Reactivity of Substituted Thiophenes toward Tris(triethylphosphine)platinum(0), -palladium(0), and -nickel(0)

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The reactions of $[M(PEt_3)_3]$ (M = Pt (**1**), Pd (**2**), Ni (**3**)) with 3-chlorothiophene, 2-chlorothiophene, 3-nitrothiophene, 2-nitrothiophene, 2-methoxythiophene, 3-methoxythiophene, 2-acetylthiophene, and 3-acetylthiophene afforded thiaplatinacycles of the type $[(Et_3P)_2M(C,S\text{-}C_4H_3RS)]$, (for M = Pt, R = Cl (**4** and **5**), NO_2 (**6** and **7**), MeO (**8** and **9**), Ac (**10** and **11**); for M = Pd, R = Cl (**12** and **13**), NO_2 (**14**), MeO (**15** and **16**), Ac (**17** and **18**), for M = Ni, R = Cl (**19**)). When **3** and 2-chlorothiophene were reacted, another compound resulting from the oxidative addition of the C−Cl bond could be isolated, with the formulation $[(Et_3P)_2Ni(Cl)(\eta^1\text{-}T)]$ (**20**). Additionally the reaction of **3** with 2-nitrothiophene produced a compound derived from a C−H activation reaction, $[(Et_3P)_2Ni(H)(\eta^1\text{-}NO_2T)]$ (**21**). The thiaplatinacycles **8**−**11** were shown to be active intermediates in HDS reactions, under catalytic conditions, to give 81 cycles at 300 psi, 100 °C in THF, in the presence of metallic mercury. Crystal structures are reported for **4** and **7**.

Introduction

Recent studies of the reactivity of thiophenes toward complexes containing low-valent transition metals has shown them to be very useful models to understand the mechanism of hydrodesulfurization (HDS). The structures and reactivity patterns of organometallic compounds of thiophenes that have been uncovered help to elucidate some of the factors involved in the actual process.[2] The study of the reactivity of methyl substituted thiophenes are of particular interest, since they are present in crude oil and are highly resistant to removal by conventional HDS methods.[3] To date very few reports on the reactivity of transition metals toward methyl-substituted thiophenes have been reported.[4,9]

Furthermore, thiophenes with substituents other than methyl have been very little studied as models for HDS. However, Jones has reported[5] the ring opening of 2-methoxythiophene by $[(C_5Me_5)Rh(C_2H_4)_2]$ to give the corresponding thiarhodacycle $[(C_5Me_5)Rh(C,S\text{-MeO-}C_4H_3)]$. Bianchini discussed[6] the reactions of [(triphos)-$Rh(H)_3$] with a variety of substituted thiophenes; however, details of the isolation and characterization of some of the products have not yet been given. There has also a recent report of the 1,2-insertion of ruthenium into 3-substituted thiophenes.[7]

Work in our laboratory with $[M(PEt_3)_3]$ (M = Pt, **1**) found that it is possible to activate C−S bonds in dibenzothiophene,[8] benzothiophene, thiophene, methylthiophenes,[9] methylbenzothiophenes,[10] and methyldibenzothiophenes to yield the corresponding thiaplatinacycles.

This paper extends the study of reactivity of **1** toward several substituted thiophenes, which led to the activation of C−S, C−H, and C−Cl bonds of thiophenes and discusses the influence of the metal and thiophene substituents in such reactions. We also describe related reactions with zerovalent palladium; the thiapalladacycles reported here constitute the first examples of such compounds derived from thiophenes.

Results and Discussion

Reactions of Tris(triethylphosphine)platinum-(0) (1) with Chlorothiophenes. Heating a excess of 3-chlorothiophene (3-ClT) with **1** in toluene under argon

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(2) For recent reviews see: (a) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073. (b) Bianchini, C.; Meli, A. *J. Chem Soc., Dalton Trans.* **1996**, 801. (c) Chen, J. B.; Angelici, R. J. *Coord. Chem. Rev.* **2000**, *206*, 63.

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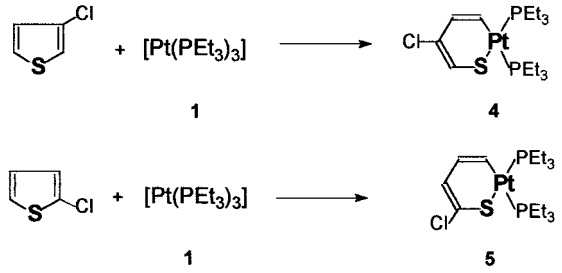
Scheme 1



and removing volatiles, the procedure we reported previously,[8a] gave the thiaplatinacycle $[(Et_3P)_2M(C,S\text{-}C_4H_3ClS)]$ (**4**; M = Pt), obtained in 67% yield after workup (Scheme 1). The analogous complex **5** from 2-chlorothiophene (2-ClT) was also formed, but in a lower yield (21%) (Scheme 1). In both reactions some free ligand and an unidentified material that did not contain a thiophenic moiety were separated by chromatography on silica gel.

Complex **4** was characterized by NMR spectroscopy and by an X-ray structure determination. The latter showed that the oxidative addition of 3-chlorothiophene was of the C−S bond and not of the C−Cl bond to the platinum. Thus, the thiaplatinacycle isomer formed has the chloro substituent in the 4-position, away from the metallic center.

The NMR spectra of crude reaction mixtures showed no evidence for any isomer other than **4** and were in agreement with the structure found by X-ray methods. In particular the $^1H-^{13}C$ HETCOR established unambiguously that the carbon directly bonded to platinum was at δ 136.1 (^1J(C−Pt) = 743 Hz, ^2J(C−*trans*-P) = 97 Hz, ^2J(C−*cis*-P) = 9.2 Hz); this carbon correlated with a proton at δ 7.7 ppm, and that proton correlated in the COSY spectrum with the proton at δ 6.9 (^3J(H−H) = 12 Hz). The ^{31}P NMR of **4** showed the characteristic pattern expected for two cis phosphines on a thiaplatinacycle, with resonances at δ −0.5 (^1J(Pt−P) = 1724 Hz, ^2J(P−P) = 23 Hz), for P trans to C, and δ 10.5 (^1J(Pt−P) = 3096 Hz, ^2J(P−P) = 23 Hz), for P trans to S.

Complex **5** was characterized similarly; the ^{31}P NMR spectrum exhibited a pattern similar to that described above, with resonances at δ 5.9 (^1J(Pt−P) = 1911 Hz, ^2J(P−P) = 16 Hz), for P trans to C, and δ 10.8 (^1J(Pt−P) = 3904 Hz, ^2J(P−P) = 16 Hz), for P trans to S. In the ^{13}C spectrum the signal assigned to the tertiary carbon directly bound to platinum is at δ 133.5 (^1J(C−Pt) = 584 Hz, ^2J(C−*trans*-P) = 78 Hz, ^2J(C−*cis*-P) = 7.5 Hz), and a signal at δ 127.6 is assigned to the quaternary carbon attached to the ring chloro substituent. The ^1H NMR spectrum in the aromatic region shows three resonances at δ 6.7, 7.05, and 7.42 for the protons on the thiaplatinacycle moiety; the signal at δ 7.05 is assigned to the proton in position 5, with ^3J(H−H) = 3.5 Hz.

X-ray Structure of Thiaplatinacycle 4. The thiaplatinacycle derived from 3-chlorothiophene is depicted in Figure 1; selected bond lengths and angles are given in Table 1. The thiaplatinacycle moiety in complex **4** is nearly planar, with a dihedral angle of only 1.3° between the plane C(4)−Pt−(S) and the mean plane through S−C(1)−C(2)−C(3)−C(4). The coordination geometry of the platinum is nearly square planar, as expected (rms deviation of the P_2SC plane, 0.065 Å; displacement of platinum, 0.018 Å): P(1)−Pt−P(2) = 98.71(13)°; S(1)−Pt−P(2) = 87.20(14)°; S(1)−Pt−C(4) = 89.8(4)°; P(1)−Pt−C(4) = 84.5(4)°. The angle P(1)−Pt−P(2) is significantly 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 **4** are Pt−S(1) = 2.299(3) Å, Pt−C(4) = 2.061(13) Å, Pt−P(1), which is trans to S(1), = 2.281(3) Å, and Pt−P(2), which is trans to C(4), = 2.350(4) Å, due to the trans influence of the σ-bonded vinylic carbon. The angles and distances are very similar to those seen with closely related platinum complexes such as the one derived from 3-methylthiophene,[9] and from a benzothiophene.[8a,10,11]

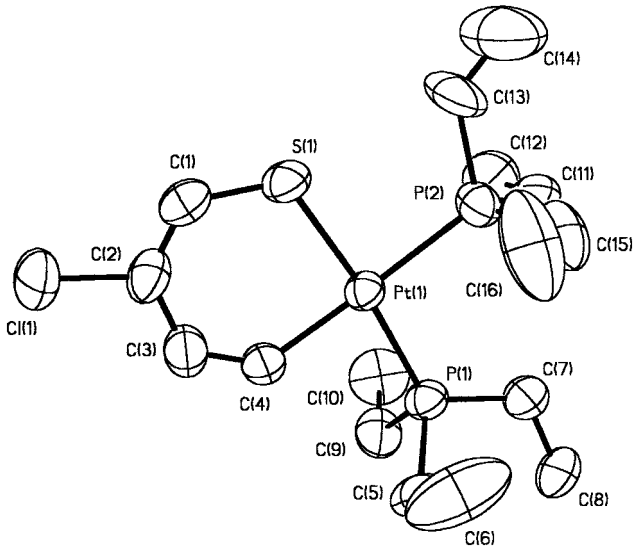


Figure 1. Molecular structure of complex **4** with thermal ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4

Pt(1)−C(5)	2.061(13)	Pt(1)−P(1)	2.281(3)
Pt(1)−S(1)	2.299(3)	Pt(1)−P(2)	2.350(4)
Cl(1)−C(2)	1.779(14)	S(1)−C(1)	1.665(16)
C(1)−C(2)	1.339(19)	C(2)−C(3)	1.39(2)
C(3)−C(4)	1.326(17)		
C(4)−Pt(1)−P(1)	84.5(4)	C(4)−Pt(1)−S(1)	89.8(4)
P(1)−Pt(1)−S(1)	173.70(14)	C(4)−Pt(1)−P(2)	174.7(4)
P(1)−Pt(1)−P(2)	98.71(13)	S(1)−Pt(1)−P(2)	87.20(14)
C(2)−C(1)−S(1)	126.7(11)	C(1)−C(2)−C(3)	129.0(14)
C(1)−C(2)−Cl(1)	116.0(11)	C(3)−C(2)−Cl(1)	114.7(13)
C(4)−C(3)−C(2)	127.1(15)	C(3)−C(4)−Pt(1)	132.0(11)
C(1)−S(1)−Pt(1)	114.8(5)		

Reactions of Tris(triethylphosphine)platinum-(0) with Nitrothiophenes. The commercially available 2-nitrothiophene (2-NO_2T) was of 85% purity and contained 15% of 3-nitrothiophene (3-NO_2T). Reaction at room temperature of this mixture with **1** afforded a mixture of compounds which was separated by column chromatography (Scheme 2). Interestingly, the main product turned to be the thiaplatinacycle derived from 3-NO_2T, which was obtained in 14% yield of the total.

