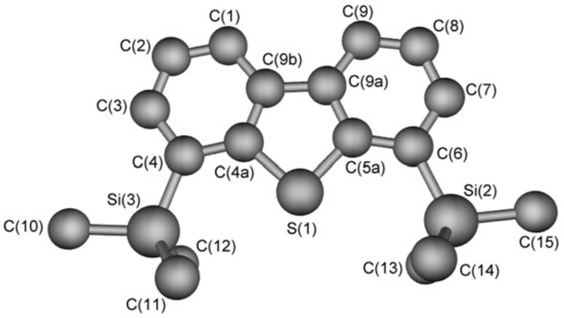


Fig. 1 Molecular structure of **2** (hydrogen atoms omitted for clarity).

4,6-Dibromodibenzothiophene (3). A bromine–carbon tetrachloride solution (1.20 mL of a 2.47 M solution, 2.96 mmol) was added to a solution of **2** (0.480 g, 1.46 mmol) in carbon tetrachloride (3.0 mL) at −15 °C. The mixture was stirred in the cold for 60 min, the cold bath was removed and the mixture stirred for a further 60 min. The volume of the mixture was increased by the addition of carbon tetrachloride (45 mL) before the reaction was quenched with water. After washing the organic layer with brine, drying over anhydrous sodium sulfate and evaporating to dryness, **3** was obtained as a pure, white crystalline solid. Yield: 0.444 g (89%). $C_{12}H_6Br_2S$ (342.05): anal. calcd. C 42.14, H 1.77; found C 41.98, H 1.75. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 7.356$ [t, $^3J_{H,H} = 7.82$ Hz, 2 H, C(2)–H, C(8)–H], 7.631 [dd, $^3J_{H,H} = 7.82$ Hz, $^4J_{H,H} = 0.96$ Hz, 2 H, C(3)–H, C(7)–H], 8.050 [dd, $^3J_{H,H} = 7.82$ Hz, $^4J_{H,H} = 0.95$ Hz, 2 H, C(1)–H, C(9)–H]. ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 116.37$ [C(4), C(6)], 120.96 [C(1), C(9)], 126.16 [C(2), C(8)], 129.96 [C(3), C(7)], 137.07 [C(9a), C(9b)], 141.08 [C(4a), C(5a)]. EI-MS: m/z 342 (M^+, 32%), 263 ($M^+ - Br$, 8%), 182 ($M^+ - 2Br$, 17%). Mp: 177–178 °C.

4,6-Bis(trimethylstannyl)dibenzothiophene (4). An aliquot of tmeda (5.0 mL, 33 mmol) in hexane (20 mL) was cooled to 0 °C under argon and a 1.6 M *n*-butyllithium in hexane solution (20.6 mL, 33 mmol) was added. The mixture was stirred for 30 min at 0 °C and for a further 30 min after removal of the cold bath. Solid dibenzothiophene (2.006 g, 10.9 mmol) and more hexane (20 mL) were added. After refluxing the mixture for 2 h, a dark brown suspension was obtained. This was cooled to −78 °C before chlorotrimethylstannane (6.573 g, 33 mmol) was added. The mixture was stirred for 30 min at −78 °C, followed by 30 min at room temperature and 30 min under reflux. Once the mixture had cooled to ambient temperature it was poured onto a saturated aqueous ammonium chloride solution (100 mL). Hexane (3 × 80 mL) was used to extract **4** from the aqueous phase. The combined hexane fractions were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to give **4** as a yellow oil. **4** undergoes extensive protodestannylation on silica gel. Sublimated dibenzothiophene was collected during the fractional distillation of **4**. Yield: 1.36 g (24%). $C_{18}H_{24}SSn_2$ (509.88): anal. calcd. C 42.40, H 4.74; found C 42.56, H 4.72. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 0.457$ (s, $^2J_{Sn\text{-}119,H} = 56.1$, $^2J_{Sn\text{-}117,H} = 53.5$ Hz, 18 H, $SnMe_3$), 7.397 [t, $^3J_{H,H} = 7.4$ Hz, 2 H, C(2)–H, C(8)–H], 7.501 [dd, $^3J_{H,H} = 6.80$, $^4J_{H,H} = 1.29$ Hz, 2 H, C(3)–H, C(7)–H], 8.087 [dd, $^3J_{H,H} = 7.76$, $^4J_{H,H} = 1.29$ Hz, 2 H, C(1)–H, C(9)–H]. ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = -9.07$ ($^1J_{Sn,C} = 347$ Hz, $SnMe_3$), 121.72 [C(1), C(9)], 123.81 [C(2), C(8)], 134.18 [C(3), C(7)], 134.45 [$^1J_{Sn,C}$ unresolved, C(4), C(6)], 135.52 [C(9a), C(9b)], 148.04 [C(4a), C(5a)]. EI-MS: m/z 510 (M^+, 6%), 495 ($M^+ - Me$, 20%), 348 ($C_{12}H_7SSnMe_3H^+$, 20%), 333 ($C_{12}H_7SSnMe_2H^+$, 100%), 301 ($C_{12}H_6SSn^+$, 36%), 184 ($C_{12}H_8S^+$, 13%), 151 ($SnMe_2{}^+$, 28%).

