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Article

Catalytic Desulfurization of Dibenzothiophene with Palladium Nanoparticles

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The thermal reduction of [(PEt$_3$)$_2$PdMe$_2$] (1 mol%), which was produced in situ from [(PEt$_3$)$_2$PdCl$_2$] (**1**) and 2 equiv of MeMgBr in toluene solvent, yielded palladium nanoparticles that in conjunction with MeMgBr effected the desulfurization of dibenzothiophene (DBT). The reaction resulted in the generation of the sulfur-free compound 2,2′-dimethylbiphenyl, in high yields (60%). The use of several stabilizing agents such as sodium 2-ethylhexanoate and hexadecylamine was also addressed herein, their use resulting in a significant improvement of the desulfurization reaction that reached up to 90% conversion of DBT into the mentioned biphenyl. The palladium nanoparticles formed during the reaction were characterized by transmission electron microscopy and exhibited a smaller size and a lesser extent of agglomeration whenever stabilizers were used.

Introduction

Environmental regulations regarding the sulfur content in fuels have become more stringent in many countries during the past few years and because of this a considerable effort has been expended to improve the efficiency of catalysts used for the hydrodesulfurization (HDS) process in the oil industry.[1] The presence of sulfur compounds in fuels is undesirable because their combustion results in formation of sulfur oxides which, after being released into the atmosphere, cause acid rain.[2] Normally, the HDS process involves the use of cobalt or nickel doped molybdenum sulfide catalysts supported over alumina that yield sulfur-free hydrocarbons and H$_2$S (eq 1), but the process requires extensive use of hydrogen at high temperatures.[3]

The removal of sulfur heterocyclic compounds such as dibenzothiophene (DBT) and its more hindered analogues, 4-methyldibenzothiophene (4-MeDBT) and 4,6-dimeth-

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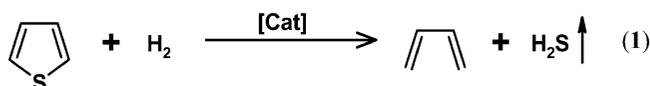
yldibenzothiophene (4,6-Me$_2$DBT), from oil (the latter being the major causes for the high sulfur levels in it) pose important challenges to the oil industry given their resistance to use HDS.[4] The use of noble metal sulfides generally improves the catalytic activities in this reaction, according to model experiments using reactor vessels,[5] and in the case of heterogeneous HDS catalysts the use of platinum group metals has indeed yielded better performances. The use of ruthenium, rhodium, and iridium based catalysts has permitted the desulfurization of a reasonable number of sulfur compounds in good yields[6] and in the case of heterogeneous catalysts those bearing palladium and platinum metal centers have reached similar or even better HDS activities than commercial catalysts.[7]

In the last few decades, metal nanoparticles have become an important alternative for heterogeneous catalysis given

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the variety of reactions in which they can be used.[8] Several examples of C−C coupling reactions catalyzed by palladium nanoparticles have been reported.[8a,b,9] The use of metal nanoparticles in HDS reactions has been studied with a variety of transition metals such as Mo, Ni, Ni/Fe, Ni/W, Mo/W, and Mo/Co, which are able to hydrodesulfurize thiophene (T) and DBT in good yields, although only poor HDS yields have been afforded in the case of 4,6-Me$_2$DBT.[10] Recently, Schlaf et al. have shown that palladium nanoparticles produced by reduction of palladium salts such as PdCl$_2$, Pd(dba)$_3$, and Pd(OAc)$_2$ are able to cleave the C−S bond of aromatic thioethers in the presence of silanes. The reaction produces thiosilanes and silthianes in DMA (eq 2).[11]

$$R = Et, Ph, vinyl, Me$$
$$R' = OMe, Cl$$
(2)

We recently reported the use of soluble nickel and platinum compounds that allow the desulfurization of DBT and its more hindered analogues 4-MeDBT and 4,6-Me$_2$DBT. The reaction occurred in the presence of Grignard reagents which yield both substituted and unsubstituted biphenyls in high yields (eq 3).[12]

(3)
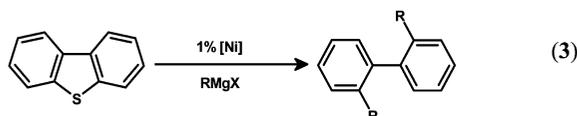
Herein we report the use of palladium nanoparticles formed by the thermal reduction of (PEt$_3$)$_2$PdMe$_2$ in the desulfurization of DBT, also using MeMgBr. The desulfurization occurs via C−C cross-coupling reaction similar to

the above-described case and yield the formation of disubstituted biphenyls. Results are significant as they illustrate one of the very few existing cases in which palladium catalysts are used for this reaction.