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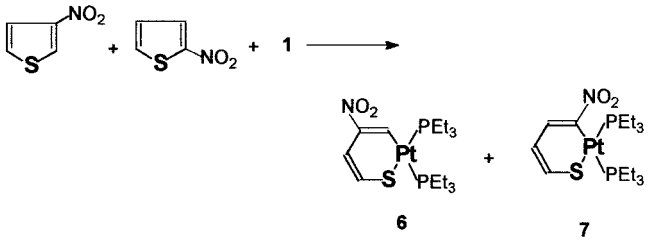
Scheme 2



This represents 93% of the 3-NO_2T present in the mixture; in other words, the 3-NO_2T reacted almost quantitatively.

In addition TLC showed the presence of a second isomeric complex, **7**, which crystallized from the hexane extracts of the original reaction mixture at −30 °C. Those crystals were suitable for an X-ray structure determination, which showed that this complex was the product of oxidative addition of the C−S bond of 2-nitrothiophene to Pt(0), giving the isomer where the nitro substituent is on the carbon directly attached to platinum in the thiaplatinacycle.

There is therefore a sharp contrast between the behavior of the chloro- and nitrothiophenes. Although the oxidative addition to Pt(0) is of a ring C−S bond in each case, in the chlorothiophenes it is of the C−S bond farthest from the Cl substituent, while in the nitrothiophenes it is the C−S ring bond nearest to the nitro substituent. Indeed, in 2-nitrothiophene the carbon bonded to the nitro group is the one that reacts. This difference probably arises from electronic rather than steric reasons; thus, it is probable that in the nitrothiophenes the closer C−S bonds are activated.

All the spectroscopy is in agreement with the proposed structure for **6**; the ^{31}P NMR shows the typical pattern described above, with two doublets with platinum satellites at δ 1.6 ppm (^1J(Pt−P) = 1879 Hz, ^2J(P−P) = 24 Hz), for P trans to C, and δ 11.0 ppm (^1J(Pt−P) = 2898 Hz, ^2J(P−P) = 24 Hz), for P trans to S. The ^{1}H NMR spectrum in the aromatic region shows three resonances at δ 7.38, 7.5, and 9.28, for protons on the thiaplatinacycle moiety. The COSY shows a correlation between the first two signals, 7.38 and 7.5 ppm, while in contrast the signal at δ 9.28 does not correlate with a proton but shows couplings to platinum and phosphorus (^2J(H−Pt) = 19 Hz, ^3J(H−P) = 24 Hz), as may be expected for a thiaplatinacycle derived from 3-NO_2T. The ^{1}H−^{13}C HETCOR allowed us to determine unambiguously that the tertiary carbon attached to the carbon directly bonded to platinum bears the proton at 9.28 ppm, as proposed for **6**.

X-ray Structure of Thiaplatinacycle 7. The thiaplatinacycle **7** derived from 2-nitrothiophene had the structure depicted in Figure 2; selected bond lengths and angles are given in Table 2. The thiaplatinacycle moiety in complex **7** is a bent structure, with a dihedral angle of 142.5° between the mean plane P(1)−Pt−P(2)−S(1)−C(4) (maximum deviation of that plane for S(1) at 0.261 Å) and the mean plane S(1)−C(1)−C(2)−C(3)−C(4) (maximum deviation of that plane for C(3) at 0.141 Å). This bent structure sharply contrasts with the virtually planar structures found in the thiaplatinacycles derived from 3-ClT discussed above and that previously reported for 3-MeT.[9] The bond angles around

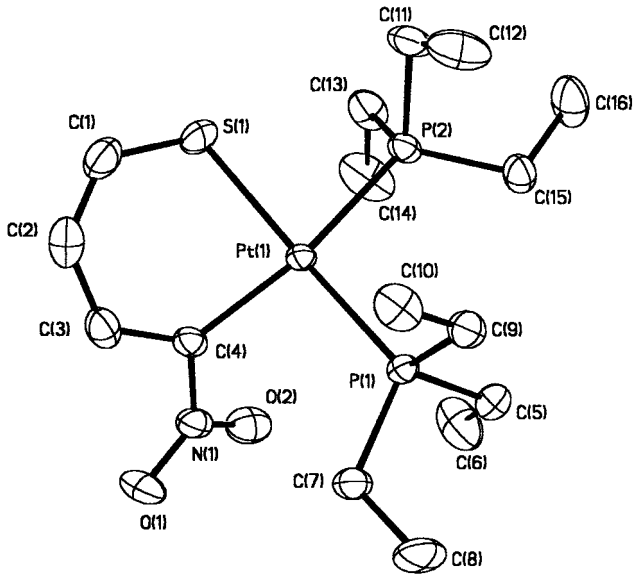


Figure 2. Molecular structure of complex **7** with thermal ellipsoids at the 30% probability level. H atoms have been omitted for clarity.

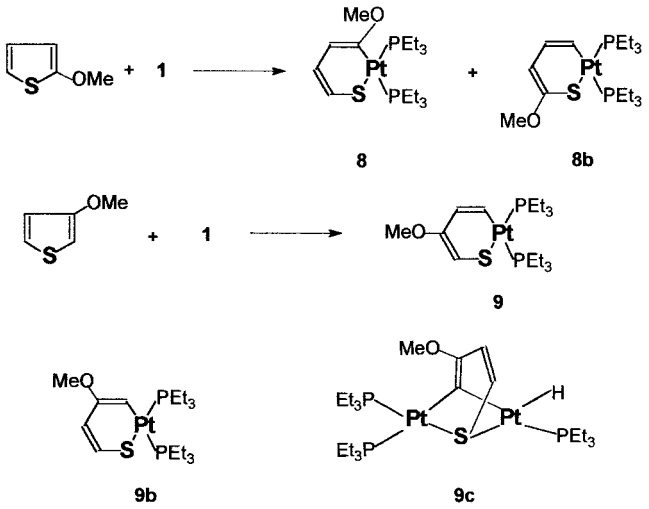
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 7

Pt(1)−C(4)	2.047(5)	Pt(1)−P(1)	2.2850(14)
Pt(1)−S(1)	2.3250(16)	Pt(1)−P(2)	2.3272(14)
C(1)−C(2)	1.323(10)	C(2)−C(3)	1.419(10)
C(3)−C(4)	1.352(7)	C(4)−N(1)	1.463(7)
S(1)−C(1)	1.719(7)		
C(4)−Pt(1)−P(1)	93.08(14)	C(4)−Pt(1)−S(1)	87.47(15)
P(1)−Pt(1)−S(1)	164.18(7)	C(4)−Pt(1)−P(2)	167.33(14)
P(1)−Pt(1)−P(2)	98.16(5)	S(1)−Pt(1)−P(2)	83.30(6)
C(1)−S(1)−Pt(1)	107.5(2)	C(15)−P(2)−Pt(1)	122.4(2)
C(13)−P(2)−Pt(1)	107.3(2)	C(11)−P(2)−Pt(1)	115.7(2)
C(2)−C(1)−S(1)	127.8(5)	C(1)−C(2)−C(3)	124.8(6)
C(4)−C(3)−C(2)	126.3(6)	C(3)−C(4)−N(1)	111.8(5)
C(3)−C(4)−Pt(1)	129.6(4)	N(1)−C(4)−Pt(1)	118.0(4)

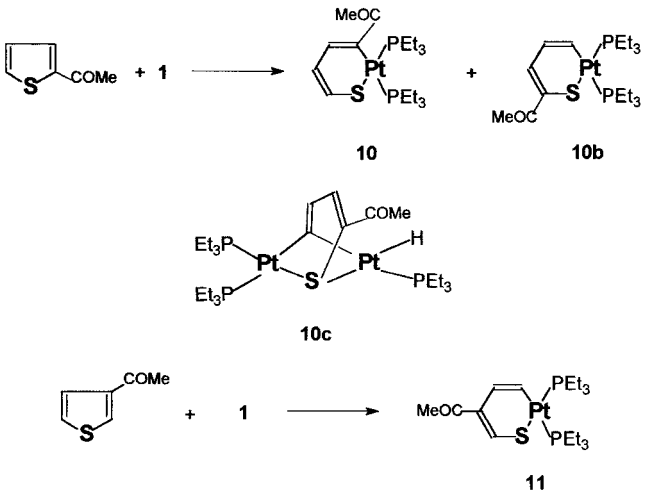
the platinum are P(1)−Pt−P(2) = 98.16(5)°, S(1)−Pt−P(2) = 83.30(6)°, S(1)−Pt−C(4) = 87.47(15)°, and P(1)−Pt−C(4) = 93.08(14)°; again the angle P(1)−Pt−P(2) is larger than 90°, due to steric repulsion between the substituents on the phosphines. The angle P(1)−Pt−C(4) is also larger than 90°, probably as a consequence of repulsion between the NO_2 and the phosphine substituents. Key bond lengths in complex **7** are Pt−S(1) = 2.3250(16) Å, Pt−C(4) = 2.047(5) Å, Pt−P(1), which is trans to S(1), = 2.2850(14) Å, and Pt−P(2), which is trans to C(4), = 2.3272(14) Å.