μ-Dibenzothienyl-1κ^4:2κ*C*^{6}-bis[*trans*-bromobis(triethylphosphane)platinum(II)] (5). At ambient temperature and under a nitrogen atmosphere **3** (0.283 g. 0.827 mmol) was added to a solution of $[Pt(PEt_3)_4]$ (1.09 g, 1.63 mmol) in toluene (10 mL). An additional 10 mL of toluene was added and the solution refluxed for 1 h. The solvent was removed *in vacuo* and the resultant white solid was washed with hexane (2 × 2 mL) and dried *in vacuo*. Colourless, cubic crystals of the compound were grown from a cold (−20 °C) toluene–hexane solution. However, the crystals became amorphous upon removal of the mother liquour or on exposure to air. Yield 0.87 g (87%). $C_{36}H_{66}Br_2P_4Pt_2S$ (1204.85): anal. calcd. C 35.89, H 5.52; found C 35.98 H 5.50. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 1.013$ (m, 36 H, CH_3), 1.696 (m, 24 H, CH_2), 6.983 [t, $^3J_{H,H} = 7.50$ Hz, 2 H, C(2)–H, C(8)–H], 7.381 [d, $^3J_{H,H} = 7.24$ 7.24 Hz, $^3J_{Pt,H} = 70.5$ Hz, 2 H, C(3)–H, C(7)–H], 7.620 [d, $^3J_{H,H} = 7.76$ Hz, 2 H, C(1)–H, C(9)–H]. ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 8.05$ (CH_3), 14.41 (t, $^1J_{P,C} = 17.1$ Hz, CH_2), 115.34 [C(1), C(9)], 123.56 [$^3J_{Pt,C} = 75.4$ Hz, C(2), C(8)], 133.15 [C(3), C(7)], 133.29 [C(4), C(6)], 134.84 [C(9a), C(9b)], 147.92 [C(4a), C(5a)]. ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = 12.47$ ($^1J_{Pt,P} = 2694$ Hz). EI-MS: m/z (M^+not detected), 773 [$M^+ - Pt(PEt_3)_2$, 45%], 694 [$M^+ - Pt(PEt_3)_2 - Br$, 66%], 431 [$Pt(PEt_3)_2$, 68%], 118 ($PEt_3{}^+$, 39%). IR (polyethylene disk): ν/cm^{-1} 318 (Pt–Br). Mp: >220 °C.

