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Analysis of a Hydrodesulfurization Process. 3. Acid Cleavage of Thiaplatinacycles[1]

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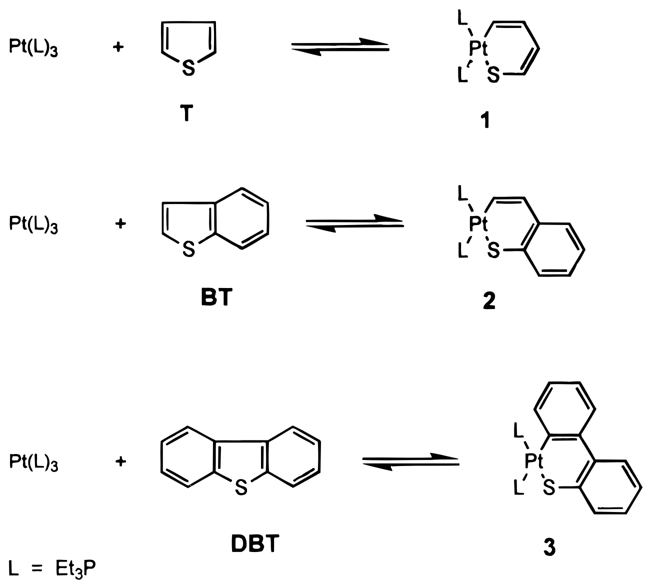
Reaction of the thiaplatinacyle $[(Et_3P)_2Pt(C_{12}H_8S\text{-}C,S)]$ (**3**; derived from reaction of $[Pt(Et_3P)_3]$ and dibenzothiophene (DBT)) with HCl gives largely 2-phenylthiophenol and a small amount of DBT. The thiaplatinacycle $[(Et_3P)_2Pt(C_8H_6S\text{-}C,S)]$ (**2**; from benzothiophene (BT)) undergoes reaction with HCl to give 2,3-dihydrobenzothiophene (22%), a small amount of 2-vinylthiophenol, and BT, while the thiaplatinacycle $[(Et_3P)_2Pt(C_4H_4S\text{-}C,S)]$ (**1**; from thiophene) regenerates thiophene with HCl; in each case the metal is found as $[(Et_3P)_2PtCl_2]$. In contrast all the thiaplatinacycles react very similarly with HBF_4 to give dinuclear $[Pt_2(Et_3P)_4(\mu\text{-}SR)_2](BF_4)_2$ (**7c**, R = 2-phenylthiophenolate (from **3**); **7b**, R = 2-vinylthiophenolate (from **2**); **7a**, R = 1-thiolatobutadiene (from **1**)). An X-ray structure determination of **7c** confirmed the structure. Reaction of the dications **7a**−**c** with HCl gave C_4H_6S (59%), 2-vinylthiophenol (83%), and 2-phenylthiophenol (91%), respectively.

Introduction

In previous papers of this series[1,3] we have reported the synthesis and structures of a variety of thiaplatinacycles (e.g., **1**−**3**) derived from the oxidative insertion of Pt(0) (from $Pt(PEt_3)_3$) into the C−S bonds of various thiophenes and their benzo and dibenzo homologues (Scheme 1). We have reported on the equilibria which govern their formation and also on some of the reactions that cleave the thiaplatinacycles. Most attention has focused on those reactions which give complete desulfurization, but we have also noted that hydrogen chloride can cleave the Pt−S and Pt−C bonds to give the thiols and $[Pt(PEt_3)_2Cl_2]$.[3] We here elaborate on these last reactions and give details of the products obtained with acids of noncoordinating anions.

Scheme 1



Results and Discussion

Reactions of the Thiaplatinacycles with HCl. As reported previously, the thiaplatinacycle $[(Et_3P)_2Pt(C_{12}H_8S\text{-}C,S)]$ (**3**; derived from dibenzothiophene (DBT)) was readily cleaved under ambient conditions by HCl gas (25 °C, 1 atm, CH_2Cl_2 solution) to give 2-phenylthiophenol (**4**) in 98% yield. Analysis by GC−MS showed that in addition a small amount of DBT (2%) was formed; NMR spectroscopy showed that the platinum was present mainly as *cis*-$[PtCl_2(PEt_3)_2]$, together with some of the *trans* isomer.

