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Thiaplatinacycles Derived from Dibenzothiophene-Containing Phosphites as Auxiliary Ligands and Their Role in Homogeneous Desulfurization Reactions

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The reaction of complex $[\mathrm{Pt}(\eta^2\text{-}C,S\text{-}\mathrm{C}_{12}\mathrm{H}_8)(\mathrm{PEt}_3)_2]$, **1**, with a variety of phosphites afforded compounds of the type $[\mathrm{Pt}(\eta^2\text{-}C,S\text{-}\mathrm{C}_{12}\mathrm{H}_8)(\mathrm{PEt}_3)(\mathrm{P(OR)}_3)]$, where R = Et, ^{i}Pr, and Ph (**2a**, **2b**, **3**, and **4**, respectively) and $[\mathrm{Pt}(\eta^2\text{-}C,S\text{-}\mathrm{C}_{12}\mathrm{H}_8)(\mathrm{P(OR)}_3)_2]$, where R = Et (**5**). Compounds **2**−**4** were used to model a desulfurization process and were compared with **1** and other similar compounds. Under comparable conditions, the amount of desulfurization depended on the σ-donor/π-acceptor properties and the steric effects of the ligands and of the use of alumina in the reaction media. X-ray crystal structures are reported for **2b** and **3**.

Introduction

The study of hydrodesulfurization (HDS) has been the focus of high interest because of the need to improve the process used to remove sulfur from organosulfur molecules present in crude oil feedstocks.[1] The commercial HDS process currently uses the cobalt- or nickel-doped molybdenum sulfide catalyst supported on alumina; however, the highest activity has been shown by platinum group metals, such as Ru, Os, Rh, Ir, Pd, and Pt, at least in model reactor studies, but they are not commercially used because of their higher cost.[2] Thus, a variety of organometallic compounds containing transition metals have been studied in homogeneous HDS reactions with thiophenes.[3] Although to date there are several reports leading to a C−S bond cleavage for thiophenes in complexes containing one metal and also several metal centers, the use of phosphites as auxiliary ligands in the organometallic modeling of HDS has been virtually ignored.

Our group, interested in the use of platinum metals to activate thiophenes, particularly with the use of $[\mathrm{Pt(PEt}_3)_3]$, has found that it is possible to activate C−S bonds in dibenzothiophene[4] and other thiophenes[5,6] to produce the corresponding thiaplatinacycles. Such derivatives have been demonstrated to be useful intermediates for organic transformations,[7] for stoichiometric hydrodesulfurizations[4,8] and as active precursors in homogeneous HDS catalytic reactions as well.[9] Very few other thiaplatinacycles derived from thiophenes have been reported, such as Jones'[10] ring-opened 4,6-dimethyldibenzothiophene reactions with $[(\mathrm{dippe})\mathrm{Pt(H)}]_2$ as a model for deep HDS and also one by Sweigart,[11] who, using arene derivatives containing carbonyl−metal moieties, “remote actived” π-coordinated thiophenes to make the coordinated thiophene more susceptible to nucleophilic cleavage than in the corresponding free thiophene.

In the present study, we investigated the effect of replacing a phosphine ligand (PEt_3) by a phosphite in the thiaplatinacycle $[\mathrm{Pt}(\eta^2\text{-}C,S\text{-}\mathrm{C}_{12}\mathrm{H}_8)(\mathrm{PEt}_3)_2]$ and its result on the reactivity of the new complexes under HDS conditions; the effect of acid and basic alumina on the reaction media was also studied.

Results and Discussion

Reaction of $[\mathrm{Pt}(\eta^2\text{-}C,S\text{-}\mathrm{C}_{12}\mathrm{H}_8)(\mathrm{PEt}_3)_2]$, 1, with Triethyl Phosphite. The reaction at room temperature of $[\mathrm{Pt}(\eta^2\text{-}C,S\text{-}\mathrm{C}_{12}\mathrm{H}_8)(\mathrm{PEt}_3)_2]$ with $\mathrm{P(OEt)}_3$ in toluene yields three different compounds, two of them with the formulation of $[\mathrm{Pt}(\eta^2\text{-}C,S\text{-}\mathrm{C}_{12}\mathrm{H}_8)(\mathrm{PEt}_3)(\mathrm{P(OR)}_3)]$, **2a** and **2b**, and one more with the formulation $[\mathrm{Pt}(\eta^2\text{-}C,S\text{-}$