Reactions of Tris(triethylphosphine)platinum(0) with Methoxythiophenes. The reaction of **1** with 2-methoxythiophene afforded thiametallacycle **8** (Scheme 3). The ^{31}P NMR spectrum exhibited the typical pattern for a thiaplatinacycle, two doublets with platinum satellites at δ 1.0 (^1J(Pt−P) = 1716 Hz, ^2J(P−P) = 21 Hz), for P trans to C, and δ 10.5 (^1J(Pt−P) 3235 Hz, ^2J(P−P) 21 Hz), for P trans to S. The significant signals in ^{1}H NMR are three resonances at δ 5.8, 6.8, and 6.9, for protons on the thiaplatinacycle moiety; the second signal is assigned to the proton on position 4, which shows couplings to protons in positions 3 and 5; that was confirmed with COSY. In the ^{13}C NMR the quaternary carbon directly bonded to platinum is at δ 169.0 ppm (^2J(C−*trans*-P) = 126 Hz, ^2J(C−*cis*-P) = 5 Hz); platinum satellites could not be observed due to the

Scheme 3



Scheme 4



weakness of this signal, as this is a quaternary carbon. This was confirmed by the ^{1}H−^{13}C HETCOR. The ^{31}P NMR spectrum of the crude reaction revealed the presence of a small amount of a second thiaplatinacycle, probably **8b**, with signals at δ 2.5 (^1J(Pt−P) = 1806 Hz, ^2J(P−P) = 22 Hz), for P trans to C, and 11.0 (^1J(Pt−P) = 3162 Hz, ^2J(P−P) = 22 Hz), for P trans to S. We suggest this compound is the isomeric form of **8**, with the platinum inserted into the C−S bond where the carbon is a tertiary carbon or opposite to the methoxy substitution. Further heating of pure **8** did not produce **8b**; consequently, we propose that each isomer is formed by an independent pathway.

The analogous reaction of **1** with 3-methoxythiophene afforded as main product complex **9** in 50% yield. The structure proposed for this complex is similar to that of **4** (Scheme 3), on the basis of the ^{31}P NMR spectrum (two doublets with platinum satellites at δ −0.1 ppm (^1J(Pt−P) = 1732 Hz, ^2J(P−P) = 23 Hz), for P trans to C, and 9.3 ppm (^1J(Pt−P) = 3084 Hz, ^2J(P−P) = 23 Hz), for P trans to S) and the ^{1}H NMR spectrum. The latter showed three protons on the thiaplatinacycle in the aromatic region at δ 6.2, 6.8, and 7.7; the second and third signals are coupled to each other, but no H−H coupling was found for the δ 6.2 signal, which was confirmed with COSY. With ^{1}H−^{13}C HETCOR we established unambiguously that the carbon directly bound to platinum was the signal at δ 135.0 (^1J(C−Pt) = 640 Hz, ^2J(C−*trans*-P) = 100 Hz, ^2J(C−*cis*-P) = 10 Hz); this carbon correlated with the proton at δ 7.7. The possibility of having as a product the thiametallacycle **9b**, with a methoxy substituent in a position closer to platinum, was discarded because this isomer is expected to have a tertiary carbon directly bound to platinum without a significant H−H coupling. Since we did not detect the formation of **9b**, we explored a variety of reaction conditions in order to form it.

However, we found that on increasing the reaction time a new compound was formed; this compound was isolated from the reaction mixture by column chromatography. It showed two signals in the ^{1}H NMR in the aromatic region at δ 6.8 and 7.5 with coupling between them (10 Hz) and a signal in the hydride region at δ −6.1, with couplings to two different platinum centers and three different phosphorus atoms (^1J(H−Pt) = 508 Hz, ^3J(H−Pt) = 148 Hz, ^2J(H−P) = 75 Hz, ^4J(H−P) 17 Hz, ^4J(H−P) = 11 Hz). The ^{13}C NMR showed four signals at low field, two for tertiary carbons at δ 95.0 and 118.4 and two for quaternary carbons at δ 127.0 and 160.0, which was confirmed with a ^{1}H−^{13}C HETCOR determination. The ^{31}P NMR spectrum showed a pattern characteristic of dinuclear platinum-phosphine complexes,[12] with three different phosphorus at δ −0.2 (^1J(P−Pt) = 2412 Hz, ^3J(P−Pt) = 41 Hz, ^4J(P−P) = 10 Hz, ^4J(P−P) = 4.5 Hz), at δ 1.7, (^1J(P−Pt) = 2264 Hz, ^3J(P−Pt) = 39 Hz, ^2J(P−P) = 11 Hz, ^4J(P−P) = 4.5 Hz) and at δ 20.5, (^1J(P−Pt) = 4463 Hz, ^3J(P−Pt) = 316 Hz, ^2J(P−P) = 11 Hz, ^4J(P−P) = 10 Hz). The above spectroscopic details and the FAB$^+$ MS, which showed *m/z* 858, lead to the structure depicted for **9c** (Scheme 3). This dinuclear compound can be envisaged to result from the reaction between **9b** and **1**, via a C−H activation of the thiaplatinacycle **9b** and PEt_3 loss from **1**.

Reactions of Tris(triethylphosphine)platinum-(0) with Acetylthiophenes. The reaction of the Pt(0) complex **1** with 2-acetylthiophene gave a mixture of the thiaplatinacycles **10** and **10b** in a 10:1 ratio, as result of the ring-opening reaction of the thiophene and the consequent C−S bond breaking at positions 2 and 5 (Scheme 4). In the ^{31}P NMR spectrum of each metallacycle are observed two doublets and their respective platinum satellites, for **10** at δ 0.1 ([^1J(Pt−P) = 1679 Hz, ^2J(P−P) = 23 Hz), for P trans to C, and δ 11.2 (^1J(Pt−P) = 3094 Hz, ^2J(P−P) = 23 Hz), for P trans to S. Similarly, the signals for **10b** are at δ 0.8 (^1J(Pt−P) = 1715 Hz, ^2J(P−P) = 23 Hz), for P trans to C, and δ 11.7 (^1J(Pt−P) = 2982 Hz, ^2J(P−P) = 23 Hz), for P trans to S. Since the mixture of isomers could not be separated by any method tried, and the ^{1}H NMR spectrum was too complicated to allow assignment of the various signals, the mixture was left at room temperature for 2 h to see if one isomer would be favored; in fact column chromatography then gave a new compound, **10c** (Scheme 4), with spectroscopic features similar to those of **9c**. For instance, in the ^{1}H NMR spectrum are observed two multiplets at δ 7.5 and 8.6 (^3J(H−H) = 8.2 Hz) and a signal in the hydride region at δ −5.9,

(12) Schwartz, D. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4014.

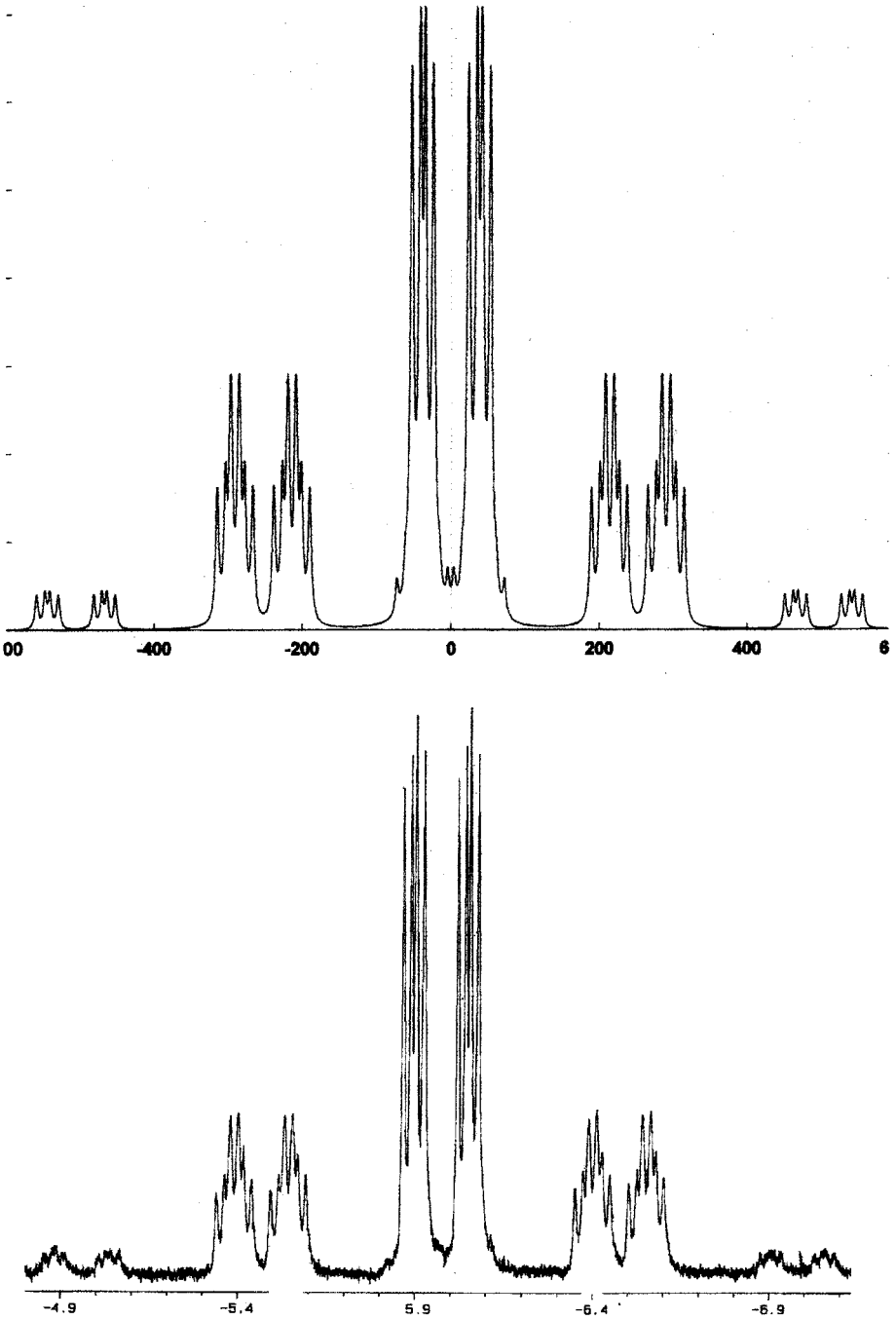
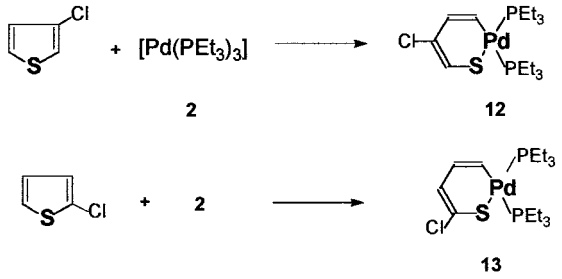


