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Analysis of a hydrodesulfurization process—2 [1]. The reactions of 2- and 3-methylthiophenes with tris(triethylphosphine)platinum(0)

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Abstract—The oxidative insertion reactions of 2-methylthiophene (2-MeT) and 3-methylthiopene (3-MeT) with $Pt(PEt_3)_3$ (**1**), were examined as models for the first step in a platinum catalysed hydrodesulfurization. 2-MeT gave a single isomer, 1-bis(triethylphosphine)platina-2-thia-3-methylcyclohexa-3,5-diene (**2**), characterized spectroscopically. 3-MeT gave two isomers (ratio 1 : 1.6), 1-bis(triethylphosphine)platina-2-thia-5-methylcyclohexa-3,5-diene (**3b**), identified spectroscopically, and 1-bis(triethylphosphine)platina-2-thia-4-methylcyclohexa-3,5-diene (**3a**), identified spectroscopically and by an X-ray crystal structure determination. The thiophenes in the thiametallacycles can be displaced by free thiophenes and measurements show that the equilibrium constants decrease in the order $[Pt(C,S\text{-3-MeT})(PEt_3)_2]+T[K_{eqm(3/0)} = 2.30$ (after 7 h)]; $[Pt(C,S\text{-3-MeT})(PEt_3)_2]+\text{2-MeT}$ $[K_{eqm(3/2)} = 2.20$ (after 12 h)]; and $[Pt(C,S\text{-2-MeT})(PEt_3)_3]+T$ $[K_{eqm(2/0)} = 1.45$ (after 20 h)]. The order of stability in the complexes is T > 2-MeT > 3-MeT. Equilibrium is attained more rapidly in the 3-MeT complexes than in those of 2-MeT. Details of the X-ray structure of the previously prepared complex **5**, $[Pt(PEt_3)_2\{C,S\text{-}C_{12}H_8S\}]$, derived from dibenzothiophene, are also given and these two structures are compared with that for complex **4**, $[Pt(PEt_3)_2\{C,S\text{-}C_8H_6S\}]$, derived from benzothiophene. Complexes **3a**, **4** and **5** share the common feature of a six-membered thiaplatinacycle, which is planar in **3a**, nearly so in **4**, but very severely distorted in **5**; however, many of the bond lengths and angles are similar. © 1997 Elsevier Science Ltd

Keywords: thiophenes; platinum; oxidative addition; X-ray structure.

Hydrodesulfurization (HDS) removes undesirable sulfur containing molecules from crude oil. This prevents poisoning of the reforming catalysts and produces sulfur-free fuels and is generally carried out using a sulfided metal catalyst (e.g. CoMoS or NiMoS on alumina) at high temperature and under pressure [2]. However, the highest HDS activity is shown by the noble metals [3], which have therefore been the subject of many model studies [4,5].

Heterocycles such as the thiophenes (T), benzothiophenes (BT) and dibenzothiophenes (DBT), and especially their alkyl derivatives, pose particular problems as they occur in substantial amounts, notably in heavier crudes, and are rather resistant to normal HDS techniques. A widely accepted current mechanistic hypothesis for HDS of such thiophenes over the noble metals is that it takes place in two steps, where the first is the oxidative insertion of the metal into the C—S bond of the thiophene, forming a thiametallacycle, while the extrusion of the sulfur occurs in the second step in the presence of a source of hydrogen or hydride. An alternative view is that one or more rings of the thiophene or annelated thiophene are first hydrogenated and that the hydrogenolysis of the C—S bond occurs subsequently.

It is generally believed that the alkyl-thiophenes and their benzo and dibenzo analogues, where the alkyl

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group is close to the ring sulfur, are inert to conventional HDS procedures because the alkyl offers substantial steric hindrance to the approach of the C—S bond to the CoMoS in the critical oxidative insertion step [6].

Platinum has recently emerged as a viable catalyst for second stage industrial hydrotreating of diesel [7]. While this step has been introduced largely to reduce the proportion of aromatics, it also significantly reduces sulfur from (*ca* 1000 to < 15 ppm) ; thus, most of the residual sulfur-containing materials that are not removed by the conventional first stage CoMoS or NiMoS catalysts are removed in this second stage. This has allowed the production of the so-called *city diesel* fuel, with very low sulfur (< 5 ppm).

We have shown, in model studies [1], that the platinum(0) complex [$Pt(PEt_3)_3$] (**1**) reacts (reversibly) with DBT, BT and T by an oxidative insertion of the Pt(0) into one C—S bond, giving a six-membered heterocyclic $\overline{\text{Pt—S—C—C—C—C}}$ ring. We have also shown that these thiaplatinacycles extrude S and Pt to give the parent hydrocarbons, thus demonstrating a full HDS sequence mediated by platinum.

As part of our further investigation, we report here on the synthesis and characterization, as well as some equilibrium studies, of the bis-triethylphosphine complexes derived from 2- and 3-methylthiophenes. The object of these investigations is to define more closely the chemistry underlying hydrodesulfurization (HDS), especially with methylated thiophenes.