In contrast, $[(Et_3P)_2Pt(C_8H_6S\text{-}C,S)]$ (**2**; derived from benzothiophene (BT)) reacted with HCl gas under the same conditions to give a mixture, separated and identified by GC−MS as BT (77%), 2,3-dihydrobenzothiophene (**5**; 22%), and 2-vinylthiophenol (**6**; 0.3%); *cis*-$[PtCl_2(PEt_3)_2]$ (79%) was also obtained. On the basis of the conversion of the DBT complex **3** to the thiophenol **4** described above, the vinylthiophenol **6** is the expected product here. It seems very likely that 2,3-dihydrobenzothiophene (**5**) is formed from 2-vinylthiophenol by an isomerization involving a H-shift from sulfur onto the vinylic double bond.[4] Since 2-vinylthiophenol is normally a reasonably stable substance, the isomerization may be catalyzed by the platinum. Thus, we conclude that an overall C−S bond cleavage has also occurred in the thiaplatinacycle **5**, derived from BT, but to a smaller extent than for the thiaplatinacycle **3**, derived from DBT.

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[1] Part 2: Garcia, J. J.; Arevalo, A.; Capella, S.; Chehata, A.; Hernandez, M.; Montiel, V.; Picazo, G.; Del Rio, F.; Toscano, R. A.; Adams, H.; Maitlis, P. M. *Polyhedron,* in press.

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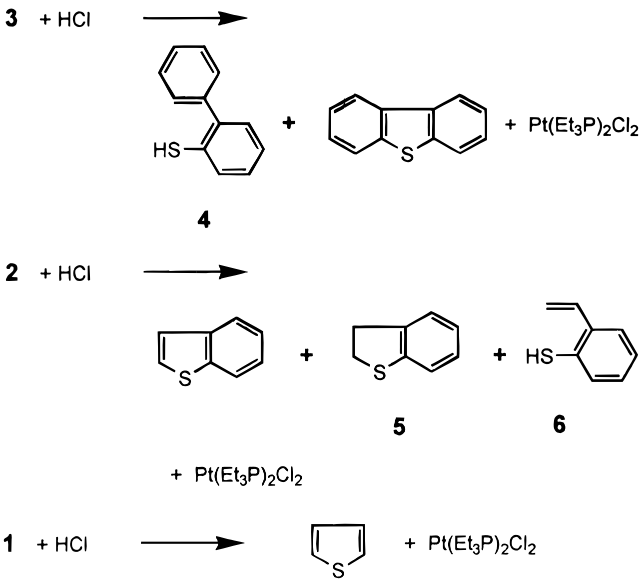
S0276-7333(97)00198-2 CCC: $14.00

Scheme 2



The third thiaplatinacycle [$(Et_3P)_2Pt(C_4H_4S$-*C,S*)] (**1**; derived from thiophene itself, reacted with HCl under the same conditions, but in this case the only products were T, formed virtually quantitatively, and *cis*-[$PtCl_2(PEt_3)_2$] (70%).

The order of reactivity for the acid cleavage reactions (**3** > **2** > **1**) differs from the hydrodesulfurizations with triethylsilane that we described earlier,[3] where the order was complex **2** > **3** > **1**. The thiaplatinacycle **1** regenerates free thiophene most easily in both cases and shows the least tendency for an overall ring cleavage, but the reactivities of the BT and DBT complexes **2** and **3** are inverted. Although related reactions with HPF_6 and HBF_4 have been reported (see below), the direct cleavage of a thiametallacycle with HCl, as occurs for complex **3** and to some extent for complex **2**, seems rather uncommon.