Figure 3. ^{1}H NMR spectra in the hydride region for complex **10c**: (top) simulated; (bottom) experimental.

with a multiplicity showing that it was coupled to two different platinum and three different phosphorus centers (^1J(H−Pt) = 499 Hz, ^3J(H−Pt) = 180 Hz, ^2J(H−P) = 76 Hz, ^4J(H−P) = 17 Hz, ^4J(H−P) = 11 Hz) (see Figure 3). In ^{13}C NMR five signals are observed at low field, two of them for tertiary carbons at δ 120.2 and 133.3 ppm, confirmed with a ^{1}H−^{13}C HETCOR, and three for quaternary carbons at 129.0, 162.5, and 196.4 ppm. The 162.5 ppm resonance is broad and is assigned to the carbon directly attached to platinum, and the 196.4 ppm signal is assigned to the carbonyl carbon. The ^{31}P NMR spectrum shows again the typical pattern for dinuclear compounds, as in **9c**, with three different phosphines at δ −0.1 (^1J(P−Pt) = 2370 Hz, ^3J(P−Pt) = 39 Hz, ^4J(P−P) = 10.5 Hz, ^4J(P−P) = 4 Hz), δ 0.9 (^1J(P−Pt) = 2226 Hz, ^3J(P−Pt) = 44 Hz, ^2J(P−P) = 10.5 Hz, ^4J(P−P) = 4 Hz) and δ 21.0 (^1J(P−Pt) = 4496 Hz, ^3J(P−Pt) = 329 Hz, ^2J(P−P) = 10.5 Hz, ^4J(P−P) = 10.5 Hz). The FAB$^+$-MS determination shows *m*/*z* 870, in agreement with a dinuclear structure. As for **9c**, a possible formation of **10c** can be envisaged to occur from the reaction of **10b** with **1**, through a C−H activation on the thiaplatinacycle and phosphine loss, respectively.

The related reaction of **1** with 3-acetylthiophene gave only one product complex, **11**, in 70% yield after workup; the proposed structure for this complex is similar to that of **9** (Scheme 4). The ^{31}P NMR displays two doublets with platinum satellites at δ 1.5 (^1J(Pt−P) = 1681 Hz, ^2J(P−P) = 22 Hz), for P trans to C, and δ 11.5 (^1J(Pt−P) = 3156 Hz, ^2J(P−P) = 22 Hz), for P trans to S. The ^{1}H NMR spectrum shows three signals for the thiaplatinacycle at δ 7.7, 8.2, and 8.6; the δ 7.7 and 8.2

Scheme 5

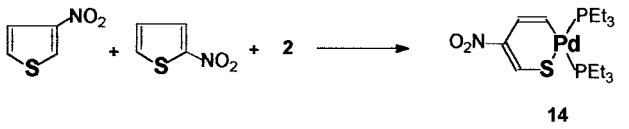


resonances show coupling to each other, but there was no H−H coupling to the third signal. These were confirmed by COSY, while ^{1}H−^{13}C HETCOR allowed us to assign unambiguously the signal at δ 138.9 (^{1}J(C−Pt) 640 Hz, ^{2}J(C−*trans*-P) = 97 Hz, ^{2}J(C−*cis*-P) = 9 Hz) as the carbon directly bound to platinum; this carbon correlated with the proton at 7.7 ppm. The possibility that the compound was the isomer analogue of **9b** was discarded for the same reasons already discussed above. The ^{31}P NMR shows the typical signals for a thiaplatinacycle, at δ 1.5, (^{1}J(Pt−P) = 1681 Hz, ^{2}J(P−P) = 22 Hz), for P trans to C, and δ 11.5 (^{1}J(Pt−P) = 3156 Hz, ^{2}J(P−P) = 22 Hz), for P trans to S.

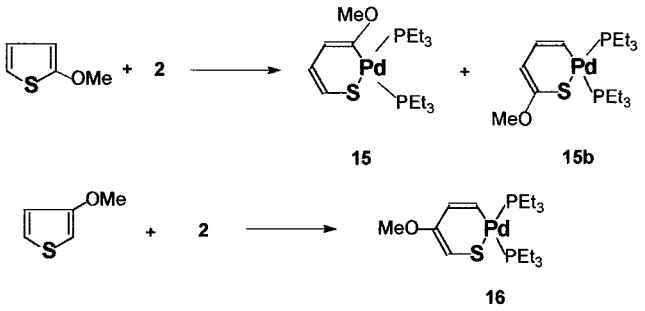
Reactions of Tris(triethylphosphine)palladium-(0) with Chlorothiophenes. Using a procedure similar to that used for platinum, the reaction of the palladium complex **2** with 3-chlorothiophene afforded the thiapalladacycle **12**, in 65% yield after workup (Scheme 5). A similar reaction of **2** with 2-chlorothiophene produced the thiapalladacycle **13** in 64% yield (Scheme 5). The ^{31}P NMR of **12** consists of two broad singlets at δ 15.8 and 18.3; ^{2}J(P−P) is not observed or is smaller than 2 Hz. The signals in the ^{1}H NMR for the thiametallacycle are at δ 6.46, 6.85, and 7.2; the first signal shows no H−H coupling, while the δ 6.85 and 7.2 signals were coupled (^{3}J(H−H) 5 Hz). These were confirmed with COSY, which also showed the additional couplings ^{4}J(H−P) = 1 Hz and ^{3}J(H−P) = 3 Hz. With ^{1}H−^{13}C HETCOR we could establish from the coupling to phosphorus that the signal at δ 7.2 was due to a proton attached to carbon directly bound to palladium. That carbon is at δ 122.5 (^{2}J(C−P) 25 Hz). In the ^{13}C NMR spectrum the remaining carbons of the thiaplatinacycle are at δ 118.2 and 132.8 (tertiary carbons) and at δ 139.4 (quaternary carbon attached to the chloro substituent); none of the carbons showed a C−P coupling constant larger than 8 Hz. Consequently, the structure for **12** is the one depicted in Scheme 5 and is isostructural with complex **4**.

Similarly, the thiapalladacycle **13** is isostructural with **5**. The ^{31}P NMR spectrum for **13** consists of two broad singlets at δ 16.0 and 18.25, again ^{2}J(P−P) is not observed or is smaller than 2 Hz. The signals for the thiametallacycle in the ^{1}H NMR spectrum are three signals at δ 6.5 (^{3}J(H−H) = 3 Hz), 6.9 (^{3}J(H−H) = 3 Hz, ^{3}J(H−H) = 5 Hz), and 7.3 (^{3}J(H−H) = 5 Hz); additionally the last signal shows a small coupling, probably due to ^{3}J(H−P) = 2 Hz. ^{1}H−^{13}C HETCOR shows that the signal at δ 7.3 is the proton attached to carbon which is directly bound to palladium. This carbon in the ^{13}C NMR is located at δ 128.7 (^{2}J(C−P) = 20 Hz); the remaining carbons for the thiaplatinacycle are at δ 126.9 and 128.5 (tertiary carbons) and at δ 141.0 (quaternary carbon attached to the chloro substituent). None of these carbons showed a C−P coupling constant larger than 10 Hz.

Scheme 6



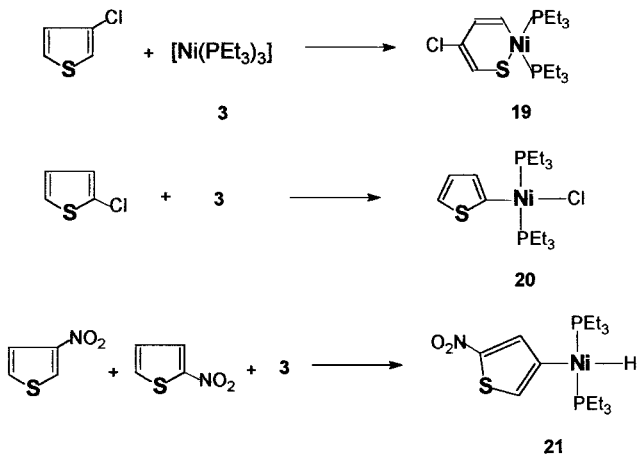
Scheme 7



Reactions of Tris(triethylphosphine)palladium-(0) with Nitrothiophenes. Using the commercial mixture of nitrothiophenes (85% of 2-NO_2T and 15% of 3-NO_2T), the reaction at room temperature of **2** with the above thiophenes gave a mixture of compounds separated by column chromatography; only complex **14** was recovered in pure form (Scheme 6). The compound depicted can be envisaged as derived from 3-nitrothiophene in 13% yield with respect to the total amount of used thiophenes; however, considering the relative composition of the used starting material, the reaction is almost quantitative (87% relative yield). In the ^{31}P NMR spectrum can be observed the typical pattern for a thiapalladacycle: it consists of two doublets at δ 22.1 and 27.7 (^{2}J(P−P) = 37 Hz). The ^{1}H NMR shows three signals in the aromatic region associated with the thiapalladacycle at δ 6.89 (^{3}J(H−H) = 5.5 Hz, ^{4}J(H−P) = 5 Hz), 7.15 (J(H−H) = 5.5 Hz, ^{3}J(H−P) = 12 Hz, ^{3}J(H−P) = 1 Hz) and 7.81 (^{4}J(H−P) = 6 Hz); the couplings between the δ 6.89 and 7.15 signals were confirmed with COSY. The relevant signals in the ^{13}C NMR are the signals for the thiapalladacycle moiety at δ 116.1, 126.1, and 135.5 (^{2}J(C−P) 39 Hz) (for tertiary carbons) and at 153.1 ppm (for a quaternary carbon attached to the nitro substituent).

