Ring Opening of Methylbenzothiophenes and Methyldibenzothiophenes by Tris(triethylphosphine)platinum(0)

Alma Arévalo,[1a] Sylvain Bernès,[1a] Juventino J. García,*[,1a] and Peter M. Maitlis[1b]

Facultad de Química, Universidad Nacional Autónoma de México, México, D. F. 04510, and Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, England

Received December 3, 1998

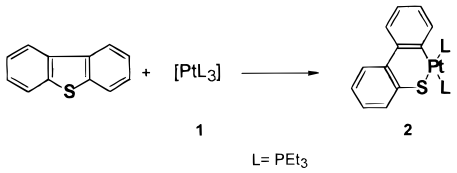
The reaction of $[Pt(PEt_3)_3]$, **1**, with 3-methylbenzothiophene and 2-methylbenzothiophene afforded the thiaplatinacycles $[(Et_3P)_2Pt(C,S\text{-}C_9H_8S)]$, **3** and **4**, respectively. In the formation of both complexes $(Et_3P)_2Pt$ has inserted into the C−S bond to the vinylic carbon. Complex **4** rearranges in solution to a dimeric thiaplatinacycle, **5**, in which the platinum has moved from lying between the vinylic C−S bond into the aromatic C−S bond. Reaction of **1** with 4-methyldibenzothiophene gave a mixture of isomeric thiaplatinacycles $[(Et_3P)_2Pt(C,S\text{-}C_{13}H_{10}S)]$, **6** and **7**. The reaction of **1** with 4,6-dimethyldibenzothiophene containing some 1,9-dimethyldibenzothiophene led to the isolation of complex **9**, $[(Et_3P)_2Pt(C,S\text{-}C_{14}H_{12}S)]$. This is derived from 1,9-dimethyldibenzothiophene, which is a byproduct in the preparation of 4,6-dimethyldibenzothiophene by a metalation pathway. The reaction of **1** with *highly pure* 4,6-dimethyldibenzothiophene gave the hydride complex, **10**, in which $(Et_3P)_2Pt$ has inserted into the C−H bond at the 3-position. The thiaplatinacycle *cis*-$[(Et_3P)_2Pt(\eta^2\text{-}C,S\text{-}C_{14}H_{12}S)]$, **8**, was obtained by reaction of *highly pure* 4,6-dimethyldibenzothiophene with *cis*-$[PtCl_2(PEt_3)_2]$ and metallic sodium under hydrogen. X-ray structures of complexes **3**, **5**, and **9** are reported.

Introduction

The hydrotreatment of crude oil reduces the undesired compounds of sulfur, nitrogen, oxygen, and metals. New regulations worldwide aim to reduce the limits for sulfur content in gas oils[2] to less than 0.05 wt % sulfur. To achieve this, it is necessary to perform a more effective process known as "deep" hydrodesulfurization (HDS). The main organosulfur derivatives remaining after HDS are the methylbenzothiophenes (MeBT) and -dibenzothiophenes (MeDBT); alkyldibenzothiophenes (alkyl-DBTs) substituted in the 4- and 4,6-positions are the most resistant to HDS and have proved the most difficult to remove.[3]

There have been rather few reports[4] so far on model homogeneous HDS studies of 4- or 4,6-methyl-substituted dibenzothiophenes, probably because of the low reactivity associated with the stericaly hindered carbon−sulfur bond in these ligands. Consequently the study of complexes that *can* activate the C−S bonds in such molecules should lead to promising steps for the future development of deep HDS catalysts.

Scheme 1



We have reported several investigations of the chemistry of thiaplatinacycles derived from thiophenes and platinum(0); those thiaplatinacycles can be envisaged to result from an oxidative insertion into a thiophene C−S bond. $Pt(PEt_3)_3$, **1**, successfully reacted with dibenzothiophene (to produce **2,** Scheme 1),[5] benzothiophene, thiophenes, and methylthiophenes.[6,7] Recently we demonstrated that using other phosphines such as PMe_3 and dppe, it is possible to activate benzothiophene[8] and 4-methyldibenzothiophene[4e] to produce the corresponding thiaplatinacycles. Related thiaplatinacycles have been reported quite recently by Sweigart and co-workers,[9] using transition-metal fragments coordinated to the π-system of thiophene, benzothiophene, and diben-

(1) (a) Facultad de Química, Universidad Nacional Autónoma de México, México, D. F. 04510. (b) Department of Chemistry, The University of Sheffield, Sheffield, S3 7HF England.

(2) Topsφe, H.; Gates, B. C. *Polyhedron* **1997**, *16*, 3212.

(3) Kabe, T.; Ishihara, A.; Tajima, H. *Ind. Eng. Chem.* **1992**, *31*, 1577.

(4) (a) Becker, S.; Fort, Y.; Vanderesse, R.; Caubère, P. *J. Org. Chem.* **1989**, *54*, 4848. (b) White, C. J.; Wang, T.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1994**, *13*, 4474. (c) Myers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905. (d) Bianchini, C.; Casares, J. A.; Masi, D.; Meli, A.; Pohl, W.; Vizza, F. *J. Organomet. Chem.* **1997**, *1*−*2*, 541, 143. (e) Iretskii, A.; Garcia, J. J.; Picazo, G.; Maitlis, P. M. *Catal. Lett.* **1998**, *51*, 1−2, 129. (f) Vicic, D. A.; Jones, W. D. *Organometallics* **1998**, *17*, 3411.