Reactions of the Thiaplatinacycles with HBF_4. In contrast to their reactions with HCl, where the heterocycle or a related organosulfur compound was formed, the thiaplatinacycles behaved quite differently with HBF_4. Again they reacted under mild conditions (HBF_4 added to a CH_2Cl_2 solution of the thiaplatinacycle at 25 °C), but the products were now all platinum complexes with very similar structures, in each case containing a ring-opened dinuclear thiolate dication: **7a**, the complex derived from thiophene, **7b**, derived from BT, and **7c**, derived from DBT. The structures of the products were deduced from NMR spectroscopy and confirmed by an X-ray determination of **7c**.

Structure of the Dication 7c. The dication derived from DBT showed the arrangement depicted in Figure 1 and illustrated in Scheme 3; selected bond lengths and angles are in Table 1. The complex is centrosymmetric and dinuclear with two platinum atoms each bearing two triethylphosphine ligands (Pt−P = 2.289(3), 2.295(3) Å) and joined by two bridging thiolates (Pt−S = 2.410, 2.418 Å), each with a 2-biphenyl substituent. The core is close to square with angles S(1)−Pt−S(1a) = 82.42° and Pt(1)−S(1)−Pt(1a) = 97.58°, while P(1)−Pt−P(2) = 97.42° and P(1)−Pt−S(1a) = 93.43°. The external angle P−Pt−P is greater than 90°, presumably due to the steric constraints imposed by the two triethylphosphines; this in turn causes the internal angle at platinum (S−Pt−S) to be less than 90°. The angles at sulfur, C(1)−S(1)−Pt(1a) = 101.2°, and C(1)−S(1)−Pt(1) = 100.1°, show that the sulfur is close to tetrahedral, with three coordinated ligands and a lone pair, as expected.

A number of other dinuclear platinum complexes with bridging thiolates have had their structures determined

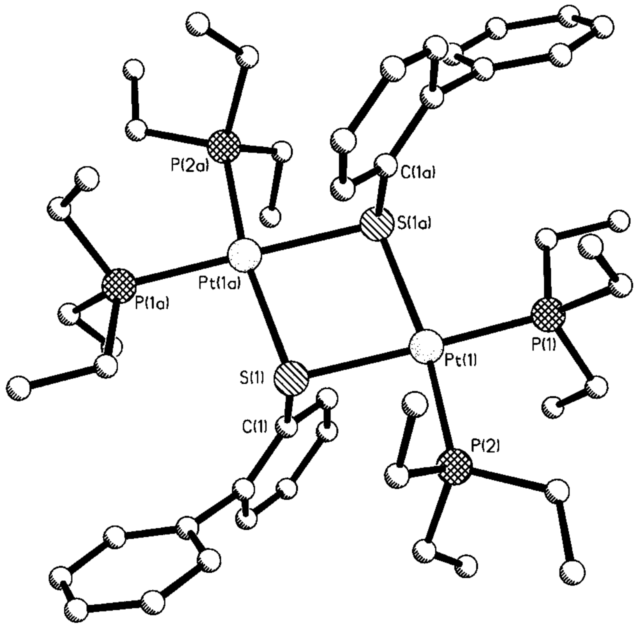


Figure 1. Molecular structure of the dication of [$Pt_2(Et_3P)_4(\mu\text{-}SC_6H_4C_6H_5)_2](BF_4)_2$ (**7c**). Anions and hydrogen atoms are omitted for clarity.