RESULTS AND DISCUSSION

2-Methylthiophene (2-MeT) and $Pt(PEt_3)_3$ (**1**) were reacted under reflux (4 h) and then the excess 2-MeT and Et_3P were removed *in vacuo* to leave an oil, which was triturated with cold hexane to give crystals of the product, 1-bis(triethylphosphine)platina-2-thia-3-methylcyclohexa-3,5-diene (**2**), which is also written as [Pt(*C*,*S*-2-MeT)$(PEt_3)_2$] [eq. (1)]. The complex was characterized by microanalysis and spectroscopically, which showed quite clearly that the isomer formed was the one where the Pt had inserted into the S—CH rather than the S—CMe bond. This is expected on steric grounds and follows the results found by others for reactions of 2-MeT [8]. The experimental method used was the same as had previously been used for the reaction with thiophene (T) itself and which gave 1-bis(triethylphosphine)platina-2-thiacyclohexa-3,5-diene in 89% yield. The low apparent yield (23%) of the thiaplatinacycle derived from 2-MeT was therefore investigated further by following the reaction by ^1H and ^{31}P NMR spectroscopy. This showed that only the one complex was formed from 2-MeT and in 89% yield, identical to that for the complex from T itself. We suggest that the very low isolated yield here arises from the greater solubility of the 2-MeT complex in the hexane used for washing the crystals in the work-up procedure.

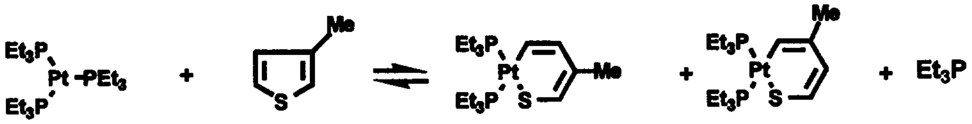
When the reaction of 3-MeT with $Pt(PEt_3)_3$ was carried out under the same conditions, one isomer, shown to be 1-bis(triethylphosphine)platina-2-thia-4-methylcyclohexa-3,5-diene (**3a**), by NMR spectroscopy and an X-ray crystal structure determination, was formed. Again the yield was low (8%) and to check on what was happening, we followed that reaction by NMR spectroscopy as well. In this case *two* complexes were formed, in the ratio of 1.6 : 1 and in total yield of 56%. The more abundant was complex **3a**, that we had already isolated; the other was characterized spectroscopically as the isomeric 1-bis(triethylphosphine)platina-2-thia-5-methylcyclohexa-3,5-diene, **3b** [eq. (2)]

Structure determination of 1-*bis*(*triethylphosphine*)*platina*-2-*thia*-4-*methylcyclohexa*-3,5-*diene* (**3a**) *and of the platinum adduct derived from dibenzothiophene*, **5**

A yellow prismatic crystal of complex **3a** was structurally analysed. The data are summarised in Tables 1 and 2 and the structure is illustrated in Fig. 1. In addition, the structure of the corresponding complex (**5**) derived from DBT, has been redetermined; the data are summarized in Tables 3 and 4 and the structure is illustrated in Fig. 2. Key bond length and bond angle data for **3a** and **5** are summarized in Table 5, where comparisons are drawn with the closely related structure of **4**, derived from BT, which has already been described [1]. In order to make the comparisons easier to follow, a unified labelling scheme has been adopted for the hetero-rings of all the complexes; this is shown in Fig. 3.

The most striking feature of the structural data for the hetero-rings of complexes **3a** and **4**, derived from 3-MeT and BT, respectively, is their similarity, within the e.s.d.'s estimated. This applies especially to the bond lengths. However, the hetero-ring of complex **5** is quite twisted leading to significantly smaller bond angles, with the exception of C_a—Pt—P_a. The much more twisted shape of complex **5** is clearly seen from an analysis of the dihedral angles of the three molecules, which show those of **5** to be 5–7 times larger than those in complexes **3a** and **4** (Table 6). For convenience and to allow comparisons, we have defined four molecular planes, using the numbering convention in Fig. 3. Thus, in the DBT complex **5** the very substantial distortions are reflected in a dihedral angle of 66.3° between planes P_a—Pt—P_b and S—C_c—C_d and of 55.3° between planes P_a—Pt—P_b and C_a—C_b—C_c ; there is also a dihedral angle of 35.3° between planes S—C_c—C_d, and C_a—C_b—C_c and even the "plane" containing the platinum is not quite flat (dihedral angle between planes P_a—Pt—P_b and S—Pt—C_a is 13.7°). By contrast in the BT complex **4**, the key dihedral angles are much smaller : only those between planes P_a—Pt—P_b and S—C_c—C_d 11.2°, and between planes P_a—Pt—P_b and C_a—C_b—C_c 9.7°, are

1 2 (1)



1 3a 3b (2)

significantly larger than zero. The molecule is thus much more nearly planar.

In the 3-MeT complex **3a** four ($C_aC_bC_c$ and Pt) of the six atoms making up the thiaplatinacycle ring are accurately coplanar, with only C_d fractionally below (0.009) and S fractionally above (0.007 Å) that plane. As a consequence the dihedral angles are quite small; the largest angle (of 3.9°) is that between the planes P_a—Pt—P_b and S—Pt—C_a. We can then state that the amount of distortion in the thiaplatinacycles decreases quite sharply in the order **5** > **4** > **3a**. It is likely that this order arises from nonbonded interactions between the ethyl hydrogens at the triethylphosphine and the hydrogens on the benzo-rings, as we noted earlier from our NMR studies [1]. These interactions are expected to be largest for the complex with two benzo-rings (i.e. **5**), intermediate for the complex **4**, which has one benzo-ring, and least (i.e. zero) for complex **3a**, which has no benzo-ring.