(5) (a) Garcia, J. J.; Mann, B. E.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1995**, *117*, 2179. (b) Garcia, J. J., Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 12200.

(6) Garcia, J. J.; Arévalo, A.; Montiel, V.; Del Rio, F.; Quiroz, B.; Adams, H.; Maitlis, P. M. *Organometallics* **1997**, *16*, 3216.

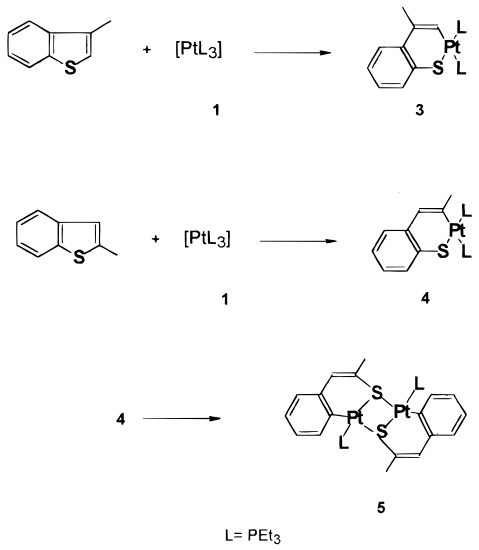
(7) Garcia, J. J.; Arévalo, A.; Capella, S.; Chehata, A.; Hernandez, M.; Montiel, V.; Picazo, G.; Del Rio, F.; Toscano, R.; Adams, H.; Maitlis, P. M. *Polyhedron* **1997**, *16*, 3185.

(8) Iretski, A.; Adams, H.; Garcia, J. J.; Picazo, G.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1998**, 61.

(9) Dullaghan, C. A.; Zhang, X.; Greene, D. L.; Carpenter, G. B.; Sweigart, D. A.; Camiletti, C.; Rajaseelan, E. *Organometallics* **1998**, *17*, 3316.

10.1021/om980974o CCC: $18.00
Publication on Web 04/01/1999

Scheme 2



zothiophene and adding $Pt(PPh_3)_3$ as nucleophile, producing a C−S cleavage. We here present a report on the activation of C−S and C−H bonds of methylbenzothiophenes and methyldibenzothiophenes by tris(triethylphosphine)platinum(0).

Results and Discussion

Reactions of Tris(triethylphosphine)platinum(0) with Methylbenzothiophenes. Following a procedure similar to that reported previously,[5a] the thiaplatinacycle $[(Et_3P)_2Pt(C,S\text{-}C_9H_8S)]$, **3**, from 3-methylbenzothiophene (3-MeBT) and **1** was obtained in 77% yield (Scheme 2). The analogous thiaplatinacycle **4** from 2-methylbenzothiophene (2-MeBT) was also formed but in a lower yield, 38%. The differences in yield between these isomeric ligands in the formation of the corresponding thiaplatinacycles illustrate the dramatic decrease in reactivity on having a methyl substituent close to the sulfur atom. Both complexes are stable at room temperature and resistant to air. However, complex **4** showed a slow rearrangement in solution to give the dimeric thiaplatinacycle $[\{(Et_3P)Pt(C,\mu\text{-}S\text{-}C_9H_8S)\}_2]$, **5**, with loss of a phosphine (Scheme 2). The complex was characterized by an X-ray structure determination, which showed that the platinum and the sulfur had exchanged positions during the dimerization. Dimerization with loss of a phosphine had been observed previously[5a] for complex **2** on heating the sample (12 h, 70 °C); in this case a rearrangement was impossible to distinguish. Other analogous structures have been reported for dimeric dibenzorhodiathiacycles;[10] the isomer isolated here, **5**, is the one where the metal has inserted into the bond between the aromatic C and the S. Jones et al. have proposed that this isomer is favored for thermodynamic reasons.[11] In most other reported structures of thiametalacycles derived from benzothiophenes the metal lies between the vinyl carbon and the sulfur, and Jones has suggested this to be the kinetically favored isomer. The mechanistic details for the conversion of **4** to **5** are still unknown; however we propose that such a process may proceed with a rearrangement of **4** to its isomer with the C(aryl)−S bond inserted, followed by loss of phosphine and dimerization to give **5**.

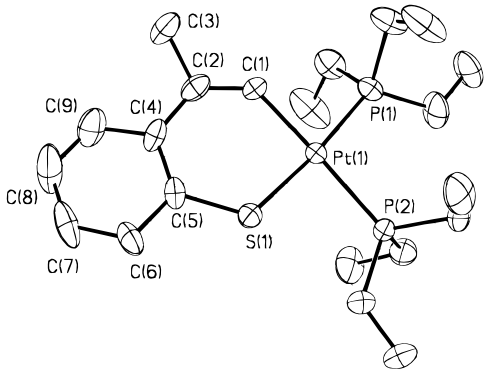


Figure 1. Molecular structure of complex **3** with thermal ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3