Scheme 3

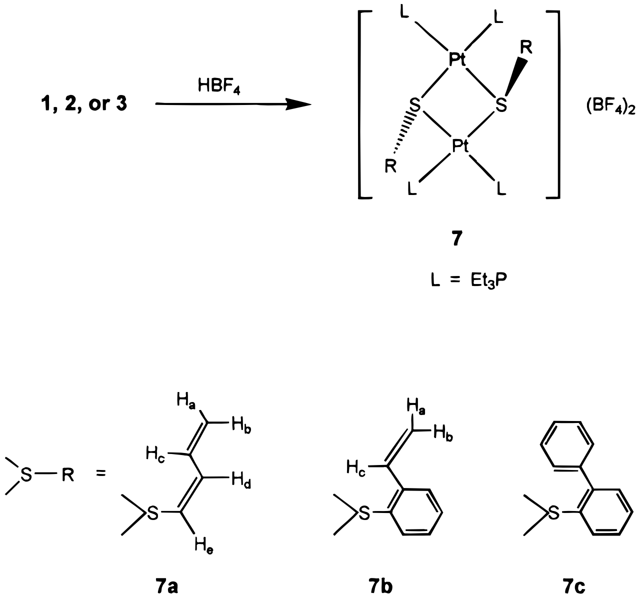


Table 1. Selected Bond Lengths and Angles for the Dication of [$Pt_2(Et_3P)_4(\mu\text{-}SC_6H_4C_6H_5)_2](BF_4)_2$ (7c)

Pt(1)−P(1)	2.289(3)	Pt(1)−P(2)	2.295(3)
Pt(1)−S(1a)	2.410(2)	Pt(1)−S(1)	2.418(2)
S(1)−C(1)	1.819(10)	S(1)−Pt(1a)	2.410(2)
P(1)−Pt(1)−P(2)	97.42(10)	P(1)−Pt(1)−S(1a)	93.43(9)
P(2)−Pt(1)−S(1a)	165.73(9)	P(1)−Pt(1)−S(1)	168.92(9)
P(2)−Pt(1)−S(1)	88.48(9)	S(1a)−Pt(1)−S(1)	82.42(8)
C(1)−S(1)−Pt(1a)	101.2(3)	C(1)−S(1)−Pt(1)	100.1(4)
Pt(1a)−S(1)−Pt(1)	97.58(8)		

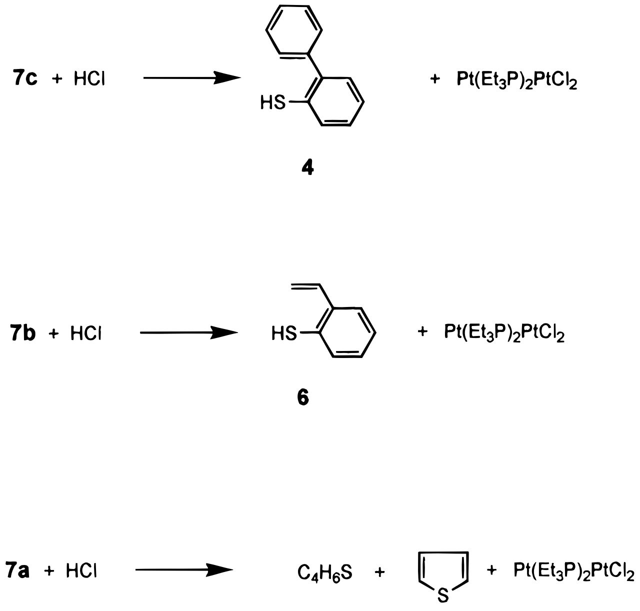
by X-ray methods; they include charged and uncharged, planar and bent molecules.[5] The reported Pt−S bond lengths in the Pt_2S_2 core vary between 2.26 and 2.4 Å, while the internal angles S−Pt−S are 80−84°. The structure closest to **7c** is that of the centrosymmetric dinuclear dication $[\{(dppe)Pt(\mu\text{-}SR)\}_2](BPh_4)_2$.[6] This shows Pt−S bonds at 2.384 and 2.402 Å, very similar to ours, and S−Pt−S angles of 83.9 and 84.6°. These are slightly larger than the S−Pt−S angle we see in complex **7c** and must be due to the effect of the dppe chelate ligand which has a smaller bite angle at the metal (P−Pt−P of 84.6°) than does $Et_3P{-}Pt{-}PEt_3$ in complex **7c**.