Combined Fenske–Hall molecular orbital and molecular mechanics calculations very recently carried out by Harris and her collaborators on a series of thiametallacycles have led to the same conclusion, namely that the differences in the thiametallacycle geometry, planar and bent, arise primarily from steric rather than electronic factors [9].

For complex **3a** the question arises whether the planar thiaplatinacyclic ring should be described as delocalized. We have compared our structural data with those for $[C_5Me_5Ir\{C,S\text{-}2,5\text{-}MeC_4H_2S\}]$, complex **6**, where significant aromatic properties have been claimed [10,11]. As shown in Table 5, the bond lengths of the thiametallacycles **3a** and **6** are very similar, within the precision allowed by the e.s.d.'s. However, Harris has suggested that electron delocalization requires electron deficiency in the metal complex and that our platinum complexes are not deficient in that sense [9]. Further studies will clearly be needed to answer this question.

Relative stabilities of the various 1-*bis*(*triethylphosphine*)*platina*-2-*thia*-4-*methylcyclohexa*-3,5-*dienes*; *equilibrium studies*

We have found that on heating one of the thiaplatinacycles with a different monocyclic thiophene, the new thiophene displaces the one in the thiaplatinacycle relatively easily. This has allowed us to establish the relative stabilities of the various thiaplatinacycles by measuring the equilibria in a series of exchange reactions. All the reactions were carried out in toluene-d_8, in sealed NMR tubes under argon, at 60°C using a metallacycle/thiophene ratio of (1/1.5). The reagents were mixed in the NMR tube and the reaction was monitored by ^{31}P and ^1H NMR spectroscopy. No reaction occurred without heating.

The equilibrium constant $K_{eqm(0/2)}$, 0.65, for reaction (0/2; Table 7), between $[Pt(C,S\text{-}T)(PEt_3)_2]$ and 2-MeT, was calculated as $[Pt(C,S\text{-}2\text{-}MeT)(PEt_3)_2][T]/[Pt(C,S\text{-}T)(PEt_3)_2][2\text{-}MeT]$; equilibrium was achieved after 20 h. For the other reactions the values (Table 7) were obtained similarly; reagents are on the left and products on the right.

The data for the forward and back reactions are reasonably self-consistent; those which take the longest time (20 *vs* 7 or 12 h) to achieve equilibrium show a little decomposition and some solid is deposited. The reactions using $[Pt(C,S\text{-}3\text{-}MeT)(PEt_3)_2]$ were made with an enriched mixture of isomers, in a starting ratio of 3.5/1, where the most abundant isomer is **3a** with the methyl in the "far" position from the C—Pt bond. When the complex $[Pt(C,S\text{-}3\text{-}MeT)(PEt_3)_2]$ is the product, only one isomer is detected, the 1-bis(triethylphosphine)platina-2-thia-4-methylcyclohexa-3,5-diene (**3a**).

The equilibria show that in the thiaplatinacycles, T is favoured over 2-MeT, which in turn is favoured over 3-MeT in the approximate ratio 1 : 0.65 : 0.45. This measure of the relative thermodynamic ability

Table 1. X-ray crystal structure determination of complex **3a**, $[(Et_3P)_2Pt(C,S\text{-}3\text{-}MeT)]$: crystal data, details of data collection, and of solution and refinement

Empirical formula	$C_{17}H_{36}P_2PtS$
Colour	Yellow
Habit	Prism
Crystal size (mm)	$0.40 \times 0.20 \times 0.16$
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit-cell dimensions	$a = 11.291(2)$ Å $b = 12.932(2)$ Å $c = 14.988(3)$ Å $\beta = 96.07(2)°$
Volume (Å^3)	2176.3(8)
Z	4
Formula weight	529.5
Density (calc.) (mg m^{-3})	1.616
Absorption coefficient (mm^{-1})	6.685
$F(000)$	1048
Data collection	
Diffractometer used	Siemens P4/PC
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)
Temperature (K)	293
Monochromator	Highly oriented graphite crystal
2θ range (°)	3.0–50.0
Scan type	ω
Scan speed	Variable ; 4.00–60.00° min^{-1} in ω
Scan range (ω) (°)	1.40
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	3 measured every 97 reflections
Index ranges	$0 < h < 13$, $0 < k < 15$, $-17 < l < 17$, plus Friedel pairs
Reflections collected	8080
Independent reflections	3841 ($R_{int} = 4.71\%$)
Observed reflections	2251 [$F > 4.0\sigma(F)$]
Absorption correction	Face-indexed numerical
Min./Max. transmission	0.3121/0.3701
Solution and refinement	
System used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct methods (SIR92)
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma[w(F_o - F_c)^2]$
Hydrogen atoms	Riding model, fixed isotropic $U = 0.08$ Å^2
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
Number of parameters refined	190
Final R indices (obs. data)	$R = 5.84\%$, $wR = 6.01\%$
Goodness-of-fit	1.15
Largest and mean Δ/σ	0.161, 0.010
Data-to-parameter ratio	11.8 : 1
Largest difference peak (e Å^{-3})	2.13 ; close to Pt atom
Largest difference hole (e Å^{-3})	-1.03

of methylthiophenes to participate in the oxidative insertion process indicates that there is some destabilizing effect of a methyl on the thiaplatinacycle, but that is small (corresponding to a $\Delta G°$ of *ca* 2.5 kJ mol^{-1} at most). Since the oxidative insertion may be regarded as the attack of the electron rich platinum(0) centre on the thiophene, additional electron density provided by methyl substituents to the thiophene ring would be expected to disfavour the reaction.