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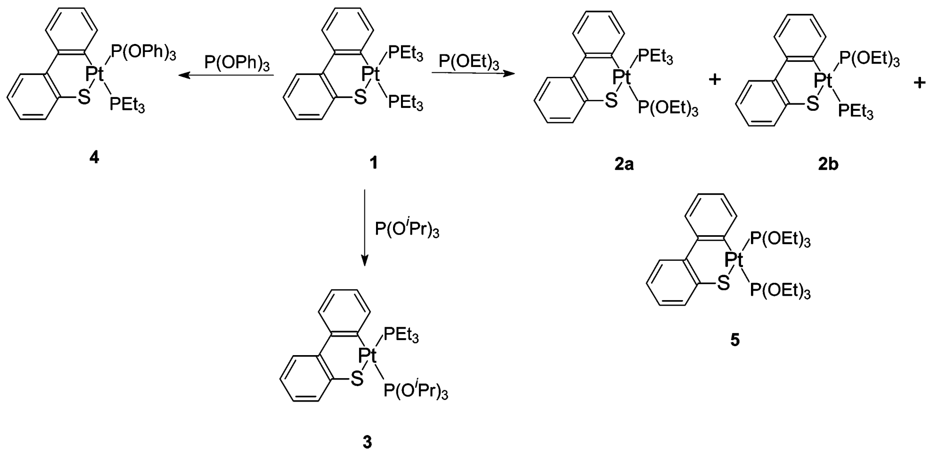
Scheme 1



$C_{12}H_8)(P(OEt)_3)_2]$, **5** (Scheme 1). As expected, both compounds **2a** and **2b** are isomeric forms, one with the phosphite *trans* to carbon and the other with the phosphite *trans* to sulfur of the thiaplatinacycle moiety, respectively. The NMR spectra of crude reaction mixtures showed evidence of the formation of three different compounds, all of which were isolated by differences in solubility and further purification by column chromatography. ^{31}P NMR was especially useful to differentiate each particular compound, compound **2a** showing the characteristic pattern expected for two nonequivalent *cis* phosphorus atoms with resonances at δ 15.4 (^1J(Pt−P) = 3084 Hz, ^2J(P−P) = 28 Hz) for the phosphine *trans* to S and δ 123.3 (^1J(Pt−P) = 3065 Hz, ^2J(P−P) = 28 Hz) for the phosphite *trans* to C; complex **2b** exhibited a similar pattern, with resonances at δ 10.6 (^1J(Pt−P) = 1691 Hz, ^2J(P−P) = 28 Hz) for the phosphine *trans* to C and δ 104.7 (^1J(Pt−P) = 5405 Hz, ^2J(P−P) = 28 Hz) for the phosphite *trans* to S. These assignments are in agreement with the values previously observed for thiaplatinacycles containing only monodentate phosphines as auxiliary ligands.[4−6] Complex **2b** was also characterized by an X-ray structure determination, the latter confirming that the phosphite ligand was *trans* to sulfur. Complex **5** was characterized considering the above quoted chemical shifts and coupling constants; the ^{31}P NMR spectrum exhibited a pattern similar to those described above, with resonances at δ 107.0 (^1J(Pt−P) = 2938 Hz, ^2J(P−P) = 44 Hz) for the phosphite *trans* to C and δ 123.3 (^1J(Pt−P) = 5160 Hz, ^2J(P−P) = 44 Hz) for the phosphite *trans* to S. As can be seen from the data quoted above, the value of ^1J(Pt−P) for the phosphite ligand *trans* to carbon is always smaller than the corresponding value of ^1J(Pt−P), where the phosphite is *trans* to sulfur, as expected; this is due to the higher *trans* influence of the σ-bonded sp^2 carbon.