Reactions of Tris(triethylphosphine)palladium-(0) with Methoxythiophenes. The reaction of **2** with 2-methoxythiophene gave a mixture of complexes **15** and **15b**, resulting from the ring-opening reaction of the above thiophene (Scheme 7). The ^{31}P NMR shows four doublets (in a ratio of 1.5:1) at δ 10.1 (^{2}J(P−P) = 10.8 Hz), 10.9 (^{2}J(P−P) = 10.8 Hz), 10.2 (^{2}J(P−P) = 10.9 Hz), and 10.7 (^{2}J(P−P) = 10.9 Hz), respectively. In the ^{1}H NMR six multiplets are observed in the aromatic region for a metallacycle, separated into two sets of three signals (in a ratio of 1.5:1), respectively, at δ 6.66 (^{3}J(H−H) = 3.9 Hz, ^{3}J(H−H) = 4.8 Hz), 7.07 (^{3}J(H−H) = 4.8 Hz), and 7.17 (^{3}J(H−H) = 3.9 Hz) for the major isomer and at δ 6.76, (^{3}J(H−H) = 3.6 Hz, ^{3}J(H−H) = 3.9 Hz), 7.23 (^{3}J(H−H) = 3.6 Hz), and 7.58 (^{3}J(H−H) = 3.9 Hz, ^{3}J(H−P) = 1.5 Hz), for the minor isomer. The instability of the sample did not allow for ^{13}C NMR or ^{1}H−^{13}C HETCOR; however, on comparing this with the results

Scheme 8



obtained for platinum, we propose that the major isomer is **15** and the minor isomer is **15b**. The related reaction with 3-methoxythiophene afforded as the main product complex **16** in 15% yield (Scheme 7). Apparently small amounts of a second complex can be observed in the NMR, but not in an important yield. In the ^{31}P NMR are observed two doublets at δ 27.4 and 27.9 (^2J(P−P) = 6 Hz). For ^{1}H NMR are observed three multiplets at δ 6.3, 6.8, and 7.8, for three protons on the thiapalladacycle; the second and third signals were shown to be coupled, and no H−H coupling was observed for the first signal. As for **15**, due to the low stability of the sample ^{13}C NMR could not be obtained; consequently, the structure of **16** is proposed in analogy to complex **9**.

Reactions of Tris(triethylphosphine)palladium(0) with Acetylthiophenes. The reaction of **2** with 2-acetylthiophene and 3-acetylthiophene gave in both cases the corresponding thiaplatinacycles **17** and **18**, respectively, on the basis of the signals observed for the reaction mixture. Notably, the ^{31}P NMR gave evidence for the formation of such thiapalladacycles, but unfortunately the separation and isolation of these compounds could not be completed due to decomposition nor could a particular isomeric form be confirmed, due to the fact that long-term ^{13}C and HETCOR finished with a decomposed sample. In particular, **18** exhibited two different isomers in the reaction mixture; the ^{31}P NMR spectrum showed four doublets at δ 12.6 (^2J(P−P) = 7.2 Hz), 16.7 (^2J(P−P) = 7.2 Hz), 12.8 (^2J(P−P) = 6.4 Hz), and 17.0 (^2J(P−P) = 6.4 Hz).

Reactions of Tris(triethylphosphine)nickel(0) with Chlorothiophenes. When the nickel complex **3** was reacted with 3-chlorothiophene. the thianickelacycle [(Et$_3$P)$_2$Ni(*C*,*S*-C$_4$H$_3$ClS)] (**19**) was obtained in 65% yield after workup (Scheme 8). This compound is analogous to complex **4** and exhibits similar spectroscopic features; for instance the ^{31}P NMR with two doublets at δ 31.5 (^2J(P−P) = 5 Hz) and 52.8 (^2J(P−P) = 5 Hz). The relevant signals in the ^{1}H NMR are three signals at δ 7.3, 7.7, and 8.9 for the thiametallacycle; the signal at δ 7.3 is a slightly broad singlet without any H−H couplings, and the signals at δ 7.7 and 8.9 were shown to be coupled (^3J(H−H) = 4 Hz). Additionally, the signal at 8.9 ppm showed ^3J(H−P) = 10 Hz; this is assigned to the proton attached to the carbon directly bound to nickel. The ^{13}C NMR shows three singlets at δ 124.3, 126.1, and 153.1 ppm and a doublet for tertiary carbon at δ 135.6 (^2J(C−P) = 27.6 Hz). The closely related reaction of **3** with 2-chlorothiophene, carried out under the same reaction conditions, afforded the complex [(Et$_3$P)$_2$Ni(Cl)(η^1-C$_4$H$_3$S)] (**20**), as a result of the oxidative addition of the C−Cl bond (Scheme 8). The ^{31}P NMR spectrum shows only one singlet at δ 12.4. The ^{1}H NMR spectrum in the aromatic region shows three signals at δ 6.5, 6.9, and 7.36 (^3J(H−H) = 5 Hz). In the ^{13}C NMR spectrum the signals associated with the thiophenic moiety are four singlets at δ 127.1, 128.5, 129.9, and 140.4; the first three signals are for tertiary carbons and the last is for a quaternary carbon, and no carbon−phosphorus coupling is observed.

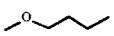
Reactions of Tris(triethylphosphine)nickel(0) with Nitrothiophenes. Following the same procedure as above, the complex [(Et$_3$P)$_2$Ni(H)(η^1-C$_4$H$_2$NO$_2$S)] (**21**) was derived from the C−H activation reaction between the nickel complex **3** and the commercial mixture of nitrothiophenes (2-NO$_2$T and 3-NO$_2$T, 85% and 15%, respectively), particularly from 2-nitrothiophene. The ^{31}P NMR shows one slightly broad signal at δ 52.8 ppm. In the ^{1}H NMR the relevant signals are broad singlets at δ 7.1 and 7.5, without any observable H−H coupling; the signal associated with the hydride could not be observed at room temperature or on lowering the temperature to −45 °C. In the infrared spectrum the hydride could be observed at 2150 cm^{-1}. The sample decomposed in solution to a paramagnetic byproduct; consequently the ^{13}C NMR could not be obtained.

Catalytic Studies. Complexes **8**−**11** were used as catalyst precursors for the hydrodesulfurization of the parent thiophene. Under relatively mild conditions all the above thiaplatinacycles were active precursors for the hydrodesulfurization reaction; these experiments are summarized in Table 3. From the analysis of such results we can observe that the activity of such compounds is higher in THF than in toluene at the same temperature; however, when the temperature is increased to 150 °C, a lower activity is detected, probably associated with the decomposition of the corresponding thiaplatinacycles. All of them melt with decomposition in the range 120−140 °C. As described in the Experimental Section, since no evolution of H$_2$S was detected and because the reactor's walls finished cleanly polished and a black precipitate was also observed, metallic mercury was added to the reactor experiments to give a homogeneous system. As a consequence of this, the activity was increased up to 81 cycles in THF at 100 °C. The dark insoluble residues of all the experiments were treated with hydrochloric acid, releasing H$_2$S in all cases.

Conclusions

We have demonstrated that it is possible to activate a C−S bond in 3-chlorothiophene, 2-chlorothiophene, 3-nitrothiophene, 2-nitrothiophene, 2-methoxythiophene, 3-methoxythiophene, 2-acetylthiophene, and 3-acetylthiophene, by reaction with the electron-rich complexes tris(triethylphosphine)platinum(0) (**1**), tris(triethylphosphine)palladium(0) (**2**), and tris(triethylphosphine)-nickel(0) (**3**). The products isolated and characterized were the thiametallacycles **4**−**11** for platinum, **12**−**18** for palladium, and **19** for nickel. The nickel complex led to C−Cl activation reactions in the case of chlo-

Table 3. Hydrodesulfurization Studies of Thiaplatinacycles

Complex	Substrate	Solvent	Temperature (°C)	Co-catalyst	Main desulfurized products	Cycles
8	2-MeOT	Toluene	100	None		21
8	2-MeOT	THF	100	None		57
8	2-MeOT	THF	100	Hg (33 mmol)		80
9	3-MeOT	Toluene	100	None		36
9	3-MeOT	THF	100	None		60
9	3-MeOT	THF	150	None		37
9	3-MeOT	THF	100	Hg (33 mmol)		81
11	3-AcT	Toluene	100	None		26
11	3-AcT	THF	100	None		34

rothiophenes and C−H activation products in the case of nitrothiophenes. It was also demonstrated that thiaplatinacycles **8**−**11** are important precursors or intermediates in homogeneous catalytic HDS processes, where the presence of a second metal increases the activity of the system.

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 determined 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, ^{31}P NMR spectra are relative to external H_3PO_4. Infrared spectra were obtained on a Perkin-Elmer 1600 FT spectrophotometer and GC-MS determinations on a Varian Saturn 3. Galbraith Laboratories carried out elemental analyses. The synthesis of $[Pt(PEt_3)_3]$ was carried out using the previously reported procedure.[13] All thiophenes were purchased from Aldrich and dried over molecular sieves. All complexes were purified by column chromatography, using silica gel and using hexane or hexane/acetone (1:1 v/v) as eluent, unless otherwise stated.

Preparation of [(Et$_3$P)$_2$Pt(*C,S*-C$_4$H$_3$ClS)] (4). Complex **4** was prepared from $[Pt(PEt_3)_3]$ (0.33 g, 0.6 mmol), **1**, and 3-chlorothiophene (0.2 mL, 2.2 mmol) in toluene (10 mL) under argon. The solution was then heated to 70 °C for 10 min with stirring. After this time the solvent and the excess phosphine was distilled out and the color changed from orange-red to yellow. The heating was then stopped, and the mixture was evaporated to dryness with increasing vacuum (0.01 mmHg) and cooled to room temperature. Freshly distilled dried toluene was added (5 mL) to give a yellow solution, which was purified by column chromatography on silica gel with hexane/acetone as eluent (from 9:1 to 3:1). Yield: 67%. Anal. Calcd for $C_{16}H_{33}ClP_2PtS$: C, 34.9; H, 6.0; S, 5.8. Found: C, 35.4; H, 6.0; S, 5.9. FAB$^+$: *m/z* 549. NMR spectra were obtained in $CDCl_3$. ^{1}H: δ (ppm) 1.1−1.9 (m, 30H, from Et−P), 6.9 (dd, 1H, ^3J(H−H) = 12 Hz, ^4J(H−*trans*-P) = 18 Hz, ^3J(H−Pt) = 75 Hz); 7.15 (d, 1H, ^3J(H−Pt) = 87 Hz, ^4J(H−*trans*-P) = 15 Hz); 7.7 (ddd, 1H, ^3J(H−*trans*-P) = 26 Hz, ^3J(H−*cis*-P) = 8 Hz, ^3J(H−H) = 12 Hz). ^{31}P: δ (ppm) −0.5 (^1J(Pt−P) = 1724 Hz, ^2J(P−P) = 23 Hz), 10.5 (^1J(Pt−P) = 3096 Hz, ^2J(P−P) = 23 Hz). ^{13}C: δ (ppm) 8.3 (d, CH_3, Et−P); 16−17.5 (m, −CH_2−P); 114.0 (d, CH, C(2), ^2J(C−Pt) 39 Hz, ^3J(C−*trans*-P) = 8 Hz); 125.18 (s, CH, C(4), ^2J(C−Pt) 131 Hz); 125.26 (s, C, C(3), ^3J(C−Pt) 12 Hz); 136.1 (dd, CH, C(5), ^1J(C−Pt) 743 Hz, ^2J(C−*trans*-P) = 97 Hz, ^2J(C−*cis*-P) = 9.2 Hz).