We conclude that there is a weak electronic effect, but the fact that the 2-methylthiophene is somewhat favoured over the 3-methyl argues against a single

Table 2. X-ray crystal structure determination of complex **3a**, $[(Et_3P)_2Pt(\mathit{C,S}\text{-}3\text{-MeT})]$: selected bond lengths (Å) and angles (°)

Pt—P(1)	2.294(4)	C(2)—C(3)—C(6)	120.6(19)
Pt—P(2)	2.285(5)	C(4)—C(3)—C(6)	115.8(18)
Pt—S(1)	2.285(5)	C(3)—C(4)—C(5)	129.0(18)
Pt—C(5)	2.041(16)	Pt—C(5)—C(4)	134.0(14)
S(1)—C(2)	1.703(17)		
C(2)—C(3)	1.328(28)		
C(3)—C(4)	1.424(30)		
C(3)—C(6)	1.536(26)		
C(4)—C(5)	1.308(23)		
P(1)—Pt—P(2)	98.0(2)		
P(1)—Pt—S(1)	175.0(1)		
P(2)—Pt—S(1)	87.0(2)		
P(1)—Pt—C(5)	85.8(5)		
P(2)—Pt—C(5)	173.9(5)		
S(1)—Pt—C(5)	89.2(5)		
Pt—S(1)—C(2)	113.7(7)		
S(1)—C(2)—C(3)	130.3(15)		
C(2)—C(3)—C(4)	123.4(16)		

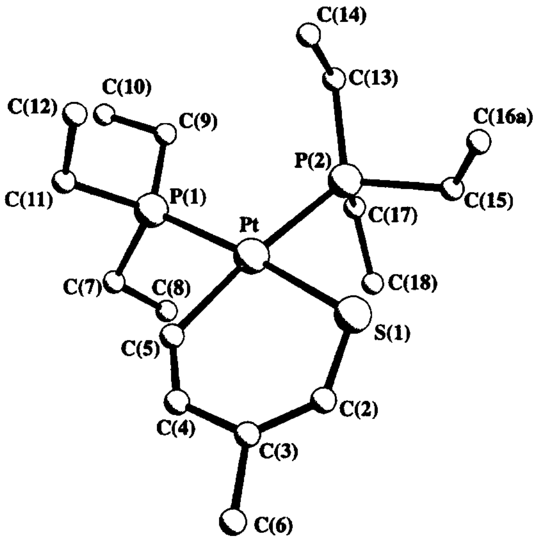


Fig. 1. Illustration of the molecular structure of complex **3a**, $[(Et_3P)_2Pt(\mathit{C,S}\text{-}3\text{-MeBT})]$.

methyl having any major steric influence. A complication is that qualitative measurements indicated that those reactions wherein 2-MeT participated were significantly slower than those of T or 3-MeT. This argues for a steric effect which is kinetic rather than thermodynamic.

We also reacted $Pt(PEt_3)_3$ with 2,5-dimethylthiophene under similar conditions; in this case there was no evidence for the formation of a thiaplatinacycle, only slow decomposition. Bianchini *et al.* [8] also found that T and 2-MeT reacted similarly with [(triphos)RhH] [eq. (7)] and that both reacted more easily than 3-MeT; they also found no reactivity of $2,5\text{-}Me_2T$. This lack of reactivity contrasts with the results found by Jones and Dong, who were able to oxidatively insert the 16-electron $(C_5Me_5)Rh(PMe_3)$ into the C—S bonds of $2,5\text{-}Me_2T$ as well as of T, 2-MeT and 3-MeT to give the thiarhodiacycle [eq. (6)] in each case [12]. While Jones and Dong [8] found little difference between the rates of reaction of $(C_5Me_5)Rh(PMe_3)$ with thiophene itself and the 2- and 3-Me-Ts; they noted that although $2,5\text{-}Me_2T$ reacted more sluggishly, an almost quantitative yield of the complex derived from it was obtained.

The lack of reactivity of 2,5-dimethylthiophene with $[Pt(PEt_3)_3]$ and [(triphos)RhH] may well imply that the steric congestion around the metal in the $[Pt(PEt_3)_3]$ and in [(triphos)RhH] is much greater than in $(C_5Me_5)Rh(PMe_3)$. This suggests that steric factors can become significant where the sulfur is strongly shielded and oxidative insertion is then inhibited.

One must conclude that the steric and electronic effects on metallacycle formation from the thiophenes are rather unusual. Insufficient data are yet available to allow further discussion of these intriguing effects; one can only speculate whether those operating on the new platinum on zeolite second stage hydrotreating catalysts are different to those that control the activity of the conventional CoMoS or NiMoS catalysts.