Pt(1)−C(1)	2.034(12)	Pt(1)−S(1)	2.280(4)
Pt(1)−P(1)	2.294(4)	Pt(1)−P(2)	2.344(3)
S(1)−C(5)	1.729(14)	C(1)−C(2)	1.34(2)
C(1)−Pt(1)−P(1)	85.1(4)	C(1)−Pt(1)−S(1)	89.3(4)
P(1)−Pt(1)−S(1)	174.18(14)	C(1)−Pt(1)−P(2)	176.8(4)
P(1)−Pt(1)−P(2)	97.84(14)	S(1)−Pt(1)−P(2)	87.77(13)
C(5)−S(1)−Pt(1)	115.0(5)	C(1)−C(2)−C(4)	129.7(14)

Structure of Thiaplatinacycle 3. The thiaplatinacycle derived from 3-MeBT presented the arrangement depicted in Figure 1; selected bond lengths and angles are in Table 1. The benzothiaplatinacycle moiety in complex **3** is nearly planar, with a dihedral angle of only 17.6(6)° between the plane C(1)−Pt−S and the mean plane through S−C(5)···C(2)−C(1). The coordination geometry of the platinum is nearly square planar, as expected (rms deviation of P_2SC plane, 0.028 Å; displacement of platinum 0.005 Å): P(1)−Pt−P(2), 97.84(14)°; S(1)−Pt−P(2), 87.77(13)°; S(1)−Pt−C(1), 89.3(4)°; P(1)−Pt−C(1), 85.1(4)°. The angle P(1)−Pt−P(2) is larger than 90°, probably due to an important steric repulsion between the substituents on the phosphines, as a consequence, the other three angles are correspondingly smaller. Key bond lengths in complex **3** are Pt−S(1), 2.280(4) Å; Pt−C(1), 2.034(12) Å; Pt−P(1), which is trans to S(1), 2.294(4) Å; and Pt−P(2), which is trans to C(1), 2.344(3). The last is an indication of the high trans influence of the σ-bonded vinylic carbon. Nearly all the above quoted angles and distances are identical or very similar to those seen with close related platinum complexes of unsubstituted benzothiophene.[5a,9]

Structure of the Dimeric Thiaplatinacycle 5. The thiaplatinacycle derived from 2-MeBT after its rearrangement from **4** to **5** presented the structure depicted in Figure 2; selected bond lengths and angles are in Table 2. In contrast with complex **3** the benzothiaplatinacycle moiety in **5** is not planar, with a dihedral angle of 67.3(4)° between the plane C(2)−Pt(1)−S(1) and the mean plane through C(2)···C(9). The coordination geometry of the platinum is nearly square planar, as expected (rms deviation of PS_2C plane, 0.029 Å; displacement of platinum 0.182 Å): S(1)−Pt(1)−S(1A), 83.6(2)°; S(1)−Pt(1)−C(5), 86.2(7)°; C(5)−Pt(1)−P(1), 90.8(7)°; P(1)−

(10) Jones, W. D.; Chin, R, M. *J. Am. Chem. Soc.* **1992**, *114*, 9851.
(11) Myers, A. W.; Jones, W. D.; McClements, S. M. *J. Am. Chem. Soc.* **1995**, *117*, 11704.

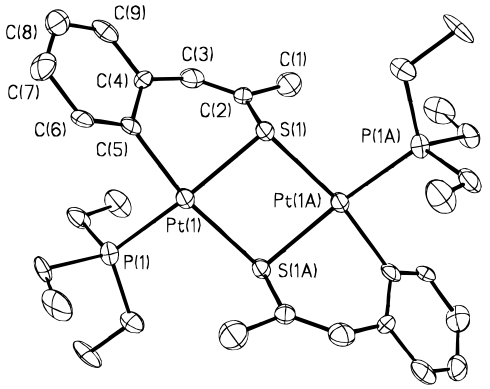


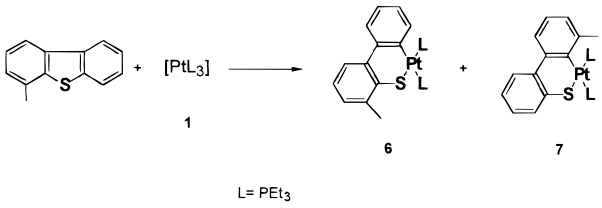
Figure 2. Molecular structure of complex **5** with thermal ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5[a]

Pt(1)−S(1)	2.372(6)	Pt(1)−P(1)	2.254(7)
Pt(1)−C(5)	2.040(19)	Pt(1)−S(1A)	2.404(5)
S(1)−C(2)	1.806(18)	C(2)−C(3)	1.309(35)
S(1)−Pt(1)−P(1)	166.3(2)	S(1)−Pt(1)−C(5)	86.2(7)
P(1)−Pt(1)−C(5)	90.8(7)	S(1)−Pt(1)−S(1A)	83.6(2)
P(1)−Pt(1)−S(1A)	98.1(2)	C(5)−Pt(1)−S(1A)	169.1(7)
Pt(1)−S(1)−C(2)	95.5(9)	Pt(1)−S(1)−Pt(1A)	96.4(2)
C(2)−S(1)−Pt(1A)	113.7(7)	C(2)−C(3)−C(4)	126.7(18)

[a] Symmetry operation implied by A label: $1-x, -y, -z$.