Preparation of [(Et$_3$P)$_2$Pt(*C,S*-C$_4$H$_3$ClS)] (5). Complex **5** was prepared from **1** and 2-chlorothiophene, following the same procedure, amounts, and purification methods as described for complex **4**. Yield: 21%. Anal. Calcd for $C_{16}H_{33}ClP_2PtS$: C, 34.9; H, 6.0; S, 5.8. Found: C, 35.6; H, 5.9; S, 5.9. FAB$^+$: *m/z* 549. NMR spectra were obtained in $CDCl_3$. ^{1}H: δ (ppm) 1.1−1.7 (m, 30H, from Et−P), 6.7 (pt, 1H, ^3J(H−H) = 3.5 Hz, ^3J(H−*trans*-P) = 7 Hz, ^2J(H−Pt) = 28 Hz); 7.05 (t, 1H, ^3J(H−H) = 3.5 Hz); 7.42 (d, 1H, ^3J(H−H) = 3.5 Hz). ^{31}P: δ (ppm) 5.9, (^1J(Pt−P) = 1911 Hz, ^2J(P−P) = 16 Hz), 10.8, (^1J(Pt−P) = 3904 Hz, ^2J(P−P) = 16 Hz). ^{13}C: δ (ppm) 8.3 (m, CH_3, Et−P); 16−17.0 (m, −CH_2−P); 112.85 (d, CH, ^3J(C−

(13) Yoshida, T.; Matsuda, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 119.

trans-P) = 5.8 Hz); 127.6 (s, C); 130.4 (s, CH, ^2J(C−Pt) = 80 Hz); 133.5 (dd, CH, ^1J(C−Pt) = 584 Hz, ^2J(C−*trans*-P) = 78 Hz, ^2J(C−*cis*-P) = 7.5 Hz).

Preparation of [(Et$_3$P)$_2$Pt(*C,S*-C$_4$H$_3$NO$_2$S)] (6 and 7). Both compounds were prepared from [Pt(PEt$_3$)$_3$] (0.33 g, 0.6 mmol), **1**, and the commercial mixture of 2-nitrothiophene and 3-nitrothiophene (0.31 g, 2.4 mmol) in toluene (10 mL) under argon. The solution was kept at room temperature for 30 min with stirring, during which time the color changed from orange to red. After this time the solvent and the excess phosphine were distilled out with increasing vacuum (0.01 mmHg); after 3 h the residue was redisolved in 5 mL of toluene, and this solution was purified by column chromatography, on silica gel with 4:1 hexane/acetone to 1:1 hexane/acetone as eluent. Yield: 14% for **6** and 10% for **7**. Anal. Calcd for $C_{16}H_{33}NO_2P_2PtS$: C, 34.3; H, 5.9; S, 5.7. Found for **6**: C, 33.8; H, 5.8; S, 5.7. Found for **7**: C, 34.0; H, 5.8; S, 6.1. NMR spectra for **6** were obtained in $CDCl_3$. ^{1}H: δ (ppm) 1.1−2.0 (m, 30H, from Et−P), 7.38 (dd, 1H, ^3J(H−H) = 10 Hz, ^5J(H−*trans*-P) = 3 Hz); 7.5 (ddd, 1H, ^4J(H−*cis*-P) = 1 Hz, ^4J(H−*trans*-P) = 16 Hz, ^3J(H−H) = 10 Hz); 9.28 (m, 1H, ^3J(H−*trans*-P) = 24 Hz, ^3J(H−*cis*-P) = 5 Hz, ^2J(H−Pt) = 19 Hz). ^{31}P: δ (ppm) 1.6, (^1J(Pt−P) = 1879 Hz, ^2J(P−P) = 24 Hz), 11.0, (^1J(Pt−P) = 2898 Hz, ^2J(P−P) = 24 Hz). ^{13}C: δ (ppm) 8.5 (d, CH_3, Et−P); 16−18 (m, −CH_2−P); 116.8 (s, CH, ^2J(C−Pt) = 81 Hz); 126.8 (d, CH, ^3J(C−*trans*-P) = 11 Hz); 131.5 (dd, CH, ^1J(C−Pt) not observed, ^2J(C−*trans*-P) = 96.7 Hz, ^2J(C−*cis*-P) = 11.5 Hz); 144.3 (s, C, C−NO_2).

Preparation of [(Et$_3$P)$_2$Pt(*C,S*-C$_4$H$_3$OMeS)] (8). Compound **8** was prepared from [Pt(PEt$_3$)$_3$] (0.2 g, 0.36 mmol), **1**, and 2-methoxythiophene (0.1 mL, 1.08 mmol) in toluene (10 mL) under argon. The solution was then heated to reflux for 20 min with stirring, during which time the color changed from orange to red. After this, the solvent and the excess phosphine were distilled out; at this point, the heating was stopped and the mixture was evaporated to dryness with increasing vacuum (0.01 mmHg), cooled to room temperature, and dried for 5 h. Freshly distilled dried toluene was added (3 mL) to give a reddish solution which was purified by column chromatography, on silica gel with 5:1 hexane/acetone to 1:1 hexane/acetone as eluent; the third fraction gave a red-orange residue. Yield: 60%. Anal. Calcd for $C_{17}H_{36}OP_2PtS$: C, 37.4; H, 6.6; S, 5.8. Found: C, 38.9; H, 6.7; S, 6.0. FAB$^+$: *m/z* 545. NMR spectra were as follows. ^{1}H: δ (ppm) 0.9−1.6 (m, 30H, from Et−P); 3.4 (s, 3H, OMe); 5.8 (dd, 1H, ^3J(H−H) = 7.2 Hz, ^4J(H−*trans*-P) = 13.4 Hz, ^3J(H−Pt) = 46 Hz); 6.8 (dd, 1H, ^3J(H−H) = 7.2 Hz, ^3J(H−H) = 9.2 Hz); 6.9 (dd, 1H, ^3J(H−H) = 9.2 Hz, ^4J(H−*trans*-P) = 12.8 Hz). ^{31}P: δ (ppm) 1.0, (^1J(Pt−P) = 1716 Hz, ^2J(P−P) = 21 Hz), 10.5, (^1J(Pt−P) = 3235 Hz, ^2J(P−P) = 21 Hz). ^{13}C: δ (ppm) 8−9 (m, CH_3, Et−P); 16−19.0 (m, −CH_2−P); 54.3 (s, CH_3O, ^3J(C−Pt) = 22 Hz); 98.8 (d, CH, ^3J(C−*trans*-P) = 10 Hz, ^2J(C−Pt) = 73 Hz); 112.8 (d, CH, ^3J(C−*trans*-P) = 6 Hz; 122.5 (d, CH, ^3J(C−Pt) = 77 Hz, ^4J(C−P) 3 Hz); 169.3 (dd, C, ^2J(C−*trans*-P) = 126 Hz, ^2J(C−*cis*-P) = 5 Hz, ^1J(C−Pt) = not observed).

Preparation of [(Et$_3$P)$_2$Pt(*C,S*-C$_4$H$_3$OMeS)] (9 and 9c). By a procedure similar to that described for **8**, complex **9** was prepared and purified, to give a pale yellow product. Yield: 50%. Anal. Calcd for $C_{17}H_{36}OP_2PtS$: C, 37.4; H, 6.6; S, 5.8. Found: C, 37.6; H, 6.5; S, 5.9. FAB$^+$: *m/z* 545. NMR spectra for **9** are as follows. ^{1}H: δ (ppm) 1.1−2.0 (m, 30H, from Et−P); 3.6 (s, 3H, OMe); 6.2 (d, 1H, ^4J(H−*trans*-P) = 16 Hz, ^3J(H−Pt) = 82 Hz); 6.8 (dd, 1H, ^3J(H−H) = 12 Hz, ^4J(H−P) = 19 Hz, ^3J(H−Pt) = 77 Hz); 7.7 (ddd, 1H, ^3J(H−H) = 12 Hz, ^3J(H−*trans*-P) = 26 Hz, ^3J(H−*cis*-P) = 9 Hz). ^{31}P: δ (ppm) −0.1 (^1J(Pt−P) = 1732 Hz, ^2J(P−P) = 23 Hz), 9.3 (^1J(Pt−P) = 3084 Hz, ^2J(P−P) = 23 Hz). ^{13}C: δ (ppm) 8−9 (m, CH_3, Et−P); 16−17 (m, −CH_2−P); 54.4 (s, CH_3O); 90.5 (d, CH, ^3J(C−*trans*-P) = 8 Hz); 121.7 (s, CH); 135.8 (dd, CH, ^1J(C−Pt) = 640 Hz, ^2J(C−*trans*-P) = 100 Hz, ^2J(C−*cis*-P) = 10 Hz); 154.2 (s, C). When the reaction time was increased to 4 h, **9c** was formed, FAB$^+$: *m/z* 858. NMR spectra for **9c** are as follows. ^{1}H: δ (ppm) −6.1 (ddd, 1H, ^1J(H−Pt) = 543.3 Hz, ^3J(H−Pt) = 473.4 Hz, ^2J(H−P) = 76.05 Hz, ^4J(H−P) = 16.67 Hz, ^4J(H−P) = 10.95 Hz); 0.8−1.8 (m, 45H, from Et−P); 3.7 (s, 3H, OMe); 6.8 (d, 1H, ^3J(H−H) = 10 Hz); 7.5 (d, 1H, ^3J(H−H) = 10 Hz). ^{31}P: δ (ppm) −0.2 (^1J(P−Pt) = 2412 Hz, ^3J(P−Pt) = 41 Hz, ^4J(P−P) = 10 Hz, ^4J(P−P) = 4.5 Hz); 1.7 (^1J(P−Pt) = 2264 Hz, ^3J(P−Pt) = 39 Hz, ^2J(P−P) = 11 Hz, ^4J(P−P) = 4.5 Hz); 20.5 (^1J(P−Pt) = 4463 Hz, ^3J(P−Pt) = 316 Hz, ^2J(P−P) = 11 Hz, ^4J(P−P) = 10 Hz). ^{13}C: δ (ppm) 8−9 (m, CH_3, Et−P); 18−19 (m, −CH_2−P); 56.2 (s, CH_3O); 95.0 (s, br, CH); 118.4 (s, br, C); 127.1 (s, CH); 159.3 (s, br, C).