CONCLUSION

$Pt(PEt_3)_3$ oxidatively inserts thiophene (T), 2-methylthiophene (2-MeT) and 3-methylthiophene (3-MeT) to give the corresponding thiaplatinacycles. The ring-opened thiophenes can be displaced by the free thiophenes and equilibrium studies show that the ease of formation decreases in the order T > 2-MeT > 3-MeT. For a monomethylthiophene steric effects are very small. 2-MeT gave a single isomer, 1-bis(tri-

Table 3. X-ray crystal structure determination of complex **5**, $[(Et_3P)_2Pt(C,S\text{-DBT})]$: crystal data, details of data collection, and of solution and refinement

Structure determination summary	
Empirical formula	$C_{24}H_{38}P_2PtS$
Colour	Yellow
Habit	Prism
Crystal size (mm)	0.62 × 0.48 × 0.44
Crystal system	Monoclinic
Space group	$P2_1$
Unit-cell dimensions	$a = 10.447(2)$ Å $b = 17.178(3)$ Å $c = 14.910(2)$ Å $\beta = 105.46(2)^\circ$
Volume (Å^3)	2578.9(7)
Z	4
Formula weight	615.6
Density (calc.) (mg m^{-3})	1.586
Absorption coefficient (mm^{-1})	5.654
$F(000)$	1224
Data collection	
Diffractometer used	Siemens P4/PC
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)
Temperature (K)	293
Monochromator	Highly-oriented graphite crystal
2θ range (°)	3.0–60.0
Scan type	ω
Scan speed	Variable; 4.00–60.00° min^{-1} in ω
Scan range (ω) (°)	1.10
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
Standard reflections	3 measured every 97 reflections
Index ranges	$0 < h < 14$, $0 < k < 24$, $-20 < l < 20$
Reflections collected	8140
Independent reflections	7750 ($R_{int} = 2.81\%$)
Observed reflections	6130 [$F > 4.0\sigma(F)$]
Absorption correction	Face-indexed numerical
Min./Max. transmission	0.0810/0.1701
Solution and refinement	
System used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct methods (SIR92)
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma[w(F_o-F_c)^2]$
Absolute structure	$\eta = 0.95(6)$
Extinction correction	$\chi = 0.00025(4)$, where $F^* = F[1+0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic $U = 0.08$ Å^2
Weighting scheme	$w^{-1} = \sigma^2(F)+0.0008F^2$
Number of parameters refined	506
Final R indices (obs. data)	$R = 4.61\%$, $wR = 5.10\%$
Goodness-of-fit	1.01
Largest and mean Δ/σ	0.010, 0.002
Data-to-parameter ratio	12.1 : 1
Largest difference peak (e Å^{-3})	1.98
Largest difference hole (e Å^{-3})	−2.00

ethylphosphine)platina-2-thia-3-methylcyclohexa-3,5-diene (**2**), while 3-MeT gave two (ratio 1 : 1.6). One was 1-bis(triethylphosphine)platina-2-thia-5-methylcyclohexa-3,5-diene, while the other was 1-bis(triethylphosphine)platina-2-thia-4-methylcyclohexa-3,5-diene (**3a**). Comparison of the X-ray structure of **3a** with that of the previously prepared complexes **5**, $[Pt(PEt_3)_2\{C,S\text{-}C_{12}H_8S\}]$, derived from dibenzothiophene and **4**, $[Pt(PEt_3)_2\{C,S\text{-}C_8H_6S\}]$, derived from benzothiophene, shows that all three

Table 4. X-ray crystal structure determination of complex **5**, $[(Et_3P)_2Pt(C,S\text{-}DBT)]$, selected bond lengths (Å) and angles (°)

Pt(1)—P(1A)	2.261(4)	P(1A)—Pt(1)—P(2A)	99.1(2)
Pt(1)—P(2A)	2.325(5)	P(1A)—Pt(1)—S(5A)	168.5(2)
Pt(1)—S(5A)	2.341(5)	P(2A)—Pt(1)—S(5A)	86.5(2)
Pt(1)—C(13A)	2.052(16)	P(1A)—Pt(1)—C(13A)	92.8(4)
S(5A)—C(12A)	1.748(19)	P(2A)—Pt(1)—C(13A)	165.2(5)
C(10A)—C(11A)	1.500(21)	S(5A)—Pt(1)—C(13A)	83.4(4)
C(10A)—C(13A)	1.429(23)	Pt(1)—S(5A)—C(12A)	99.8(6)
C(11A)—C(12A)	1.380(28)	C(11A)—C(10A)—C(13A)	120.9(15)
		C(10A)—C(11A)—C(12A)	121.7(16)
		S(5A)—C(12A)—C(11A)	123.6(12)
		Pt(1)—C(13A)—C(10A)	125.1(10)

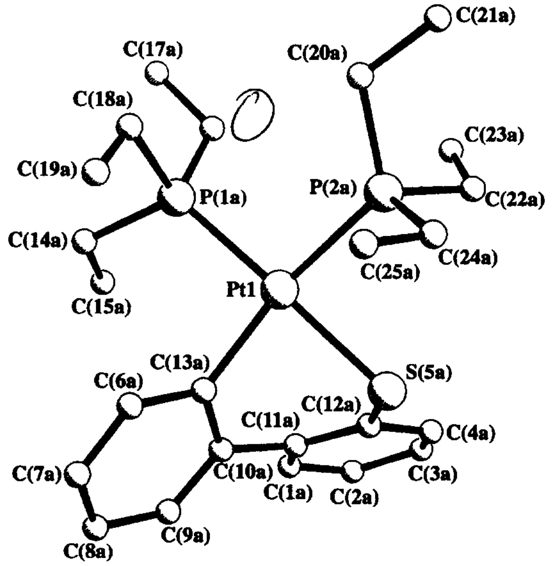


Fig. 2. Illustration of the molecular structure of complex **5**, $[(Et_3P)_2Pt(C,S\text{-}DBT)]$.

complexes contain a six-membered thiaplatinacycle, which is planar in **3a**, nearly so in **4**, but very severely twisted in **5**. However, many of the bond lengths and angles are similar in the three complexes and it is probable that the non-planarity of the hetero-ring arises from non-bonded steric interactions between the triethylphosphines and the benzo-hydrogens.