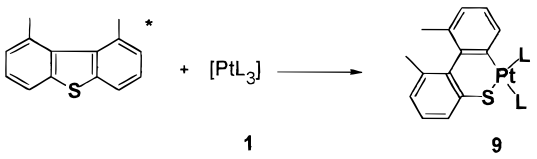
Scheme 3



Pt(1)−S(1A), 98.1(2)°. The angle P(1)−Pt(1)−S(1A) is larger than 90°, probably due to an important repulsion between the substituents on the phosphine and the methyl substituent in position 2; as a consequence, two of the other three angles are correspondingly smaller. The angles at sulfur C(2)−S(1)−Pt(1), 95.5(9)°, and C(2)−S(1)−Pt(1A), 113.7(7)°, show that the sulfur is close to tetrahedral, with three bonded atoms and a lone pair, as expected for a sp^3 hybridization. Key bond lengths in complex **5** are Pt(1)−S(1), 2.372(6) Å; Pt(1)−C(5), 2.040(19) Å; Pt(1)−P(1), which is trans to S(1), 2.254(7) Å; and Pt(1)−S(1A), which is trans to C(5), 2.404(5) Å. A number of other binuclear platinum complexes with bridging thiolates have had their structures determined by X-ray diffraction, including some obtained from our group.[6] The reported Pt−S bond lengths in the Pt_2S_2 core vary between 2.26 and 2.4 Å, while the internal angles S−Pt−S are 80−84°. The above quoted distances for **5** are well in agreement with such ranges.

Reactions of Tris(triethylphosphine)platinum-(0) with 4-Methyldibenzothiophene. The reaction of **1** with 4-methyldibenzothiophene afforded a mixture of isomers with the formulation $[(Et_3P)_2Pt(C,S\text{-}C_{13}H_{10}S)]$, **6** and **7** (Scheme 3), in a 1.6:1 ratio, respectively (60% total yield). The isomers **6** and **7** were observed in ^{31}P NMR, with resonances at δ 8.2 [^1J(Pt−P) 1771 Hz, ^2J(P−P) 14 Hz], and 8.4 [^1J(Pt−P) 1746 Hz, ^2J(P−P) 13 Hz], P trans to C and 10.2 [^1J(Pt−P) 3233 Hz, ^2J(P−P) 13 Hz], and 10.9 [^1J(Pt−P) 3243 Hz, ^2J(P−P) 14 Hz]. The ^1H NMR shows methyl resonances at δ (ppm) 2.21 and 2.29 (ratio 1:1.6). Since the last signal is the more intense, we tentatively assign it to complex **6**, the models of which indicate could be favored on steric grounds. Values of ^1J(Pt−P) allow us to assign signals at 8.2 and 8.4 ppm to phosphorus trans to carbon; consequently signals at 10.2 and 10.9 ppm are associated with phosphorus trans to sulfur.

Scheme 4



* Obtained as byproduct in the lithiation/methylation method to prepare 4,6-dimethyldibenzothiophene. [12]

A similar isomeric mixture of thiaplatinacycles was also obtained from 4-MeDBT but with PMe_3 and dppe as ligands instead of PEt_3.[4e]

Reactions of Tris(triethylphosphine)platinum-(0) with Dimethyldibenzothiophenes. When 4,6-dimethyldibenzothiophene is prepared by the standard lithiation/methylation method, which involves the lithiation of dibenzothiophene with butyllithium, followed by a methylation with dimethyl sulfate, it contains a mixture of dimethyldibenzothiophenes,[12] among them 4,6-dimethyldibenzothiophene and 1,9-dimethyldibenzothiophene as shown by Haenel et al.[12c] Thus when this mixture was reacted with Pt(0), it did not give the expected thiaplatinacycle **8**. Instead we could only isolate complex **9** (in 10% yield). The formation of complex **9** can most easily be explained as arising from the reaction between **1** and 1,9-dimethyldibenzothiophene, which is an *impurity* in the 4,6-dimethyldibenzothiophene when made by the lithiation pathway (Scheme 4). Complex **9** was characterized by an X-ray structure determination.

To avoid the lithiation/methylation method, we prepared *pure* 4,6-dimethyldibenzothiophene using the ring closure method, reported recently by Meille et al.,[13] starting from *o*-thiocresol and 2-bromonitrotoluene. The purity was checked by GC−MS, which showed only traces of di-*o*-tolylsulfide as byproduct. Using similar reaction conditions as in the preparation of **9** and following the reaction by ^{31}P and ^1H NMR, no evidence for the formation of **8** or **9** could be obtained. However, on using longer reaction times, a new complex, **10**, was formed (Scheme 5); this was shown to be a hydride. The NMR spectroscopic data for **10** are consistent with a hydride [^1H NMR at δ −16.95 ppm, triplet due the coupling of the hydride to two cis phosphines ^2J(H−P) 14 Hz, plus satellites due to the coupling ^1J(H−Pt) 1268 Hz; ^{31}P NMR shows equivalent phosphines at δ 3.4 ppm, ^1J(P−Pt) 3296 Hz]. A complex similar to **10**, resulting

(12) (a) Gerdil, R.; Lucken, E. A. C. *J. Am. Chem. Soc.* **1965**, *87*, 213. (b) Kuehm-Caubère, C.; Adach-Becker, S.; Fort, Y.; Caubère, P. *Tetrahedron*. **1996**, *52*, 9087. (c) Haenel, M. W.; Fieseler, H.; Jakubik, D.; Gabor, B.; Goddard, R.; Krüger, C. *Tetrahedron Lett.* **1993**, *34*, 2107.