Preparation of [(Et$_3$P)$_2$Pt(*C,S*-C$_4$H$_3$COMe)] (10, 10b, and 10c). By a procedure similar to that described for **8**, the mixture of complex **10** and **10b** was prepared and purified, to give an orange oily residue. **10**: yield 60%. **10b**: yield 6%. Anal. Calcd for $C_{18}H_{36}OP_2PtS$: C, 38.7; H, 6.5; S, 5.7. Found: C, 38.4; H, 6.6; S, 5.9%. FAB$^+$: *m/z* 557. NMR spectra for **10** are as follows. ^{31}P: δ (ppm) 0.1 (^1J(Pt−P) = 1679 Hz, ^2J(P−P) = 23 Hz), 11.2 (^1J(Pt−P) = 3094 Hz, ^2J(P−P) = 23 Hz). NMR spectra for **10b** are as follows. ^{31}P: δ (ppm) 0.8 (^1J(Pt−P) = 1715 Hz, ^2J(P−P) = 23 Hz), 11.7 (^1J(Pt−P) = 2982 Hz, ^2J(P−P) = 23 Hz). When the reaction time of the above mixture was increased to 2 h, **10c** was formed. FAB$^+$: *m/z* 870. NMR spectra for **10c** are as follows. ^{1}H: δ (ppm) −5.9 (ddd, 1H, ^1J(H−Pt) = 524.4 Hz, ^3J(H−Pt) = 485 Hz, ^2J(H−P) = 76.6 Hz, ^4J(H−P) = 17.8 Hz, ^4J(H−P) = 11.2 Hz); 0.8−2.0 (m, 45H, from Et−P); 3.0 (s, 3H, COMe); 7.53 (m, 1H, ^3J(H−H) = 8.2 Hz); 8.6 (m, 1H, ^3J(H−H) = 8.2 Hz). ^{31}P: δ (ppm) −0.1 (^1J(P−Pt) = 2370 Hz, ^3J(P−Pt) = 39 Hz, ^4J(P−P) = 10.5 Hz, ^4J(P−P) = 4 Hz); 0.9 (^1J(P−Pt) = 2226 Hz, ^3J(P−Pt) = 44 Hz, ^2J(P−P) = 10.5 Hz, ^4J(P−P) = 4.0 Hz); 21.0 (^1J(P−Pt) = 4496 Hz, ^3J(P−Pt) = 329 Hz, ^2J(P−P) = 10.5 Hz, ^4J(P−P) = 10.5 Hz). ^{13}C: δ (ppm) 8−9 (m, CH_3, Et−P); 18−21 (m, −CH_2−P); 28.6 (s, CH_3CO); 120.2 (s, br, CH); 129.0 (s, br, C); 133.3 (s, CH); 162.5 (s, br, C); 196.4 (s, CO).

Preparation of [(Et$_3$P)$_2$Pt(*C,S*-C$_4$H$_3$COMeS)] (11). By a procedure similar to that described for **8**, complex **11** was prepared and purified, to give an orange product. Yield: 70%. Anal. Calcd for $C_{18}H_{36}OP_2PtS$: C, 38.7; H, 6.5; S, 5.7. Found: C, 38.6; H, 6.3; S, 5.9. FAB$^+$: *m/z* 557. NMR spectra for **11** are as follows. ^{1}H: δ (ppm) 0.8−2.0 (m, 30H, from Et−P); 2.25 (s, 3H, COMe); 7.7 (m, 1H, ^3J(H−H) = 11.5, ^3J(H−*trans*-P) = 22 Hz, ^3J(H−*cis*-P) = 1.6 Hz, ^2J(H−Pt) not observed); 8.2 (m, 1H, ^3J(H−H) = 11.5 Hz, ^4J(H−P) = 20 Hz); 8.6 (d, 1H, ^4J(H−*trans*-P) = 17 Hz, ^3J(H−Pt) = 91 Hz). ^{31}P: δ (ppm) 1.5 (^1J(Pt−P) = 1681 Hz, ^2J(P−P) = 22 Hz), 11.5 (^1J(Pt−P) = 3156 Hz, ^2J(P−P) = 22 Hz). ^{13}C: δ (ppm) 8−9 (m, CH_3, Et−P); 16−17 (m, −CH_2−P); 26.0 (s, CH_3CO); 120.0 (s, C); 133.5 (s, CH, ^3J(C−Pt) = 98 Hz); 137.2 (s, br, CH); 138.9 (dd, CH, ^1J(C−Pt) = 640 Hz, ^2J(C−*trans*-P) = 97 Hz, ^2J(C−*cis*-P) = 9 Hz); 195.1 (s, C, CO).

Preparation of [(Et$_3$P)$_2$Pd(*C,S*-C$_4$H$_3$ClS)] (12). Complex **12** was prepared from [Pd(PEt$_3$)$_3$] (0.23 g, 0.49 mmol), **2**, and 3-chlorothiophene (0.17 mL, 1.83 mmol) in toluene (10 mL) under argon. The solution was kept at room temperature for 2 h and then heated to 70 °C for 10 min with stirring; the color changed from orange to yellow. After this time the solvent and the excess phosphine was distilled out; at this point, the heating was stopped and the mixture was evaporated to dryness with increasing vacuum (0.01 mmHg) and cooled to room temperature. Freshly distilled dried toluene was added (4 mL) to give a yellow solution, which was purified by column chromatography, on silica gel with 9:1 hexane/acetone to 3:1 hexane/acetone as eluent; the second eluted fraction was collected, concentrated, and dried for 3 h, to give a yellow solid. Yield: 65%. Anal. Calcd for $C_{16}H_{33}ClP_2PdS$: C, 41.6; H, 7.2; S, 6.9. Found: C, 41.4; H, 7.1; S, 7.0. FAB$^+$: *m/z* 461. NMR spectra in $CDCl_3$ are as follows. ^{1}H: δ (ppm) 1.1−1.9 (m, 30H, from Et−P); 6.46 (d, 1H, ^4J(H−*trans*-P) = 1.2 Hz); 6.85 (dd, 1H, ^3J(H−H) = 4.8 Hz, ^4J(H−P) = 1.5 Hz); 7.2 (dd, 1H, ^3J(H−

H) = 4.8 Hz, ^3J(H−*trans*-P) = 2.7 Hz). ^{31}P: δ (ppm) 15.8 (s, broad), 18.3 (s, broad). ^{13}C: δ (ppm) 8.0 (d, CH_3, Et−P); 13.5−14.2 (m, $-CH_2-$P); 118.2 (s, CH); 122.5 (d, CH, ^2J(C−P) = 25 Hz); 132.8 (s, CH); 139.4 (s, C).

Preparation of [(Et$_3$P)$_2$Pd(*C,S*-C$_4$H$_3$ClS)] (13). As described for **12**, complex **13** was prepared and purified, to give a yellow solid. Yield: 64%. Anal. Calcd for $C_{16}H_{33}ClP_2PdS$: C, 41.6; H, 7.2; S, 6.9. Found: C, 41.5; H, 7.1; S, 7.1. NMR spectra in $CDCl_3$ are as follows. ^{1}H: δ (ppm) 1.1−1.9 (m, 30H, from Et−P), 6.5 (d, 1H, ^3J(H−H) = 3 Hz); 6.9 (dd, 1H, ^3J(H−H) = 3 Hz, ^3J(H−H) = 5 Hz); 7.3 (d, 1H, ^3J(H−H) = 5 Hz). ^{31}P: δ (ppm) 16.0 (s, broad); 18.25 (s, broad). ^{13}C: δ (ppm) 8.0 (d, CH_3, Et−P); 13.5−14.2 (m, $-CH_2-$P); 126.9 (s, CH); 128.5 (s, CH); 128.7 (d, CH, ^2J(C−P) 20 Hz); 141.0 (s, C).

Preparation of [(Et$_3$P)$_2$Pd(*C,S*-C$_4$H$_3$NO$_2$S)] (14). This compound was prepared and purified under the same conditions used for complex **12**, to give a red solid. Yield: 13%. Anal. Calcd for $C_{16}H_{33}NO_2P_2PdS$: C, 40.7; H, 7.0; S, 6.7. Found: C, 40.6; H, 6.9; S, 6.8. NMR spectra in $CDCl_3$ are as follows. ^{1}H: δ (ppm) 1.0−2.0 (m, 30H, from Et−P); 6.89 (dd, 1H, ^3J(H−H) = 5.5 Hz, ^4J(H−P) = 6 Hz); 7.15 (ddd, 1H, ^3J(H−H) = 5.5 Hz, ^3J(H−P) = 12 Hz, ^3J(H−P) = 1 Hz); 7.81 (d, 1H, ^4J(H−P) = 6 Hz). ^{31}P: δ (ppm) 22.1 (d, ^2J(P−P) = 37 Hz); 27.7 (d, ^2J(P−P) = 37 Hz). ^{13}C: δ (ppm) 8.0 (d, CH_3, Et−P); 15.1 (d, $-CH_2-$P), 17.4 (d, $-CH_2-$P); 116.1 (s, CH); 126.1 (s, CH); 135.5 (d, CH, ^2J(C−P) = 39 Hz); 153.1 (s, C).