EXPERIMENTAL

Reactions were carried out using standard Schlenk techniques, under argon or dry nitrogen. NMR spectra were run on either a Varian VXR-300 or on a Varian Unity Plus 500 spectrometer in C_6D_6, toluene-d_8, or $CDCl_3$ solution. Microanalyses were performed by Galbraith Laboratories, USA.

1-*Bis(triethylphosphine)platina*-2-*thia*-3-*methyl-cyclohexa*-3,5-*diene* (**2**)

A solution of tris(triethylphosphine)platinum [13] in hexane (10 cm^3 containing 0.072 g, 0.13 mmol cm^{-3}) was prepared. A large excess of 2-methylthiophene (3.8 cm^3, 39 mmol) was added to the residue, $Pt(PEt_3)_3$ (0.72 g, 1.3 mmol) left from 10 cm^3 of this solution after removal of solvent *in vacuo* and the mixture was refluxed (110°C) with constant stirring (4 h). The methylthiophene was then removed *in vacuo*, dry hexane (10 cm^3) was added to the residue. On addition of further cold hexane (5 cm^3) and cooling (ice/acetone bath) this gave a red solid which was filtered; yield, after drying, 0.16 g (23%) of product. Found: C, 38.4; H, 6.8; S, 6.2. Calc. for $C_{17}H_{36}P_2PtS$: C, 38.5; H, 6.85; S, 6.1%. NMR spectroscopic data: ^1H NMR (in $CDCl_3$): δ 1.1 (m, 18H, Me), 1.96 (m, 2H, CH_2), 2.38 (m, 3H, Me), 6.54 [d, 1H, H_c $J(H_b—H_c)$, 7 Hz], 7.06 (m, 1H, H_a) and 7.26 (m, 1H, H_b). ^{13}C NMR ($CDCl_3$): δ C_d 126.8; C_c 125.1; C_b 122.7; C_a 131.8 [$^2J(P_b–C_a)$ 94.5; $^2J(P_a—C_a)$ 9.2 Hz]; CH_2 28.5; Me, 16.3; Me, 8.0. ^{31}P NMR (in toluene-d_8): δ P_a +11.6; P_b, 1.5; [$^2J(P_a—P_b)$ 23; $^1J(Pt—P_b)$ 1660; $^1J(Pt—P_a)$ 3088 Hz].

1-*Bis(triethylphosphine)platina*-2-*thia*-4-*methyl-cyclohexa*-3,5-*diene* (**3a**)

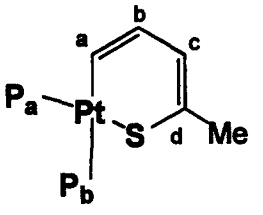
1-Bis(triethylphosphine)platina-2-thia-4-methyl-cyclohexa-3,5-diene (**3a**, 0.06 g, 8%) was made in identical fashion from 10 cm^3 of the solution of tris(triethylphosphine)platinum in hexane (0.072 g, 0.13 mmol cm^{-3}) and 3-methylthiophene (2 cm^3, 20.7 mmol). Found: C, 38.6; H, 6.9; S, 6.3. Calc. for $C_{17}H_{36}P_2PtS$: C, 38.5; H, 6.85; S, 6.1%. NMR spectroscopic data: ^1H NMR δ ($CDCl_3$): 1.1 (m, 18H, Me), 1.9 (m, 12H, CH_2), 2.0 (s, 3H, Me), 6.8 (m, 2H, H_d and H_b), 7.6 (m, 1H, H_a). ^{13}C NMR: δ ($CDCl_3$) C_d 112.8; C_c 125.9; C_b 130.4; C_a 133.6 [$^2J(P_b—C_a)$, 97.2; $^2J(P_a—C_a)$, 9.3 Hz]; Me 25.7; CH_2 16.5; Me 8.3. ^{31}P NMR (in toluene-d_8): δ P_a +11.0; P_b, 0.9;

Table 5. Comparison of bond lengths and angles for complexes **3a**, **4**, **5** and [$C_5Me_5Ir\{C,S\text{-}2,5\text{-}MeC_4H_2S\}$], **6**, (from ref. [10])