(13) Meille, V.; Schulz, E.; Lemaire, M.; Faure, R.; Vrinat, M. *Tetrahedron* **1996**, *52*, 3953.

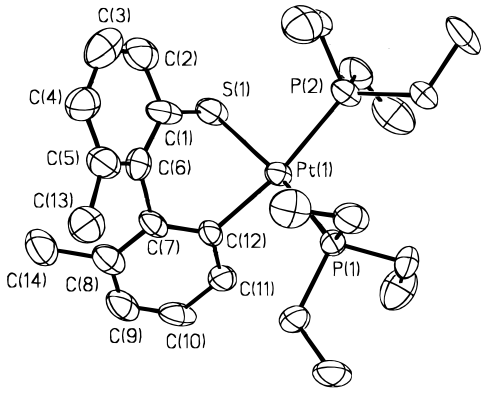
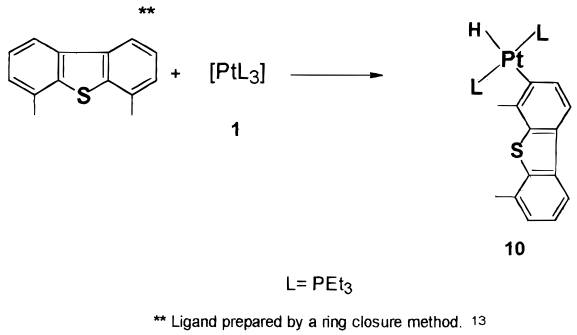
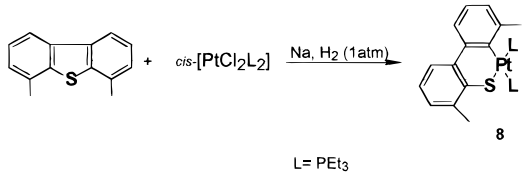


Figure 3. Molecular structure of complex **9** with thermal ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

Scheme 5



Scheme 6



from a C−H activation process, was recently reported;[4d] following that example, we tentatively propose that the site of C−H activation is at position 3 on the benzene ring.

We have been able to obtain complex **8**, but to achieve that, a different synthetic approach was needed. This new synthesis (Scheme 6) involved the reaction of *cis*-$[PtCl_2(PEt_3)_2]$ and 4,6-Me_2DBT with metallic sodium under H_2 at 1 atm. The advantage of this procedure was that it avoided the difficult step of removing the excess triethylphosphine, which is needed during the C−S bond breaking if one starts from **1** in Scheme 4. Complex **8** was obtained by this route in 30% yield; it showed the typical signal pattern for a thiaplatinacyle in the ^{31}P NMR, with resonances at δ (ppm) 3.2 [^1J(Pt−P) 2270 Hz, ^2J(P−P) 19 Hz] and 4.25 [^1J(Pt−P) 3094 Hz, ^2J(P−P) 19 Hz]. In addition the ^{1}H NMR showed methyl resonances at δ 1.8 and 2.1 ppm.

Structure of Thiaplatinacycle 9. As we have described above, the thiaplatinacycle **9** prepared from the *impure* 4,6-dimethyldibenzothiophene is actually derived from 1,9-dimethyldibenzothiophene. The structure is illustrated in Figure 3; selected bond lengths and angles are in Table 3. Complex **9** shows distortions of several planes and angles similar to the related complex 2 from the dibenzothiophene itself. Within the esd's

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 9

Pt(1)−C(12)	2.052(12)	Pt(1)−P(1)	2.255(3)
Pt(1)−P(2)	2.347(3)	Pt(1)−S(1)	2.370(4)
S(1)−C(1)	1.64(2)		
C(12)−Pt(1)−P(1)	92.3(4)	C(12)−Pt(1)−P(2)	168.1(4)
P(1)−Pt(1)−P(2)	99.55(13)	C(12)−Pt(1)−S(1)	81.3(4)
P(1)−Pt(1)−S(1)	169.9(2)	P(2)−Pt(1)−S(1)	87.15(13)
C(1)−S(1)−Pt(1)	90.1(5)		

other bond lengths and angles are nearly identical to those reported previously for complex **2**, for instance the dihedral angle of 81.5(7)° between planes P(1)−Pt(1)−P(2) and S(1)−C(6)−C(1) and of 63.7(5)° between planes P(1)−Pt(1)−P(2) and C(12)−C(7)−C(6). There is also a dihedral angle of 46(1)° between planes S(1)−C(6)−C(1) and C(12)−C(7)−C(6). Interestingly the plane containing the platinum atom is also distorted; a dihedral angle of 8.0(1)° is seen between P(1)−Pt(1)−P(2) and S(1)−Pt(1)−C(12). Key bond lengths in complex **9** are Pt(1)−C(12), 2.052(12) Å; Pt(1)−S(1), 2.370(4) Å; Pt(1)−P(1), 2.255(3) Å; and Pt(1)−P(2), 2.347(3) Å. The Pt−P distances reflect a strong trans influence by the carbon.