μ-Dibenzothienyl-1κ^4:2κ*C*^{6}-bis[*cis*-chloro(cod)platinum(II)] (6). $[Pt(\eta^4\text{-cod})Cl_2]$ (1.21 g, 3.23 mmol) and dichloromethane (25 mL) were added to a Schlenk flask containing **4** (0.82 g, 1.6 mmol). The resulting mixture was refluxed for 3 days. Thereafter the solvent was removed *in vacuo* and the white solid obtained was washed with hexane. Yield: 1.3 g (95%). $C_{28}H_{30}Cl_2Pt_2S$ FM (859.68): anal. calcd. C 39.12, H 3.52; found C 38.95, H 3.50. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 2.38$–2.44 (m, 8 H, cod CH_2), 2.65–2.69 (m, 8 H, cod CH_2), 4.756 (br s, $^2J_{Pt,H} = 74.5$ Hz, 4 H, cod CH), 5.903 (br s, $^2J_{Pt,H}$ unresolved, 4 H, cod CH), 7.13–7.15, [m, 4 H, C(2)–H, C(8)–H, C(3)–H, C(7)–H], 7.647 [dd, $^3J_{H,H} = 6.72$ Hz, $^4J_{H,H} = 2.31$ Hz, 2 H, C(1)–H, C(9)–H]. ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 28.23$ (cod CH_2), 32.16 (cod CH_2), 99.98 (cod CH), 115.80 (cod CH), 117.25 [C(1), C(9)], 124.63 [C(2), C(8)], 130.90 [C(3), C(7)], 135.61 [C(4), C(6)], 140.19 [C(9a), C(9b)], 147.00 [C(4a), C(5a)]. EI-MS: m/z (M^+ not detected), 520 [$M^+ - Pt(cod)Cl$, 5%] 377 ($C_{12}H_6PtS^+$, 6%), 338 [$Pt(cod)Cl^+$, 19%], 303 [$Pt(cod)^+$, 20%], 184 ($C_{12}H_8S^+$, 57%). IR (polyethylene disk): ν/cm^{-1} 316 (Pt–Cl).

X-Ray crystallographic study

Crystals of **2** and **3** suitable for X-ray diffraction studies were grown as previously described. Data were collected on a SMART CCD 1K diffractometer for **2** and on an Enraf-Nonius CAD4 diffractometer for **3**, both operating with graphite-monochromated Mo-*K*α radiation ($\lambda = 0.7107$ Å) and $\omega - 2\theta$ scans. The intensity data were refined by full-matrix, least-squares techniques against F^2. The structures were solved by direct methods using SHELX97-2.[40] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and refined with a common isotropic thermal parameter.†

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References

1 J. K. Stille, in *The Chemistry of the Metal-Carbon Bond*, eds. F. R. Hartley and S. Patia, John Wiley and Sons Ltd., New York, 1985, pp. 656–666.
2 R. J. Puddephatt, in *The Chemistry of the Metal–Carbon Bond*, ed. F. R. Hartley and S. Patia, John Wiley and Sons Ltd., New York, 1982, pp. 250–252 and references therein.
3 H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, 1997, **16**, 4696.
4 Y. Xie, S. C. Ng, B.-M. Wu, F. Xue, T. C. W. Mak and T. S. A. Hor, *J. Organomet. Chem.*, 1997, **531**, 175.
5 Y. Xie, B.-M. Wu, F. Xue, S.-C. Ng, T. C. W. Mak and T. S. A. Hor, *Organometallics*, 1998, **17**, 3988.
6 K. R. J. Thomas, J. T. Lin and K.-J. Lin, *Organometallics*, 1999, **18**, 5285.
7 L.-Y. Chia and W. R. McWhinnie, *J. Organomet. Chem.*, 1980, **188**, 121.
8 J. Manna, C. J. Kuehl, J. A. Whiteford and P. J. Stang, *Organometallics*, 1997, **16**, 1897.
9 D. P. Arnold, Y. Sakata, K. Sugiura and E. I. Worthington, *Chem. Commun.*, 1998, 2331.
10 S. Kotani, K. Shiina and K. Sonogashira, *J. Organomet. Chem.*, 1992, **429**, 403.
11 S. W. Carr, P. G. Pringle and B. L. Shaw, *J. Organomet. Chem.*, 1988, **341**, 543.
12 K. A. Fallis, C. Xu and G. K. Anderson, *Organometallics*, 1993, **12**, 2243.
13 J. K. Stille, in *The Chemistry of the Metal-Carbon Bond*, eds. F. R. Hartley and S. Patia, John Wiley and Sons Ltd., New York, 1985, pp. 716–717.
14 P. K. Byers, *Coord. Chem. Rev.*, 1995, **146**, 431.
15 H.-K. Yip, C. M. Che and S.-M. Peng, *J. Chem. Soc., Dalton Trans*, 1993, 179.
16 J. Ashby and C. C. Cook, in *Advances in Heterocyclic Chemistry*, eds. A. R. Katritzky and A. J. Boulton, Academic Press, New York, 1974, vol. 16, p. 254.
17 R. Gerdil and E. A. C. Lucken, *J. Am. Chem. Soc.*, 1965, **87**, 213.
18 L. Benati, P. C. Montevecchi and A. Tundo, *J. Chem. Soc., Chem. Commun.*, 1978, 530.
19 C. R. Neumoyer and E. D. Amstutz, *J. Am. Chem. Soc.*, 1947, **69**, 1920.