A rather similar diiridium complex, $[\{(triphos)IrH\}_2(\mu\text{-}SC_6H_4C_6H_5)_2](PF_6)_2$, is formed by the action of HPF_6 on the thiairidacycle $[\{(triphos)IrH\}_2(SC_6H_4C_6H_4\text{-}C,S)_2]$, derived from $(triphos)Ir(H)_3$ and DBT.[7]

The Bis(μ-butadienylthiolato)- and the Bis(μ-vinylthiophenolato)diplatinum Dications 7a and 7b. Most interesting are the closely related platinum organosulfur complexes formed in good yield from the thiaplatinacycles **1** and **2**. These have butadiene-1-thiol (1-thia-2,4-pentadiene) and 2-vinylthiophenol as ligands. The structures of the dications **7a** and **7b** are assigned by analogy to **7c**, since they are formed in very similar reactions and show similar stoichiometries, and also from their spectra. Although no confirmatory X-ray structure is yet available, in both cases the spectra clearly indicate that the ligand is bound to the platinum only through the sulfur and that there is no ancillary π-bonding of the double bond. Complex **7b**, like complex **7c**, is quite a stable molecule; however, the butadienethiolate complex **7a** is much more reactive and quite rapidly turns to a brown polymeric gum, even on standing under argon at −5 °C, presumably because of the high reactivity of the free diene moiety.

The ^1H NMR spectrum of **7b** shows the vinylic resonances on the vinylthiophenolate clearly, with the expected *cis* (11 Hz) and *trans* (17 Hz) couplings; the *gem* coupling was <1 Hz and was undetectable. The ^1H NMR spectrum of the thiapentadiene ligand of **7a** at −20 °C shows the five protons (δ 5.36 (CH_a), 5.5 (CH_b), 6.37 (SCH_e), 6.6 (CH_d), 7.4 (CH_c); $J(c{-}a) = J(c{-}d) = 10, 16$ Hz) with the expected couplings, [$J(c{-}a) = J(e{-}d) = 10$ Hz (*cis*) and $J(c{-}b)$ 16 Hz (*trans*); in addition the spectrum also shows the vicinal protons c and d coupled together ($J(c{-}d) = 10$ Hz). The magnitude of that coupling suggests that the dihedral angle between the two C−H bonds is close to zero, implying that the C_4H_5 ligand is planar.

Scheme 4



Bianchini and his co-workers have reported that the cationic thiairidacycle $[(triphos)Ir(SC_8H_6\text{-}C,S)]^+$ (as the PF_6^- salt) from the insertion of $(triphos)Ir(H)_3$ into BT reacts with hydrogen in THF (5 atm/20 °C) to give a dinuclear complex, $[\{(triphos)IrH\}_2(\mu\text{-}SC_6H_4Et)_2](PF_6)_2$. This complex is related to **7b**, but the bridging ligand is not *o-vinyl*thiophenolate as in **7b** but *o-ethyl*thiophenolate.[8]

Although complexes derived from thiophene itself which contain the ring-opened thiophene are well-known, most are η^3- or η^4-bonded, mainly to Rh or Ir;[9,10] no compound with the thiapentadiene η^1-bonded, analogous to **7a**, from T appears to have yet been reported.

The NMR parameters observed for **7a** are quite different from those displayed by the various η^3- and η^4-bonded C_4H_nS ligands in complexes reported by other workers. In particular we see no coupling of any of the vinylic resonances to ^{31}P, which would be expected, and which is found, in complexes where the double bond is also coordinated in some way to the metal. There was also no sign of any coupling to ^{195}Pt.

Reactions of the Dicationic Diplatinum μ-Thiolato Complexes 7a−c with HCl. When the dications were treated with HCl, the appropriate organic thiols were liberated: 2-vinylthiophenol (83%) and 2-phenylthiophenol (91%) from **7b** and **7c**, respectively (Scheme 4). The dication **7a** (derived from thiophene) reacted with HCl to yield an organic product containing an extremely unstable oil which rapidly polymerized and which was identified mass spectrometrically as thiapentadiene or an isomer thereof (C_4H_6S, 59%) and thiophene (15%). $[PtCl_2(PEt_3)_2]$ was also obtained.