X-ray Structure of Thiaplatinacycle 2b. The thiaplatinacycle derived from dibenzothiophene-containing triethylphosphine and triethyl phosphite is depicted in Figure 1; selected bond lengths and angles are given in Table 1. The thiaplatinacycle moiety in complex **2b** is severely twisted, in a very similar way to the previously reported structure for **1**[5] and similar to complex **3** (vide infra). A few important structural features for **2b** are the following: the angle P(1)−Pt−P(2) = 100.98(6)° is a bit more open compared with the corresponding value for **1**, which is 99.1(2)°, and for **3**, which is 97.76(4)°; consequently, the three remaining angles are slightly smaller, since the P−Pt−P angles are significantly larger than 90°; this can be due to steric repulsion between the phosphine and the phosphite. This is slightly larger for **2b** in the solid state. Key bond lengths in complex **2b** are Pt−S(5) = 2.355(2) Å, Pt−C(13) = 2.076(5) Å, Pt−P(1), which is *trans* to S(5), = 2.210(2) Å, and Pt−P(2), which is *trans* to C(13), = 2.330(2) Å. Again the difference in distances is due to the *trans* influence of the σ-bonded sp^2 carbon. In general, the distances quoted above are very similar to those seen in the closely related platinum complexes, such as **1**,[5] where the Pt−P(1) distance, *trans* to sulfur, is 2.261(4) Å, just a bit longer than the corresponding distance in **2b**, probably due to the phosphite π-acceptor properties.

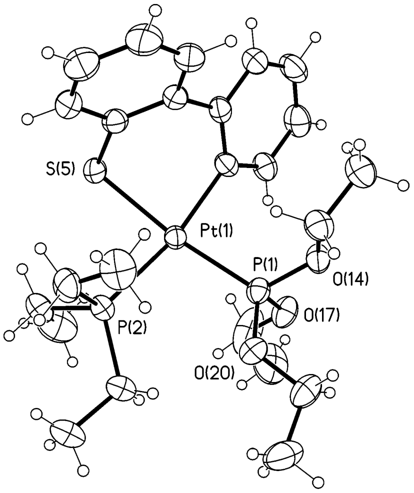


Figure 1. Molecular structure of complex **2b** with thermal ellipsoids at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2b

Pt(1)−C(13)	2.076(5)	Pt(1)−P(1)	2.210(2)
Pt(1)−P(2)	2.330(2)	Pt(1)−S(5)	2.355(2)
S(5)−C(12)	1.771(6)	C(6)−C(13)	1.391(8)
C(10)−C(13)	1.400(8)		
C(13)−Pt(1)−P(1)	89.1(2)	C(13)−Pt(1)−P(2)	168.8(2)
P(1)−Pt(1)−P(2)	100.98(6)	C(13)−Pt(1)−S(5)	84.4(2)
P(1)−Pt(1)−S(5)	172.86(6)	P(2)−Pt(1)−S(5)	85.28(6)
C(12)−S(5)−Pt(1)	95.7(2)	C(6)−C(13)−Pt(1)	122.6(5)
C(10)−C(13)−Pt(1)	119.9(4)		

Reactions of $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)_2]$, 1, with Triisopropyl Phosphite.

Similar to the reaction dis-

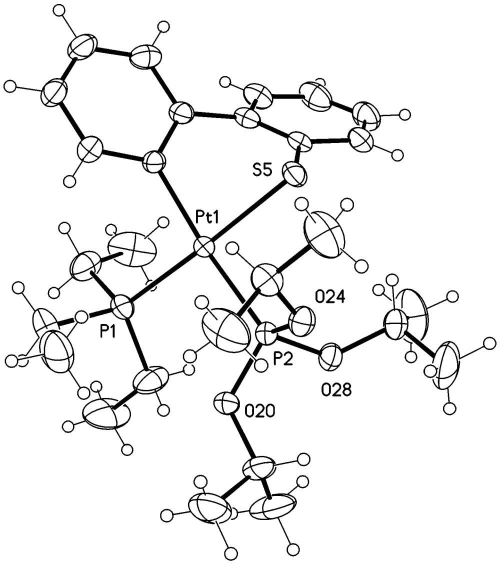


Figure 2. Molecular structure of complex **3** with thermal ellipsoids at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