Conclusions

We have demonstrated that it is possible to activate a C−S bond in 2-methylbenzothiophene, 3-methylbenzothiophene, 4-methyldibenzothiophene, and 1,9-dimethyldibenzothiophene, by reaction with the electron-rich complex tris(triethylphosphine)platinum(0), **1**. The products are the thiaplatinacycles **3**, **4**, **5**, **6**, **7**, and **9** respectively. The reaction of **1** with *highly pure* 4,6-dimethyldibenzothiophene led to a C−H bond activation instead of a C−S bond activation, producing the corresponding hydride **10**. We have also shown that it is possible to produce **8** by inserting a platinum into the C−S bond in 4,6-dimethyldibenzothiophene using *cis*-$[PtCl_2(PEt_3)_2]$ and metallic sodium under H_2.

Experimental Section

All reactions were carried out using standard Schlenk techniques, under argon. Solvents were dried and distilled before use. Deuterated solvents (Aldrich) for NMR experiments were dried over molecular sieves. All other chemicals, filter aids, and chromatographic materials were reagent grade and used as received. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Unity (300 MHz) or a Varian Unity Plus (500 MHz) spectrometer in toluene-d_8 or benzene-d_6, unless otherwise stated, chemical shifts (δ) are relative to the deuterated solvent, and ^{31}P spectra are relative to external H_3PO_4. Infrared spectra were obtained in a Perkin-Elmer 1600 FT spectrophotometer. GC−MS determinations were performed on a Varian Saturn 3. Galbraith Laboratories, carried out elemental analyses. The synthesis of $[Pt(PEt_3)_3]$ was carried out using a previously reported procedure.[14] 3-Methylbenzothiophene was purchased from Lancaster; 2-methylbenzothiophene,[15] 4-methyldibenzothiophene,[16] 4,6-dimethyldibenzothiophene,[12,13] and $[PtCl_2(PEt_3)_2]$[17] were prepared by the reported methods. All complexes were purified by column

(14) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 119.
(15) Shirley, D. A.; Cameron, M. D. *J. Am. Chem. Soc.* **1952**, *74*, 664.
(16) Gilman, H.; Jacoby, A. L. *J. Org. Chem.* **1938**, *3*, 108.
(17) Parshall, G. W. *Inorg. Synth.* **1970**, *12*, 26.

Table 4. Summary of Crystallographic Results for 3, 5, and 9, Respectively

	$C_{21}H_{38}P_2PtS$	$C_{30}H_{46}P_2Pt_2S_2$	$C_{26}H_{42}P_2Pt_1S_1$
fw	579.60	922.91	643.69
cryst size/mm	0.4 × 0.4 × 0.4	0.2 × 0.2 × 0.05	0.7 × 0.2 × 0.1
color, shape	yellow, regular	yellow, irregular	pale yellow, irregular
d (calc)/g cm^{-3}	1.584	1.877	1.543
space group	$P2_12_12_1$	$P2_1/c$	Cc
a/Å	9.638(2)	12.036(3)	9.314(3)
b/Å	13.272(1)	12.433(2)	18.210(2)
c/Å	18.998(1)	11.968(2)	16.924(3)
β/deg		114.22(1)	105.18(2)
V	2430.05(45)	1633.2(8)	2770.3(11)
Z	4	2	4
μ/mm^{-1}	5.99	8.80	5.27
2θ range /deg	3−60	3−50	3−52
no. of reflns coll	4908	3704	3496
no. of unique reflns (R_{int})	4679 (5.69%)	2880 (8.32%)	3222 (2.96%)
no. of reflns with $I > 2\sigma(I)$	3171	1750	2651
transmission range	not applied	not applied	0.138−0.169
no of data/params	4679/227	2880/163	3222/272
GOF on F^2	1.064	0.930	1.049
R indices ($I > 2\sigma(I)$)/%	5.87, 12.52	6.22, 7.73	3.97, 9.03
R indices (all data)/%	9.52, 14.41	11.13, 10.10	5.53, 9.94
max resid density /e Å^{-3}	4.34	3.07	1.41
Flack param	0.00(2)		−0.020(9)
syst used	SHELXTL 5.03	SHELXTL 5.03	SHELX 97−2

chromatography, using silica gel and eluting from hexane to hexane/acetone, 1:1 (v/v), unless otherwise stated.