Although a number of workers have reported cleavage of DBT, BT, and T at the C-S bond, the resulting ring-opened sulfur-containing intermediate products have usually resulted from addition of metal hydrides to the

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rings.[8,10,11] In general bases have been used to liberate organic thiols (as the salts) from heavy metal thiolate complexes, but some reactions with acids have also been reported.

Conclusions

We have found that the thiophenes oxidatively insert Pt(0) to give a variety of thiaplatinacycles. The platinum−carbon bonds there are cleaved by HBF_4 to yield dinuclear thiolate complexes. Both these and the thiaplatinacycles are further cleaved by HCl to give organic thiols, but the efficiency of the route via the dications is much higher. Furthermore, the cleavage reactions with HCl are most efficient for the complexes derived from DBT and least efficient for those from T itself: complexes derived from T regenerate free T most easily, while those derived from DBT have a low tendency to regenerate DBT.

We have as yet no mechanistic information on these reactions with acids, but it is plausible that those with HBF_4 involve a protonation, while those with HCl (carried out in very nonpolar media) involve an oxidative-addition−reductive-elimination sequence via a Pt(IV) intermediate. The driving force for the cleavage of a Pt−S bond by HCl may well be the formation of the very stable $[PtCl_2(PEt_3)_2]$. Such reactions are not unknown elsewhere; for example, Bianchini et al. have noted the cleavage of Ir−S bonds by HCl.[10]

One further point of interest is that “stabilized” forms of thiapentadiene and vinylthiophenol can be generated, which promise interesting applications in organic synthesis.

Experimental Section

All reactions and manipulations were carried out under argon using standard Schlenk techniques unless otherwise stated. Solvents were dried and distilled before use. Deuterated solvents (Aldrich) for NMR experiments were dried over molecular sieves. All other chemicals were reagent grade and were used as received. ^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian Unity (300 MHz) or a Varian Plus (500 MHz) spectrometer; chemical shifts (δ) are relative to the deuterated solvent. Infrared spectra were obtained using a Perkin-Elmer PE-1600 FT spectrophotometer. GC−MS analyses were performed on a Hewlett-Packard HP5890 series II chromatograph equipped with a mass detector. Mass spectra were obtained on a JEOL JMS-SX102A spectrometer using FAB in a 3-nitrobenzyl alcohol matrix. Elemental analyses were carried out by the University of Sheffield Microanalytical Service and on a Fisons EA-1108 microanalyzer at FQ, UNAM.

Reaction of $[Pt(SC_{12}H_8)(PEt_3)_2]$ (3) with HCl. Gaseous HCl was gently bubbled (5 min) through a stirred solution of complex **3** (0.25 g, 0.4 mmol) in CH_2Cl_2 (7 cm^3). The initial ivory solution turned pale yellow, and a white solid precipitated. After standing (30 min) the mixture was evaporated to dryness *in vacuo*, pentane (10 cm^3) was added, and the solution was filtered; the pentane-soluble part was analyzed by GC−MS and shown to be composed of 2-phenylthiophenol (98%) and dibenzothiophene (2%). The precipitate was mainly *cis*-$PtCl_2(PEt_3)_2$ (0.17 g, 0.34 mmol; 85%), identified by its NMR spectra in $CDCl_3$[12] (^{1}H, δ 1.17 (m, 18H, CH_3), 2.06 (m, 12H, CH_2); ^{31}P, δ 9.4 ($^{1}J(Pt-P) = 3503$ Hz). The spectra show that a small amount of the *trans* isomer is also present.