Pt(1)−C(13)	2.061(4)	Pt(1)−P(1)	2.2771(12)
Pt(1)−P(2)	2.2794(12)	Pt(1)−S(5)	2.3534(11)
S(5)−C(12)	1.765(6)	C(6)−C(13)	1.391(6)
C(10)−C(13)	1.413(6)		
C(13)−Pt(1)−P(1)	90.42(12)	C(13)−Pt(1)−P(2)	169.51(12)
P(1)−Pt(1)−P(2)	97.76(4)	C(13)−Pt(1)−S(5)	84.46(12)
P(1)−Pt(1)−S(5)	168.52(5)	P(2)−Pt(1)−S(5)	88.61(4)
C(12)−S(5)−Pt(1)	97.67(14)	C(6)−C(13)−Pt(1)	119.5(4)
C(10)−C(13)−Pt(1)	124.1(3)		

cussed above, but with a gentle warming to 80 °C, complex **1** reacted with $P(O^iPr)_3$ in toluene to yield only one product with the formulation $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)(P(O^iPr)_3)]$, **3** (Scheme 1), where the phosphite ligand is in *trans* position to carbon and the phosphine is *trans* to sulfur of the thiaplatinacycle moiety. No other compound was detected by ^{31}P NMR in the crude reaction mixture. Simple evaporation and hexane washing yielded an analytically pure sample. ^{31}P NMR showed the expected pattern for two nonequivalent *cis* phosphorus with resonances at δ 14.8 ($^1J(Pt-P) = 3118$ Hz, $^2J(P-P) = 29$ Hz) for the phosphine *trans* to S and δ 120.5 ($^1J(Pt-P) = 3062$ Hz, $^2J(P-P) = 29$ Hz) for the phosphite *trans* to C, which is all similar to the pattern exhibited by complex **2a**. An X-ray structure determination confirmed such a proposal. Further warming of the reaction mixture up to 24 h produced no other isomeric form that could be detected by NMR spectroscopy.

X-ray Structure of Thiaplatinacycle 3. The thiaplatinacycle derived from dibenzothiophene-containing triethylphosphine and triisopropyl phosphite is depicted in Figure 2; selected bond lengths and angles are given in Table 2. The thiaplatinacycle moiety in complex **3** is severely twisted in a very similar way to the previously reported structure for **1**[5] and quite similar to complex **2b**. Even when among the three thiaplatinacycles, complex **3** presents the least distorted P(1)−Pt−P(2) angle, 97.76(4)°, which is significantly larger than 90° due to the phosphite−phosphine repulsion. Key bond lengths for complex **3** are the following: Pt−S(5) = 2.3534(11) Å, Pt−C(13) = 2.061(4) Å, Pt−P(1), which is *trans* to S(5), = 2.2771(12) Å, and Pt−P(2), which is *trans* to C(13), = 2.2794(12) Å, in contrast to complexes **1** and **2b**. In this case both Pt−P distances are nearly the same; that is, the strong *trans* influence of a σ-bonded sp^2 toward a phosphite results almost in the same magnitude as the *trans* influence of a thiolate type ligand toward an alkyl phosphine.

Table 3. Results of Hydrodesulfurization Experiments

compound	products %Ph-Ph	products %DBT	products with acid alumina %Ph-Ph	products with acid alumina %DBT	products with basic alumina %Ph-Ph	products with basic alumina %DBT
1	9[a]	89[a]	52	31	74	15
2a	83	16	90	10	93	4
2b	85	15	89	11	94	5
3	41	59	70	30	90	7
4	40	60	75	25	88	12
[Pt(DBT)(dppe)]	22[a]	34[a]	74[a]	16[a]	74	15

[a] Data from ref 8 for comparison purposes.