Bond lengths (Å)	Complex **3a**, from 3-MeT	Complex **4**, from BT [1]	Complex **5**, from DBT	Irdiathiabenzene, **6** [10]
Pt—P_a (*trans* to S)	2.294(4)	2.301(5)	2.261(4)	
Pt—P_b (*trans* to C)	2.356(5)	2.386(5)	2.325(5)	
Pt—C_a	2.041(16)	2.035(19)	2.052(16)	1.986(6)[a]
C_a—C_b	1.308(23)	1.301(27)	1.429(23)	1.394(9)
C_b—C_c	1.424(30)	1.483(29)	1.500(21)	1.41(1)
C_c—C_d	1.328(28)	1.403(25)	1.380(28)	1.375(9)
C_d—S	1.703(17)	1.756(18)	1.748(19)	1.713(6)
S—Pt	2.285(5)	2.315(5)	2.341(5)	2.203(2)[b]
Bond angles (°)				
P_a—Pt—P_b	98.0(2)	97.6(2)	99.1(2)	
C_a—Pt—S	89.2(5)	88.6(6)	83.4(4)	
P_a—Pt—C_a	85.8(5)	86.8(6)	92.8(4)	
P_b—Pt—S	87.0(2)	87.0(2)	86.5(2)	
Pt—S—C_d	113.7(7)	114.2(6)	99.8(6)	
Pt—C_a—C_b	134.0(14)	137.3(16)	125.1(10)	
C_a—C_b—C_c	129.0(18)	128.4(18)	120.9(15)	
C_b—C_c—C_d	123.4(16)	121.5(16)	121.7(16)	
C_c—C_d—S	130.3(15)	128.7(15)	123.6(12)	
P_a—Pt—S	175.0(1)	175.4(2)	168.5(2)	
P_b—Pt—C_a	173.9(5)	174.8(6)	165.2(5)	

[a] Ir—C_a for complex **6**.

[b] Ir—S for complex **6**.



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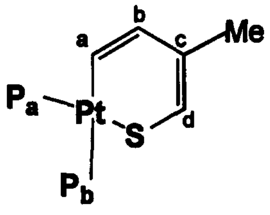
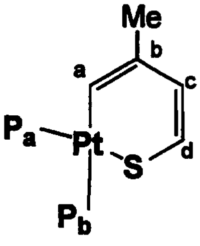
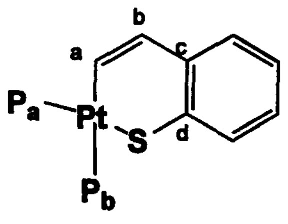


3a



3b



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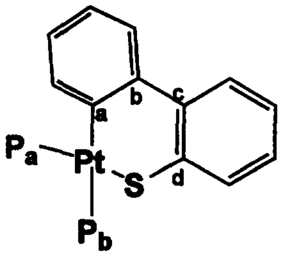

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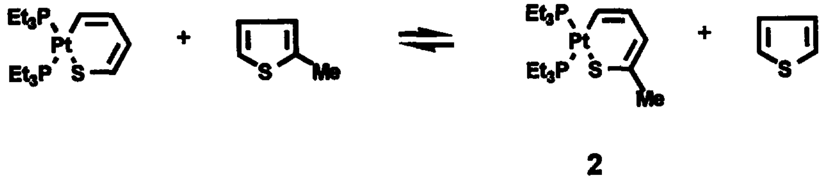
Fig. 3. Numbering convention used for the comparison of the X-ray structures of complexes **3a**, **4** and **5**, and for the discussion of NMR data of complexes **2**, **3a** and **3b**; P_a is the triethylphosphine *trans* to S, P_b the one *trans* to C_a.



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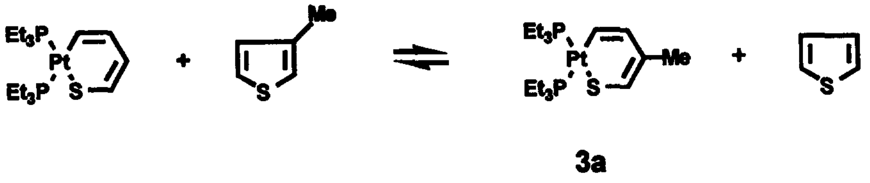

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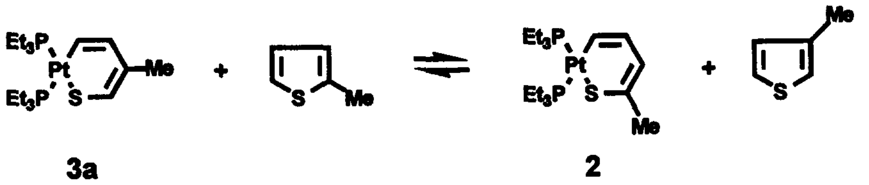


(5)

Table 6. Dihedral angles comparing **3a** (from 3-MeT), **4** (from BT) and **5** (from DBT)

Dihedral angle between planes:	For complex **3a** (from 3-MeT)	For complex **4** (from BT)	For complex **5** (from DBT)
P_a—Pt—P_b/C_c—C_d—S	7.1	11.2	66.3
P_a—Pt—P_b/C_a—Pt—S	3.9	2.9	13.7
P_a—Pt—P_b/C_a—C_b—C_c	6.6	9.7	55.3
C_c—C_d—S/C_a—C_b—C_c	1.1	5.1	35.5

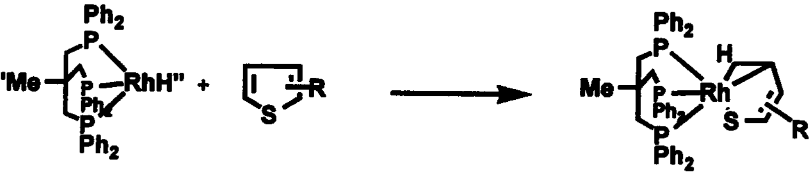
Table 7. Equilibrium constants for thiophene/2-methylthiophene/3-methylthiophene displacement reactions