Reaction of $[Pt(SC_8H_6)(PEt_3)_2]$ (2) and of $[Pt(SC_4H_4)(PEt_3)_2]$ (1) with HCl. These reactions used a similar procedure but were carried out at −10 °C (ice-acetone bath), and the CH_2Cl_2 solutions were analyzed directly by GC−MS. Complex **2**, derived from benzothiophene, gave an organic fraction composed of benzothiophene (77%), 2,3-dihydrobenzothiophene (22%), and 2-vinylthiophenol (0.3%); *cis*-$PtCl_2(PEt_3)_2$ (79%) was also obtained. Complex **1** ($Pt(SC_4H_4)(PEt_3)_2$) derived from thiophene reacted with HCl in the same way to yield *cis*-$PtCl_2(PEt_3)_2$ (70%), while the pentane-soluble organic part was thiophene (100%).

Reaction of $[Pt(SC_{12}H_8)(PEt_3)_2]$ (3) with HBF_4. A 10-fold excess of aqueous HBF_4 (0.9 cm^3, 0.75 g, 8.6 mmol) was added to a solution of the complex **3** (0.49 g, 0.8 mol) in CH_2Cl_2 (10 cm^3; 0.8 mol). The mixture was stirred (30 min) and then evaporated to dryness. Addition of pentane (10 cm^3) gave a precipitate which was purified by column chromatography (with ethyl acetate as eluent) and then concentrated and crystallized to yield a white solid, $[Pt_2(PEt_3)_4(SC_{12}H_9)_2](BF_4)_2$ (**7c**), mp 202−205 °C (95%). Anal. Calcd for $C_{48}H_{78}B_2F_8P_4Pt_2S_2 \cdot CH_2Cl_2$: C, 39.45; H, 5.4; S, 4.3. Found: C, 39.5; H, 5.1; S, 4.7. NMR in acetone-d_6: ^{31}P, δ 15.2 (d, $^{1}J(Pt-P) = 2956$ Hz); ^{19}F, δ −153.2; ^{1}H, δ 1.04 (m, 18H, CH_3), 1.9 (m, 12H, CH_2), 7.4−7.8 and 8.8 (m, 9H). It was also identified by its mass spectrum, *m/z* 1319, corresponding to $[Pt_2(PEt_3)_4(SC_{12}H_8)_2HBF_4]^+$. A single-crystal X-ray analysis was carried out.

Crystal Data for Complex 7c: $C_{48}H_{78}B_2F_8P_2Pt_2S_2$, $M_r = 1406.90$, crystallized from acetone/hexane as yellow blocks; crystal dimensions 0.55 × 0.42 × 0.22 mm; orthorhombic; $a = 14.895(3)$, $b = 18.935(4)$, $c = 20.411(8)$ Å; $V = 5757(3)$ $Å^3$; $Z = 4$; $D_c = 1.623$ g cm^{-3}; space group *Pbca* (D_2^{15}, No. 61); Mo Kα radiation ($\bar{\lambda} = 0.710\ 73$ Å), μ(Mo Kα) = 5.095 mm^{-1}, $F(000) = 2784$.

Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the ω-scan method. Of the 4547 reflections measured, all of which were corrected for Lorentz and polarization effects and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.289 and 0.847), 2905 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0463$ (wR2 = 0.1307 for all 3650 unique data, 298 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for all non-hydrogen atoms. Minimum and maximum final electron densities were −1.126 and 1.455 e $Å^{-3}$. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 15.3123P]$, where $P = (F_o^2 + 2F_c^2)/3$, was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93[13] as implemented on the Viglen 486dx computer. The structure is illustrated in Figure 1, and selected bond lengths and angles are collected in Table 1.