Reactions of $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)_2]$, 1, with Triphenyl Phosphite. Following the very same procedure used for **3**, complex **1** reacted with $P(OPh)_3$ to yield a product with the formulation $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)(P(OPh)_3)]$, **4** (Scheme 1), where the phosphite ligand is in *trans* position to sulfur and the phosphine is *trans* to carbon of the thiaplatinacycle moiety. The spectroscopic evidence is in agreement with such a proposal; for instance, in the ^{31}P NMR complex **4** exhibited a pattern with resonances at δ 10.1 ($^1J(Pt-P) = 1645$ Hz, $^2J(P-P) = 27$ Hz) for the phosphine *trans* to C and δ 94.3 ($^1J(Pt-P) = 5623$ Hz, $^2J(P-P) = 27$ Hz) for the phosphite *trans* to S. These assignments are in agreement with the values previously observed for complex **2b** (vide supra). An important diagnostic signal in the ^{13}C NMR is the quaternary carbon directly bonded to platinum at δ 153.1 ($^2J(C-trans\text{-}P) = 108$ Hz, $^2J(C-cis\text{-}P) = 7$ Hz); no platinum satellites could be observed due to the weakness of this signal of the quaternary carbon.

Hydrodesulfurization Experiments. As earlier mentioned, it has been shown that thiaplatinacycles are useful precursors or intermediates in HDS reactions. Considering this and following a procedure previously reported,[8] a series of experiments were performed to evaluate the relevance of having a coordinated phosphite and the effect of alumina in such a process. Complexes **1**−**4** undergo HDS with hydrogen alone under relatively mild conditions (H_2, 20 atm, 100 °C, 20 h, toluene, Table 3). In contrast with our previous findings with thiaplatinacycles containing only alkyl phosphines as auxiliary ligands, here all thiaplatinacycles containing a phosphite and a phosphine carry out desulfurization in relatively good yields without the use of alumina, complex **2b** being the best (85%). HDS of complexes **1**−**4** is significantly enhanced by the presence of acid alumina, the complexes being of the type $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)(P(OR)_3)]$, the ones which afford the best yields. In addition, the use of basic alumina improves even more such yields, again complex **2b** being the best of the series (94%). However, comparable yields can be attained with **3** (90%) and **4** (88%).

The higher HDS yields exhibited by thiaplatinacycles with phosphites can be associated with the higher stability of the Pt−P bond compared with that of the thiaplatinacylces with two alkyl monophosphines.

Indeed, the use of diphosphines such as dppe (1,2-bis(diphenylphosphino)ethane) affords a better yield than that with alkylic monophosphines, but a bit lower when compared with phosphite-containing thiaplatinacycles. For compounds **2b** to **4** the observed trends seem to be related to the corresponding cone angle for phosphites, the best yield being observed for the complex containing the phosphite with the smaller cone angle. Perhaps associated with such small cone angle for $P(OEt)_3$ all the expected compounds derived from the phosphine substitution were observed and isolated. In contrast, for $P(O^iPr)_3$ and $P(OPh)_3$ only one particular isomer could be observed and isolated.

Conclusions

The phosphine substitution by a phosphite in $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)_2]$ is a feasible process to produce complexes of the type $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)(P(OR)_3)]$ in good yields and purity, avoiding the reductive elimination of DBT. Even when the conditions for achieving a complete HDS cycle for DBT have not yet been established, these results do indicate the importance in the reaction of the thiaplatinacycle as intermediates or precursors. We have also demonstrated that the presence of at least one σ-donor/ π-acceptor ligand, with a small cone angle, such as triethyl phosphite, is a key factor for improvement of HDS and the promoter effect of both acid and basic alumina.

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. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were determined on a Varian Unity (300 MHz) or a Bruker (500 MHz) spectrometer in $CDCl_3$, unless otherwise stated; chemical shifts (δ) are relative to the deuterated solvent, and ^{31}P NMR spectra are relative to external H_3PO_4. Infrared spectra were obtained in a Perkin-Elmer 1600 FT spectrophotometer. Mass determinations (FAB^+) were performed on a JEOL SX-102 A, using a nitrobenzilic alcohol matrix, and GC−MS determinations were performed on a Varian Saturn 3. Galbraith Laboratories carried out elemental analyses. Melting points were determined in a Electrothermal digital melting point apparatus. The synthesis of $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)_2]$ was carried out using the previously reported procedure.[4] All phosphites were purchased from Strem and dried over molecular sieves.