$[Pt(C,S\text{-}T)(PEt_3)_2] + 2\text{-MeT} \rightleftharpoons [Pt(C,S\text{-}2\text{-MeT})(PEt_3)_2] + T$	(0/2)
$[Pt(C,S\text{-}2\text{-MeT})(PEt_3)_2] + T \rightleftharpoons [Pt(C,S\text{-}T)(PEt_3)_2] + 2\text{-MeT}$	(2/0)
$[Pt(C,S)(PEt_3)_2] + 3\text{-MeT} \rightleftharpoons [Pt(C,S\text{-}3\text{-MeT})(PEt_3)_2] + T$	(0/3)
$[Pt(C,S\text{-}3\text{-MeT})(PEt_3)_2] + T \rightleftharpoons [Pt(C,S\text{-}T)(PEt_3)_2] + 3\text{-MeT}$	(3/0)
$[Pt(C,S\text{-}2\text{-MeT})(PEt_3)_2] + 3\text{-MeT} \rightleftharpoons [Pt(C,S\text{-}3\text{-MeT})(PEt_3)_2] + 2\text{-MeT}$	(2/3)
$[Pt(C,S\text{-}3\text{-MeT})(PEt_3)_2] + 2\text{-MeT} \rightleftharpoons [Pt(C,S\text{-}2\text{-MeT})(PEt_3)_2] + 3\text{-MeT}$	(3/2)

Measured equilibrium constants,
$K_{eqm(0/2)} = 0.65$ (after 20 h); $K_{eqm(2/0)} = 1.45$ (after 20 h);
$K_{eqm(0/3)} = 0.45$ (after 7 h); $K_{eqm(3/0)} = 2.30$ (after 7 h); $K_{eqm(2/3)} = 0.46$ (after 7 h);
$K_{eqm(3/2)} = 2.20$ (after 12 h).

[$^2J(P_a$—$P_b)$ 23; ^1J(Pt—P_b) 1690; ^1J(Pt—P_a) 3062 Hz]. The other isomer, 1-bis(triethylphosphine)platina-2-thia-5-methylcyclohexa-3,5-diene, showed resonances at ^{31}P NMR: δ P_a+11.3; P_b, 1.2 [$^2J(P_a$—$P_b)$ 23; ^1J(Pt—P_b) 1673; ^1J(Pt—P_a) 3078 Hz]. The crude product analysed correctly for a mixture of two isomers. Found: C, 38.5; H, 6.95; S, 6.2. Calc. for $C_{17}H_{36}P_2PtS$: C, 38.5; H, 6.85; S, 6.1%. Although the ^{1}H NMR spectrum was very complex, peaks due to complex **3b** could be detected at δ 2.2 (s, Me) and 7.2 (m, probably H_c and H_d).

An attempt to carry out the same reaction using 2,5-dimethylthiophene (1.8 cm^3, 10 mmol) and tris(triethylphosphine)platinum (0.72 g, 1.3 mmol



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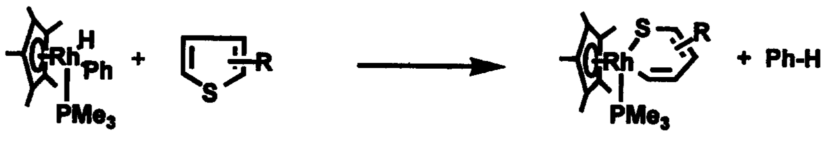

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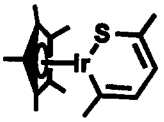

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cm^{-3}), by refluxing for 24 h, was unsuccessful; no product could be isolated.

X-ray crystal structure determination of complex **3a**, $[(Et_3P)_2Pt(C,S\text{-}3\text{-}MeT)]$

A sample for X-ray crystallography was crystallized from toluene–heptane; crystal data, details of data collection, and of solution and refinement are given in Table 1 and selected bond lengths and angles in Table 2. The X-ray structure analysis clearly shows that one of the ethyl groups on the phosphine ligand (P2) is orientationally disordered and Fig. 1 shows only the main conformer.

X-ray crystal structure determination of complex **5**, $[(Et_3P)_2Pt(C,S\text{-}DBT)]$

This was prepared as described, from $[Pt(Et_3P)_3]$ and dibenzothiophene [1]. A crystal for X-ray crystallography was crystallized at 0°C from toluene–hexane; crystal data, details of data collection, and of solution and refinement are given in Table 3; atomic coordinates are in Table 5, and selected bond lengths and angles in Table 4. The structure is illustrated in Fig. 2.

Atomic coordinates for complexes **3a** and **5** have been deposited with the Cambridge Crystallographic Data Centre.

Equilibrium studies. On heating one of the thiaplatinacycles with a different monocyclic thiophene in toluene-d_8, in sealed NMR tubes under argon, at 60°C using a metallacycle/thiophene ratio of (1/1.5), the new thiophene displaced that in the thiaplatinacycle. The reagents were mixed in the NMR tube and the reaction was usually monitored by ^{31}P NMR spectroscopy (45° pulse, 1 s acquisition, 4 s total delay between pulses and decoupling at the end of the sequence to minimize NOE); the integrals were also checked by comparison with mixtures of known compositions.

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