Preparation of [(Et$_3$P)$_2$Pt(*C,S*-C$_9$H$_8$S)], 3. Complex **3** was prepared from [Pt(PEt$_3$)$_3$] (0.66 g, 0.72 mmol) and 3-MeBT (0.72 g, 4.8 mmol) in toluene (10 mL) under argon. The solution was then heated to reflux for 4 h. After this time the solvent and the excess of phosphine distilled out and the color changed from orange-red to yellow. At this point, the heating was stopped and the mixture was evaporated to dryness with increasing vacuum (0.01 mmHg) and cooling to room temperature. Freshly distilled dried hexane was added (10 mL) with stirring to yield a yellow precipitate, which was washed three times with hexane to afford a yellow precipitate, which was purified by column chromatography. Yield: 77%. Anal. Calcd for $C_{21}H_{38}P_2PtS$: C 43.5, H 6.6, S 5.5. Found: C 42.7, H 6.4, S 5.1. NMR spectra in $CDCl_3$, ^{1}H: δ (ppm) 1.1−1.9 (m, 30H, from Et-P), 2.47 (s, 3H CH$_3$−BT), 7.0−7.05 (m, 2H, H(5), H(6)); 7.2−7.3 (m, H(2)); 7.5 (dd, H(4), ^3J 8, ^4J 2 Hz), 7.86 (dd, H(7), ^3J 8, ^4J 2 Hz). ^{31}P: δ (ppm) 1.8, ^1J(Pt−P) 1738 Hz, ^2J(P−P) 21 Hz; 10.5, ^1J(Pt−P) 3147 Hz, ^2J(P−P) 21 Hz. ^{13}C: δ (ppm) 8.3 (d, CH$_3$, Et−P); 15.5−16.6 (m, −CH$_2$−P); 28.9 (s, CH$_3$−BT); 121.7 (s, CH, C(4)); 123.5 (s, CH, C(5)); 126.4 (s, CH, C(6)); 129.2 (s, CH, C(7)); 130.2 (s, C); 130.3 (s, C); 131.4 (dd, CH, ^2J(Pt−transC) 85 Hz, ^2J(P-cisC) 8 Hz, ^1J(Pt−C) not observed); 139.7 (s, C).

Preparation of [(Et$_3$P)$_2$Pt(*C,S*-C$_9$H$_8$S)], 4, and [{(Et$_3$P)-Pt(*C,μ-S*-C$_9$H$_8$S)}$_2$], 5. [Pt(PEt$_3$)$_3$] (0.47 g, 0.86 mmol) and 2-MeBT (0.51 g, 3.4 mmol) in toluene (10 mL) were reacted under argon. Yield: 38%. Anal. Calcd for $C_{21}H_{38}P_2PtS$: C 43.5, H 6.6, %S 5.5. Found: C 43.5, H 6.7, S 5.3. NMR spectra in toluene-d_8, ^{1}H: δ (ppm) 0.56−1.9 (m, 30H, H from Et−P), 2.1 (s, br, 3H CH$_3$−BT), 6.6 (s, H(3)); 7.05−7.12 (m, H(5), H(6)); 7.44 (d, H(4), ^3J 8 Hz); 7.47 (d, H(7), ^3J 8 Hz). ^{31}P: δ (ppm) 6.05, ^1J(Pt−P) 1754 Hz, ^2J(P−P) 16 Hz; 10.8, ^1J(Pt−P) 3247 Hz, ^2J(P−P) 16 Hz. ^{13}C: δ(ppm) 8.0 (d, CH$_3$, Et−P); 15.1−16.8 (m, −CH$_2$−P); 28.5 (d, CH$_3$−BT), ^3J(P−C) 8 Hz; 121.5 (s, CH); 123.4 (s, CH); 126.4 (s, CH); 129.2 (s, CH); 130.0 (s, C); 130.6 (s, CH); 131.0 (dd, C, ^2J(Pt−transC) 90 Hz, ^2J(P−cisC) 9 Hz, ^1J(Pt−C) not observed; 139.8 (s, C). Complex **5** was slowly formed on leaving a toluene solution of **4** open to air at room temperature over 4 weeks. ^{31}P: δ (ppm) 0.8, ^1J(Pt−P) 2275 Hz. Anal. Calcd for $C_{30}H_{46}P_2Pt_2S_2$: C 39.0, H 5.0, S 6.9. Found: C 38.8, H 5.1, S 7.0.

Preparation of [Pt(*C,S*-C$_{13}$H$_{10}$S)(PEt$_3$)$_2$], 6 and 7. The mixture of both was prepared from [Pt(PEt$_3$)$_3$] (0.660 g, 1.2 mmol) and 4-MeDBT (0.9689 g, 4.8 mmol) in toluene (10 mL) under argon. The solution was then heated to reflux for 4 h. After this time the solvent and the excess of phosphine were distilled out and the color changed from orange-red to yellow-brown. At this point, the heating was stopped and the mixture was evaporated to dryness with increasing vacuum (0.01 mmHg) and cooling to room temperature. Freshly distilled dried hexane was added (10 mL) with stirring to yield a yellow-brown precipitate, which was washed three times with hexane to afford a brown precipitate, which was purified by column chromatography. Yield: 25%. Anal. Calcd for $C_{25}H_{40}P_2PtS$: C 47.7, H 6.4, S 5.1. Found: C 48.0, H 6.5, S 5.3. NMR spectra in benzene-d_6, ^{1}H: δ (ppm) 0.56−1.9 (m, 30H, H from Et−P), 2.21, 2.29 (s, 3H CH$_3$−DBT), 6.8−7.8 (m 7H, arom CH$_3$−DBT). ^{31}P: δ (ppm) 8.2, ^1J(Pt−P) 1771 Hz, ^2J(P−P) 14 Hz; 8.4, ^1J(Pt−P) 1746 Hz, ^2J(P−P) 13 Hz; 10.2, ^1J(Pt−P) 3233 Hz, ^2J(P−P) 13 Hz; 10.9, ^1J(Pt−P) 3243 Hz, ^2J(P−P) 14 Hz.