Preparation of $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)(P(OEt)_3)]$, 2a, 2b, and $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(P(OEt)_3)_2]$, 5. All three compounds were formed in the same reaction from $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)_2]$ (0.5 g, 0.81 mmol), **1**, dissolved in toluene (10 mL), adding triethyl phosphite (0.55 mL, 3.25 mmol) under argon. The reaction mixture was allowed to react at room temperature for 6 h with stirring. After this time the mixture was evaporated to dryness with increasing vacuum (0.01 mmHg) and further dried for 4 h. The residue was redisolved in the minimum amount of acetone, complex **2a** being precipitated from the reaction mixture with ice cooling and addition of hexane. The remaining mixture was purified by column chromatography on silica gel with hexane/acetone as eluent (from 9:1 to 1:1); the fourth colorless fraction was evaporated to dryness to yield complex **2b**. Complex **5** was detected only in the original reaction mixture. Yield for **2a**: 70%. Anal. Calcd for **2a**, $C_{24}H_{38}O_3P_2PtS$: C, 43.43; H, 5.73; S, 4.82. Found: C, 42.98; H, 5.68; S, 5.07. FAB^+: m/z 664. Mp: 109−114 °C. NMR spectra were as follows. ^1H: δ 0.85 (m, 9H, CH_3-, Et-P); 1.2 (m, 9H, CH_3-, EtO-P); 1.7 (m, 6H, $-CH_2-$, Et-P); 4.15 (m, 6H, $-CH_2-$, EtO-P); 6.85−7.1 (m, 4H); 7.4−7.6 (m, 4H). $^{31}P\{^1H\}$: δ 15.4 (d, (^1J(Pt−P) = 3084 Hz, ^2J(P−P) = 28 Hz); 123.3 (^1J(Pt−P) = 3065 Hz, ^2J(P−P) = 28 Hz). $^{13}C\{^1H\}$: δ 8.11 (d, CH_3, ^2J(P−C) 15 Hz, Et-P); 16.5 (d, CH_3, ^3J(P−C) 2 Hz, EtO-P); 16.7 (d, $-CH_2-$, ^1J(P−C) 33 Hz, Et-P); 61.4 (m, br, $-CH_2-$, EtO-P); 123.3 (s, CH); 124.2 (s, CH); 126.0 (s, CH); 126.2 (s, CH); 126.3 (s, CH); 126.8 (d, CH, ^4J(P−C) 8 Hz); 130.4 (s, CH); 135.9 (d, CH, ^3J(P−C) 10 Hz); 136.8 (m, br, C); 143.1 (s, C); 148.9 (s, C), 164.0 (w, br, C).

Yield for **2b**: 20%. Anal. Calcd for **2b**, $C_{24}H_{38}O_3P_2PtS$: C, 43.43; H, 5.73; S, 4.82. Found: C, 42.99; H, 5.70; S, 5.00. FAB^+: m/z 664. Mp: 101−102 °C. NMR spectra were as follows. ^1H: δ 0.9−1.2 (m, 18H, CH_3-, Et-P and EtO-P); 2.0 (m, 6H, $-CH_2-$, Et-P); 3.8 (m, 6H, $-CH_2-$, EtO-P); 6.85−7.1 (m, 4H); 7.4−7.6 (m, 4H). $^{31}P\{^1H\}$: δ 10.6 (d, (^1J(Pt−P) = 1691 Hz, ^2J(P−P) = 28 Hz); 104.7 (^1J(Pt−P) = 5405 Hz, ^2J(P−P) = 28 Hz). $^{13}C\{^1H\}$: δ 8.28 (d, CH_3, ^2J(P−C) 14 Hz, Et-P); 14.8 (d, $-CH_2-$, ^1J(P−C) 29 Hz, Et-P); 15.7 (d, CH_3-, ^3J(P−C) 7 Hz, EtO-P); 61.4 (m, br, $-CH_2-$, EtO-P); 123.2 (s, CH); 124.3 (s, CH); 125.9 (s, CH); 126.2 (s, CH); 126.4 (s, CH); 126.9 (s, CH); 130.7 (s, CH); 136.9 (d, CH, ^3J(P−C) 9 Hz, ^2J(Pt−C) 45 Hz); 138.9 (pt, C, ^2J(Pt−C) 25 Hz); 143.1 (s, C); 148.6 (pt, C, ^2J(Pt−C) 75 Hz), 154.4 (d, C, ^2J(P−C) 90 Hz). For complex **5**, yield was 10% approximately determined in solution by $^{31}P\{^1H\}$ NMR, with signals at δ 107.0 (^1J(Pt−P) = 2938 Hz, ^2J(P−P) = 44 Hz); 123.3 (^1J(Pt−P) = 5160 Hz, ^2J(P−P) = 44 Hz).