Preparation of [(Et$_3$P)$_2$Pd(*C,S*-C$_4$H$_3$OMeS)] (15 and 15b). By a procedure similar to that described for **12**, except for 3 h of heating, compounds **15** and **15b** were prepared and purified, to give an orange oil. Yield: 15% for **15** and 10% for **15b**. Anal. Calcd for $C_{17}H_{36}OP_2PdS$: C, 44.6; H, 7.9; S, 7.0. Found: C, 44.7; H, 8.0; S, 7.2. NMR spectra for the isomer mixture are as follows. ^{1}H: δ (ppm) 1.1−2.0 (m, 30H, from Et−P); 3.6 and 3.58 (s, 3H, OMe); 6.66 (dd, 1H, ^3J(H−H) = 3.9 Hz, ^3J(H−H) = 4.8 Hz); 7.07 (d, 1H, ^3J(H−H) = 4.8 Hz); 7.17 (d, 1H, ^3J(H−H) = 3.9 Hz); 6.76 (dd, 1H, ^3J(H−H) = 3.6 Hz, ^3J(H−H) = 3.9 Hz); 7.23 (d, 1H, ^3J(H−H) = 3.6 Hz); 7.58 (d, 1H, ^3J(H−H) = 3.9 Hz, ^3J(H−P) = 1.5 Hz). ^{31}P: δ (ppm) 10.1 (d, ^2J(P−P) = 10.8 Hz); 10.9 (d, ^2J(P−P) = 10.8 Hz); 10.2 (d, ^2J(P−P) = 10.9 Hz); 10.7 (d, ^2J(P−P) = 10.9 Hz).

Preparation of [(Et$_3$P)$_2$Pd(*C,S*-C$_4$H$_3$OMeS)] (16). As described for the previous reaction. complex **16** was prepared and purified, to give an orange oil. Yield: 15%. Anal. Calcd for $C_{17}H_{36}OP_2PdS$: C, 44.6; H, 7.9; S, 7.0. Found: C, 44.6; H, 7.8; S, 7.1. NMR spectra are as follows. ^{1}H: δ (ppm) 1.1−2.0 (m, 30H, from Et−P); 3.57 (s, 3H, OMe); 6.3 (s, br, 1H); 6.8 (d, 1H, ^3J(H−H) = 5.0 Hz); 7.8 (d, 1H, ^3J(H−H) = 5.0 Hz). ^{31}P: δ (ppm) 27.4 (d, ^2J(P−P) = 6 Hz); 27.9 (d, ^2J(P−P) = 6 Hz).

Reaction of Tris(triethylphosphine)palladium(0) with Acetylthiophenes. This reaction was performed as described for **12**; however, the reaction produced for **17** a blue residue very difficult to purify and isolate, which decomposed very easily, and for **18** it produced an orange residue. A sealed NMR tube experiment allowed us to determine the formation of metallacycles **17** and **18**, on the basis of their characteristic ^{31}P NMR pattern. In both cases a great amount of starting material, **2**, was observed intact at the end of the experiment. NMR spectra for **17** are as follows. ^{31}P: (δ, ppm) 23.5 (d, ^2J(P−P) = 6 Hz); 26.7 (d, ^2J(P−P) = 6 Hz). NMR spectra for **18** are as follows. ^{31}P: (δ, ppm) 12.6 (d, ^2J(P−P) = 7.2 Hz); 16.7 (d, ^2J(P−P) = 7.2 Hz); 12.8 (d, ^2J(P−P) = 6.4 Hz); 17.0 (d, ^2J(P−P) = 6.4 Hz).

Preparation of [(Et$_3$P)$_2$Ni(*C,S*-C$_4$H$_3$ClS)] (19). As described for **12**, complex **19** was prepared and purified under the same procedure, to give a yellow waxy solid. Yield: 65%. Anal. Calcd for $C_{16}H_{33}ClP_2NiS$: C, 46.4; H, 8.0; S, 7.7. Found: C, 46.2; H, 8.0; S, 7.9. NMR spectra in $CDCl_3$ are as follows. ^{1}H: δ (ppm) 1.0−1.8 (m, 30H, from Et−P); 7.3 (s, br, 1H); 7.7 (d, 1H, ^3J(H−H) = 4 Hz); 8.9 (d, 1H, ^3J(H−H) = 4 Hz). ^{31}P: δ (ppm) 31.5 (d, ^2J(P−P) = 5 Hz); 52.8 (d, ^2J(P−P) = 5 Hz). ^{13}C: δ (ppm) 7.0−10.0 (m, CH_3, Et−P); 15.0−18.5 (m, $-CH_2-$P); 124.3 (s, CH); 126.1 (s, CH); 135.6 (d, CH, ^2J(C−P) = 27.6 Hz); 153.1 (s, C).

Table 4. Summary of Crystallographic Results for 4 and 7

	4	**7**
formula	$C_{16}H_{33}ClP_2PtS$	$C_{16}H_{33}NO_2P_2PtS$
fw	549.96	560.52
cryst size/mm	0.7 × 0.25 × 0.2	0.7 × 0.5 × 0.15
color, shape	orange, needle	red, regular block
d(calcd)/g cm^{-3}	1.675	1.729
space group	$P2_1/c$	$P2_1/n$
a/Å	11.632(2)	10.668(3)
b/Å	12.956(2)	15.321(2)
c/Å	14.524(2)	13.700(3)
β/deg	94.819(15)	105.93(2)
V/Å^3	2181.1(7)	2153.3(8)
Z	4	4
μ/mm^{-1}	6.792	6.769
2θ range/deg	3.52−52.0	3−60
no. of rflns collected	5320	7602
no. of unique rflns (R_{int}/%)[a]	4234 (2.48)	6206 (4.95)
no. of rflns with $F_o > 4\sigma(F_o)$	2466	4858
no. of data/params	4234/190	6206/209
GOF on F^2	1.026	1.039
R indices ($I > 2\sigma(I)$)/%[b]	5.15, 12.11	3.83, 9.42
R indices (all data)/%	10.45, 15.02	5.61, 10.23
max. resid density/e Å^{-3}	1.160	1.77
syst used	SHELX 97-2	SHELXTL 5.03

[a] $R_{int} = \sum|F_o^2 - \langle F_o^2\rangle|/\sum F_o^2$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $S = [\sum w(F_o^2 - F_c^2)^2/(m - n)]^{1/2}$.

Preparation of [(Et$_3$P)$_2$Ni(Cl)(η^1-C$_4$H$_3$S)] (20). By a procedure similar to that described for **12**, complex **20** was synthesized and purified, as a yellow solid. Yield: 50%. Anal. Calcd for $C_{16}H_{33}ClP_2NiS$: C, 46.4; H, 8.0; S, 7.7. Found: C, 46.5; H, 8.1; S, 7.8. NMR spectra in $CDCl_3$ are as follows. ^{1}H: δ (ppm) 1.0−1.4 (m, 30H, from Et−P); 6.5 (d, br, 1H, ^3J(H−H) = 5 Hz); 6.9 (t, 1H, ^3J(H−H) = 5 Hz); 7.6 (d, 1H, ^3J(H−H) = 5 Hz). ^{31}P: δ (ppm) 12.4 (s). ^{13}C: δ (ppm) 1.0−2.0 (m, CH_3, Et−P); 10.0−15.0 (m, $-CH_2-$P); 127.1 (s, CH); 128.5 (s, CH); 129.9 (s, CH); 140.4 (s, C).

Preparation of [(Et$_3$P)$_2$Ni(H)(η^1-C$_4$H$_2$NO$_2$S)] (21). By employing the procedure described for **12** and using the commercial mixture of nitrothiophenes, compound **21** was isolated as a red solid. Yield: 40%. Anal. Calcd for $C_{16}H_{33}NO_2P_2NiS$: C, 45.3; H, 7.8; S, 7.5. Found: C, 45.0; H, 7.6; S, 7.3. IR: ν (Ni−H) 2150 cm^{-1}. NMR spectra in $CDCl_3$ are as follows. ^{1}H: δ (ppm) 1.0−2.0 (m, 30H, from Et−P); 7.1 (s, br); 7.5 (s, br). ^{31}P: δ (ppm) 52.8 (s, br).

Reactions of Tris(triethylphosphine)nickel(0) with Acetyl- and Methoxythiophenes. The reactions of **3** with acetyl- and methoxythiophenes led to the formation of mixtures of unidentified compounds.

Catalytic Experiments. The catalytic experiments were carried out in a 300 mL Parr reactor made of Monel. A typical experiment was performed as follows: under argon the reactor was charged with 100 mL of THF, 0.030 g (0.055 mmol) of **8**, and 0.57 mL (5.50 mmol) of 2-methoxythiophene. The reactor was purged three times with hydrogen and finally charged up to 300 psi at room temperature. The reaction mixture was heated to the desired temperature (100 °C). Samples of the reaction mixture and the final mixture were analyzed by GC-MS on a 60 m DB-5 capillary column.

Crystallographic Studies. Single crystals suitable for X-ray studies were obtained for compounds **4** and **7** by slow evaporation of toluene solutions, at room temperature, and were handled in a noncontrolled atmosphere. A summary of crystallographic results is presented in Table 4. Diffraction data were collected at 298 K on a Siemens P4 diffractometer,

using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å), following a standard procedure.[14]

The structures were solved[15] by the Patterson method for both Pt complexes and completed with difference Fourier maps. Non-H atoms were refined anisotropically by full-matrix least squares, without constraints or restraints for the geometry. H atoms were placed on ideal positions and refined using a riding model with a fixed isotropic thermal parameter. Despite the fact that refinements were carried out using absorption-corrected data (14 and 48 ψ scans for **4** and **7**, respectively), large residuals were observed close to heavy atoms. On the other hand, in the case of **4**, attempts to refine C atoms of the PEt$_3$ groups with large thermal displacements by mean of a disordered model (in particular C(6) and C(16)) did not significantly improve the refinement.

(14) Fait, J. XSCAnS, release 2.10b; Siemens Analytical X-ray Instruments, Madison, WI, 1991.

(15) 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: Göttingen, Germany, 1997.

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Supporting Information Available: Tables of all crystallographic data for **4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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