Reaction of 1 with 4,6-Dimethyldibenzothiophene. Complex **9** was prepared as described above for **3**, from [Pt(PEt$_3$)$_3$] (0.67 g, 1.2 mmol) and impure 4,6-dimethyldibenzothiophene (0.72 g, 3.4 mmol; prepared by a lithiation/methylation pathway[12]) in toluene. Anal. Calcd for $C_{26}H_{42}P_2PtS$: C 48.5, H 6.6, S 4.98. Found: C 48.6, H 6.4, S 5.1. NMR spectra for **9** in benzene-d_6, ^{1}H: δ (ppm) 0.5−1.8 (m, 30H, H from Et−P), 2.77 (s, 6H, CH$_3$−DBT), 6.9−7.8 (m, 6H, arom Me$_2$−DBT). ^{31}P: δ (ppm) 8.3, J(Pt−P) 1766 Hz, ^2J(P−P) 14 Hz; 11.0, ^1J(Pt−P) 3221 Hz, ^2J(P−P) 14 Hz. Efforts to isolate complex **10** by crystallization or column chromatography were unsuccessful; it decomposed easily open to the air or in a silica or alumina column. It could be detected only by keeping the sample in a sealed tube under argon. NMR data for complex **10**, detected after 5 h of reflux, in toluene-d_8, ^{1}H: δ (ppm) −16.95 (t, ^2J(H−P) 14 Hz, ^1J(H−Pt) 1268 Hz); 0.8−1.1 (m, CH$_3$−, Et$_3$−P); 1.63−1.71 (m, −CH$_2$−, Et$_3$P); 2.35 (s, CH$_3$-arom); 2.37 (s, CH$_3$-arom); 6.9 (s, 2H), 7.2−7.7 (m, 3H). ^{31}P: δ (ppm) 3.4 (^1J(P−Pt) 3295 Hz).

Reaction of *cis*-[PtCl$_2$(PEt$_3$)$_2$] with *Pure* 4,6-Dimethyldibenzothiophene. Complex [Pt(*C,S*-C$_{14}$H$_{12}$S)(PEt$_3$)$_2$], **8**, was produced on reacting *cis*-[PtCl$_2$(PEt$_3$)$_2$] (0.071 g, 0.16 mmol), 4,6-dimethyldibenzothiopene (0.070 g, 0.33 mmol), and metallic sodium (0.026 g, 1.14 mmol) in THF (80 mL) under hydrogen (1 atm), heating the system to 100 °C in a Parr reactor for 24 h. After this time the reactor was cooled to room temperature, and the reaction mixture was filtered, concentrated, and chromatographed on a short silica gel column, eluting from hexane to hexane/ethyl acetate 1:1 (v/v). Anal. Calcd for $C_{26}H_{42}P_2PtS$: C 48.5, H 6.6, S 5.0. Found: C 48.4, H

6.6, S 5.3. NMR data for complex **8** in toluene-d_8, ^{1}H: δ (ppm) 0.6−0.7 (m, CH_3−, from Et−P); 1.05−1.32 (m, $-CH_2-$, from Et-P); 1.84 (CH_3-arom); 2.71 (CH_3-arom); 6.8−7.1 (m, arom.); 7.4−7.6 (m, arom.). ^{31}P: δ (ppm) 3.2 (^1J(P−Pt) 2270 Hz, ^2J(P−P) 19 Hz); 4.26 (^1J(P−Pt) 3094 Hz, ^2J(P−P) 19 Hz).

Crystallographic Studies. Single crystals suitable for X-ray studies were obtained for compounds **3**, **5**, and **9** by slow evaporation of toluene solutions, at room temperature, and were handled in a noncontrolled atmosphere. A summary of results is presented in Table 4. Diffraction data were collected at 298 K on a Siemens P4 diffractometer, using graphite-monochromated Mo Kα radiation, following a normal procedure.[18] In the case of complex **3**, despite a high linear absorption coefficient, no correction for this effect was applied, because of the almost isotropic shape of the crystal.

The structures were solved[19] by Patterson method for Pt complexes and by direct methods for **11**, followed by difference Fourier maps, and refined anisotropically by full-matrix least-squares, without constraints nor restraints for the geometry, except for H atoms, which were systematically placed on ideal positions and refined using a riding model with a fixed isotropic thermal parameter. Complexes **3** and **9** crystallize in non-centrosymmetric space groups, and the absolute configuration was determined refining a Flack parameter.[20] It should be mentioned that for **3** and **5** high residuals were observed in the last difference maps, close to the heavy atoms, and seem to correspond to inaccurate thermal motion descriptions for Pt atoms rather than actual features.

Acknowledgment. We thank the European Commission (Grant No. ERBCI1CT940062), DGAPA-UNAM (Grant No. IN211798) and CONACYT (México) for support of this work; the last also for a Ph.D. grant (to A.A.). We also thank Dr. F. Del Rio and B. Quiroz for help on NMR determinations, ENCB-IPN and USAI-UNAM for diffractometer time, and Professor W. D. Jones for a manuscript prior to publication.

Supporting Information Available: Tables of complete crystallographic data for **3**, **5**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980974O

(18) Fait, J. *XSCANS*, release 2.10b; Siemens Analytical X-ray Instruments; Madison, WI, 1991.

(19) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

(20) Sheldrick, G. M. *SHELXTL-plus*, release 5.03; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1995. Sheldrick, G. M. *SHELX97-2 Users Manual*; University of Göttingen: Germany, 1997.