Reaction of $[Pt(SC_8H_6)(PEt_3)_2]$ (2) with HBF_4. A procedure similar to that described above for complex **3** was carried out on complex **2** with HBF_4 to give $[Pt_2(PEt_3)_4(SC_8H_7)_2](BF_4)_2$ (**7b**; 89%). Anal. Calcd for $C_{40}H_{74}B_2F_8P_4Pt_2S_2$: C, 36.8; H, 5.7; S, 4.9. Found: C, 36.7; H, 5.5; S, 5.0. This was characterized by its NMR spectra in acetone-d_6: ^{31}P, δ 17.1 (d, $^{1}J(Pt-P) = 2906$ Hz); ^{19}F, δ − 153.5; ^{1}H, δ 0.97−1.27 (m,

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18H, CH_3), 1.93−2.6 (m, 12H, CH_2), 5.6−5.73 (d, 1H, CH_a, J(a−c) = 11 Hz, J(a−b) < 2 Hz), 6.1 (d, 1H, CH_b, J(b−c) = 17 Hz, J(b−a) < 2 Hz), 6.9 (m, 1H, CH_c), 7.2−8.5 (m, 4H, C_6H_4). The mass spectrum of this complex showed no molecular ion but did show fragments at m/z 836 corresponding to $[Pt_2(SC_8H_6)_2H]^+$ and m/z 136 corresponding to $HSC_6H_4CH{=}CH_2$.

Reaction of $[Pt(SC_4H_4)(PEt_3)_2]$ (1) with HBF_4. A similar reaction of complex **1** with HBF_4 gave $[Pt_2(PEt_3)_4(SC_4H_5)_2](BF_4)_2$ (**7a**; 70%). Anal. Calcd for $C_{32}H_{70}B_2F_8P_4Pt_2S_2$: C, 31.9; H, 5.8; S, 5.3. Found: C, 31.0; H, 5.7; S, 5.4.[14] It was characterized by its NMR spectra in acetone-d_6: ^{31}P, δ 17.0 (d, ^1J(Pt−P) = 2892 Hz); ^{19}F, δ −152; ^1H (−20 °C; 500 MHz), δ 1.1 (m, 18H, CH_3, PEt_3), 2.04 (m, 12H, CH_2, PEt_3), 5.36 (d, 1H, $=CH_a$, J(a−c) = 10 Hz, J(a−b) < 1 Hz); 5.5 (d, 1H, $=CH_b$, J(b−c) = 16 Hz); 6.37 (d, 1H, SCH_e, J(e−d) = 10 Hz); 6.6 (t, 1H, CH_d, J(d−e) = J(d−c) = 10 Hz); 7.4 (dt, 1H, CH_c, J(c−a) = J(c−d) = 10, J(c−b) = 16 Hz).

Reaction of $[Pt_2(PEt_3)_4(SC_{12}H_9)_2](BF_4)_2$ (7c) with HCl. Gaseous HCl was gently bubbled (5 min) through a stirred solution of complex **7c** (0.25 g; 0.177 mmol) in CH_2Cl_2 (7 cm^3). The initial yellow solution turned pale yellow, and a white solid precipitated. After standing (30 min) the soluble part was analyzed by GC-MS and shown to be composed of 2-phenylthiophenol (91%). The precipitate was mainly *cis*-$PtCl_2(PEt_3)_2$, identified by NMR.

Reaction of $[Pt_2(PEt_3)_4(SC_8H_7)_2](BF_4)_2$ (7b) and of $[Pt_2(PEt_3)_4(SC_4H_5)_2](BF_4)_2$ (7a) with HCl. Following a similar procedure, but keeping the temperature low with an ice/acetone bath, complex **7b** derived from benzothiophene gave an organic fraction which contained 2-vinylthiophenol (83%). Complex **7a** (derived from thiophene) reacted with HCl in the same way to yield an organic part containing an extremely unstable oil that rapidly polymerized and which was identified mass spectrometrically as thiapentadiene or an isomer thereof (SC_4H_6, 59%) and thiophene (15%); $[PtCl_2(PEt_3)_2]$ was also obtained.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic thermal vibrational parameters, and hydrogen atom position parameters and an ORTEP diagram for complex **7c** (6 pages). Ordering information is given on any current masthead page.

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[14] In view of the sensitivity of complex **7a**, a freshly prepared sample was weighed in a gelatin capsule under argon in a glovebox and then immediately introduced into the combustion chamber of a Fisons EA-1108 microanalyzer. The analysis was carried out in triplicate.