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† CCDC reference numbers 157702 (**2**) and 168281 (**3**). See http://www.rsc.org/suppdata/nj/b3/b307634m/ for crystallographic data in .cif or other electronic format.

20 E. Campaigne and J. Ashby, *J. Heterocycl. Chem.*, 1969, **6**, 517.

21 R. B. DuVernet, O. Wennerström, J. Lawson, T. Otsubo and V. Boekelheide, *J. Am. Chem. Soc.*, 1978, **100**, 2457.

22 R. M. Acheson and D. R. Harrison, *J. Chem. Soc. C*, 1970, 1764.

23 F. Sauter and P. Stütz, in *Houben-Weyl Methoden der Organischen Chemie*, Georg Thiem Verlag, Stuttgart, 1994, vol. E6a, pp. 903–904.

24 R. H. Mitchell, Y. Chen and J. Zhang, *Org. Prep. Proced. Int.*, 1997, **29**, 715.

25 M. W. Haenel, D. Jakubik, E. Rothenberger and G. Schroth, *Chem. Ber.*, 1991, **124**, 1705.

26 V. Meille, E. Schulz, M. Lemaire, R. Faure and M. Vrinat, *Tetrahedron*, 1996, **52**, 3953.

27 C. Kuehm-Caubère, S. Adach-Becker, Y. Fort and P. Caubère, *Tetrahedron*, 1996, **52**, 9087.

28 A. Voituriez, J.-C. Fiaud and E. Schulz, *Tetrahedron Lett.*, 2002, **43**, 4907.

29 J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res.*, 1977, **10**, 434.

30 B. Kayser, C. Missling, J. Knizek, H. Nöth and W. Beck, *Eur. J. Inorg. Chem*, 1998, 375.

31 S. Hillebrand, J. Bruckmann, C. Krüger and M. Haenel, *Tetrahedron Lett.*, 1995, **36**, 75.

32 ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.028 (m, 18 H, PCH_2CH_3), 1.263 (s, 18 H, ^{t}Bu), 1.555 (s, 6 H, Me), 1.687 (m, 12 H, PCH_2), 6.924 (m, 1 H, CH), 7.295 (d, 1 H, CH), 7.309 (d, 1 H, CH), 7.394 (d, 1 H, CH).

33 H. A. Brune, R. Hess and G. Schmidtberg, *Chem. Ber.*, 1985, **118**, 2011.

34 R. Meyer, Ph. D. Dissertation, University of Pretoria, Pretoria, South Africa, 1998.

35 M. W. Haenel, H. Fieseler, D. Jakubik, B. Gabor, R. Goddard and C. Krüger, *Tetrahedron Lett.*, 1993, **34**, 2107.

36 (*a*) F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 1; (*b*) F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.

37 R. M. Schaffrin and J. Trotter, *J. Chem. Soc. A*, 1970, 1561.

38 H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, 1973, **59**, 411.

39 T. Yoshida, T. Matsuda and S. Otsuka, *Inorg. Synth.*, 1990, **28**, 122.

40 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.