Preparation of $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)(P(O^iPr)_3)]$, 3. **3** was prespared by a procedure similar to that described above, using 0.25 g (0.40 mmol) of **1** dissolved in toluene (10 mL), adding tri-isopropyl phosphite (0.2 mL, 0.8 mmol) under argon. The reaction mixture was heated to 80 °C for 3 h with stirring. After this the reaction was evaporated to dryness to yield a viscous residue, which was further dried for 2 h. Freshly distilled dried hexane was added (3 × 3 mL) and filtered to yield a yellow residue, which was dried for 2 h. Yield for **3**: 95%. Anal. Calcd for **3**, $C_{27}H_{44}O_3P_2PtS$: C, 45.95; H, 6.24; S, 4.54. Found: C, 45.57; H, 6.43; S, 4.61. FAB^+: m/z 706. Mp: 165−167 °C with decomposition. NMR spectra were as follows. ^1H: δ 0.85−1.0 (m, 9H, CH_3-, Et-P); 1.2−1.4 (m, 18H, CH_3-, ^{i}PrO-P); 1.75 (m, 6H, $-CH_2-$, Et-P); 5.0 (m, 3H, $-CH-$, ^{i}PrO-P); 6.85−7.1 (m, 4H); 7.4−7.6 (m, 4H). $^{31}P\{^1H\}$: δ 14.8 (d, (^1J(Pt−P) = 3118 Hz, ^2J(P−P) = 29 Hz); 120.5 (^1J(Pt−P) = 3062 Hz, ^2J(P−P) = 29 Hz). $^{13}C\{^1H\}$: δ 8.1 (d, CH_3, ^2J(P−C) 24 Hz, Et-P); 16.6 (d, $-CH_2-$, ^1J(P−C) 33 Hz, Et-P); 24.3 (s, CH_3, ^{i}PrO-P); 69.9 (s, br, $-CH-$, ^{i}PrO-P); 123.2 (s, CH); 124.1 (s, CH); 125.8 (s, CH); 126.05 (s, CH); 126.1 (s, CH); 126.7 (d, CH, ^4J(P−C) 9 Hz); 130.3 (s, CH); 136.2 (d, CH, ^3J(P−C) 6.5 Hz); 139.0 (m, br, C); 143.1 (s, C); 148.8 (s, C), 164.5 (w, br, C).

Preparation of $[Pt(\eta^2\text{-}C,S\text{-}C_{12}H_8)(PEt_3)(P(OPh)_3)]$, 4. **4** was prepared following a procedure similar to that described above, using 0.25 g (0.40 mmol) of **1** dissolved in toluene (10 mL), adding triphenyl phosphite (0.3 mL, 1.15 mmol) under argon. The reaction mixture was heated to 80 °C for 3 h with stirring. After this the reaction was evaporated to dryness to yield a white viscous residue, which was further dried for 3 h. Freshly distilled dried hexane was added (3 × 3 mL) and filtered to yield an ivory residue, which was dried for 3 h. Yield for **4**: 92%. Anal. Calcd for **4**, $C_{36}H_{38}O_3P_2PtS$: C, 53.53; H, 4.70; S, 3.96. Found: C, 53.44; H, 4.63; S, 3.97. FAB^+: m/z 808. Mp: 150−152 °C. NMR spectra were as follows. ^1H: δ 0.9−1.1 (m, 9H, CH_3-, Et-P); 2.0 (m, br, 6H, $-CH_2-$, Et-P); 6.85−7.3 (m, 19H); 7.5−7.65 (m, 4H). $^{31}P\{^1H\}$: δ 10.15 (d, (^1J(Pt−P) = 1645 Hz, ^2J(P−P) = 27 Hz); 94.3 (^1J(Pt−P) = 5623 Hz, ^2J(P−P) = 27 Hz). $^{13}C\{^1H\}$: δ 8.3 (d, CH_3, ^2J(P−C) 12 Hz, Et-P); 15.1 (d, $-CH_2-$, ^1J(P−C) 29 Hz, Et-P); 120.2 (s, CH, PhO-P); 123.1 (s, CH); 124.4 (s, CH); 124.8 (s, CH, PhO-P);

Table 4. Summary of Crystallographic Results for 2b and 3

	2b	**3**
formula	$C_{24}H_{38}O_3P_2Pt_1S_1$	$C_{27}H_{44}O_3P_2PtS$
fw	663.63	705.71
cryst size/mm	0.6 × 0.4 × 0.4	0.60 × 0.45 × 0.25
color, shape	pale yellow, irregular block	pale yellow, prism
d(calc)/g cm^{-3}	1.598	1.526
space group	$P2_1/c$	$P2_1/n$
a/Å	9.104(2)	12.700(1)
b/Å	21.473(3)	16.715(2)
c/Å	14.635(2)	14.703(1)
β/deg	105.42(1)	100.14(1)
V/Å^3	2758.2(7)	3072.4(5)
Z	4	4
μ/mm^{-1}	5.30	4.763
2θ range/deg	3−56	3−55
no. of reflns collected	8206	8465
no. of unique reflns (R_{int})/%[a]	6597 (3.91%)	6995 (3.18%)
no. of reflns with $F_o > 4\sigma(F_o)$	4972	5413
no. of data/params	6597/290	6995/308
GOF on F^2	1.076	1.030
R indices ($I > 2\sigma(I)$)/%	3.68, 7.97	3.30, 7.34
R indices (all data)/%	6.16, 10.54	5.26, 8.01
max. resid density/e Å^{-3}	1.10	0.823
system used	SHELXTL 5.03	SHELXTL 5.03 and SHELX97

[a] $R_{int} =$

$$\frac{\sum|F_o^2 - \langle F_o^2\rangle|}{\sum F_o^2},\ R_1 = \frac{\sum||F_o| - |F_c||}{\sum|F_o|},\ wR_2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}},\ S = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{m - n}}$$

125.8 (s, CH); 126.1 (s, CH); 127.0 (d, CH, ^4J(P−C) 6 Hz); 127.5 (s, CH); 129.5 (s, CH, PhO-P); 130.2 (s, CH); 137.1 (d, CH, ^3J(P−C) 10 Hz); 137.8 (s, C, PhO-P); 143.1 (s, br, C); 148.2 (s, C); 150.7 (d, C, ^3J(P−C) 11 Hz), 153.1 (d, C, ^2J(P−C) 70 Hz).

Hydrodesulfurization Experiments. These experiments were carried out in a stainless steel 300 mL Parr reactor. A typical experiment was performed as follows: under argon the reactor was charged with 0.10 g of the corresponding thiaplatinacycle, 30 mL of freshly distilled toluene, and 1.0 g of alumina. The reactor was purged three times with hydrogen and finally charged up to 294 psi at room temperature. The reaction was heated to the desired temperature (100 °C) for 24 h. The final reaction mixtures were analyzed by GC−MS on a 60 m DB-5 capillary column. The used acid alumina was acid washed alumina or acidic alumina, pH of aqueous suspension 4.5 ± 0.5; the used basic alumina was with a pH of aqueous suspension of 9.5 ± 0.5.

Crystallographic Studies. Single crystals suitable for X-ray studies were obtained for compounds **2b** and **3** by slow evaporation of toluene solutions at room temperature and were handled in a noncontrolled atmosphere. A summary of relevant crystallographic results is listed in Table 4. Diffraction data were collected at 298 K on a Siemens P4/PC diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), following a standard procedure.[12] The structure of **2b** was solved[13] by Patterson methods and that for **3** by direct methods, both completed with difference Fourier maps. Refinement was carried out by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms. H atoms were placed on ideal positions and refined using a riding model with a fixed isotropic thermal parameter.

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Supporting Information Available: Experimental details and tables of complete crystallographic data for **2b** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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