Results and Discussion

Desulfurization of Dibenzothiophene with Palladium Nanoparticles. The reaction of cis-[(PEt$_3$)$_2$PdCl$_2$] (1) and 2 equiv of MeMgBr at room temperature resulted in the quantitative formation of cis- and trans-[(PEt$_3$)$_2$PdMe$_2$], in toluene-d_8 (^{31}P{^{1}H} NMR signals for cis- and trans-[(PEt$_3$)$_2$PdMe$_2$] being δ 10.42 (s) and 18.56 (s), respectively). The thermal decomposition of the two methylated compounds was followed by ^{31}P{^{1}H} NMR spectroscopy. The followup confirmed the disappearance of the corresponding ^{31}P{^{1}H} NMR signals after continuous heating at 100 °C, which coincided with the apparition of a black metallic precipitate in the NMR tube, unequivocally identified as palladium black. Catalytic desulfurization experiments over DBT were then carried out assuming 1 to behave as a nanoparticle precursor. The catalytic desulfurization reaction of DBT in the presence of two additional equivalents of MeMgBr and complex 1 (1 mol%) under toluene reflux yielded in all cases the cross-coupling product 2,2′-dimethylbiphenyl as the sole product, although variable amounts of DBT were still found to remain in solution in these experiments. Table 1 summarizes the catalytic experiments that were carried out. Indications for compounds 2, 3, and 4 in the table refer to the use of additional palladium nanoparticle precursors, the latter being [(PPh$_3$)$_2$PdCl$_2$] (2), [(dippe)PdCl$_2$] (3), and [(dppe)PdCl$_2$] (4), respectively.

The desulfurization of DBT using THF (entry 1) did not result in any catalytic activity, although the use of toluene did result in formation of the C−C cross-coupled product, 2,2′-dimethylbiphenyl, in 45% yield (entry 2). The difference in reactivity was attributed to the more coordinating nature of THF, which lowers the desulfurization activity as observed in earlier experiments concerning this reaction when using both nickel and platinum based catalysts, under homogeneous conditions. In particular, the latter behavior was explained at the time in terms of a decoordination of the bound thiophene from the metal center, which is driven by solvent displacement.[12] The same explanation is proposed in the current case. Noteworthy, a severe decrease of the catalytic activity was observed whenever solvents with higher boiling points, such as o-xylene and mesitylene, were used (entries 3−4). The use of 300 equiv of MeMgBr (entry 5) improved in the extent of desulfurization to 60%. Use of an even more concentrated system (400 equiv) did not result in any further

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Catalytic Desulfurization of Dibenzothiophene

Table 1. Desulfurization of DBT using Palladium Nanoparticles and Grignard Reagents[a]
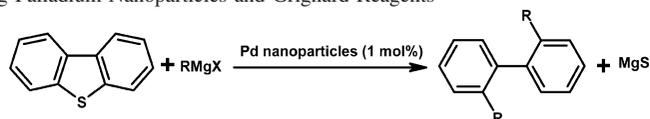
entry	complex (equiv)	thiophene (equiv)	Grignard (equiv)	solvent	organics (%)
1	**1** (1)	DBT (100)	MeMgBr (200)	THF	DBT (100%)
2	**1** (1)	DBT (100)	MeMgBr (200)	toluene	MePh-PhMe (45%); DBT (55%)
3	**1** (1)	DBT (100)	MeMgBr (200)	o-xylene	MePh-PhMe (10%); DBT (90%)
4	**1** (1)	DBT (100)	MeMgBr (200)	mesitylene	MePh-PhMe (8%); DBT (92%)
5	**1** (1)	DBT (100)	MeMgBr (300)	toluene	MePh-PhMe (60%); DBT (40%)
6	**1** (1)	DBT (100)	MeMgBr (400)	toluene	MePh-PhMe (60%); DBT (40%)
7	**1** (1)	DBT (100)	EtMgBr (300)	toluene	DBT (100%)
8	**1** (1)	DBT (100)	^{i}PrMgCl (300)	toluene	DBT (100%)
9	**2** (1)	DBT (100)	MeMgBr (300)	toluene	DBT (100%)
10	**3** (1)	DBT (100)	MeMgBr (300)	toluene	DBT (100%)
11	**4** (1)	DBT (100)	MeMgBr (300)	toluene	DBT (100%)

[a] All reactions were carried out under solvent reflux for 5 days, typically using 0.012 mmol of the corresponding palladium nanoparticle precursor. All yields in the table were determined by GC-MS, after work up.

Table 2. Desulfurization of DBT Using Palladium Nanoparticles and Grignard Reagents in the Presence of Stabilizing Agents[a]

entry	precursor (equiv)	stabilizer (equiv)	thiophene (equiv)	Grignard (equiv)	solvent	organics (%)
1	**1** (1)	**5** (0.1)	DBT (100)	MeMgBr (300)	toluene	MePh-PhMe (15%); DBT (85%)
2	**1** (1)	**6** (5)	DBT (100)	MeMgBr (300)	toluene	MePh-PhMe (25%); DBT (75%)
3	**1** (1)	**7** (5)	DBT (100)	MeMgBr (200)	toluene	MePh-PhMe (70%); DBT (30%)
4	**1** (1)	**7** (5)	DBT (100)	MeMgBr (300)	toluene	MePh-PhMe (90%); DBT (10%)
5	**1** (1)	**7** (2.5)	DBT (100)	MeMgBr (300)	toluene	MePh-PhMe (17%); DBT (83%)
6	**1** (1)	**7** (10)	DBT (100)	MeMgBr (300)	toluene	MePh-PhMe (2%); DBT (98%)
7	**1** (1)	**8** (5)	DBT (100)	MeMgBr (200)	toluene	MePh-PhMe (70%); DBT (30%)
8	**1** (1)	**8** (5)	DBT (100)	MeMgBr (300)	toluene	MePh-PhMe (90%); DBT (10%)
9	**1** (1)	**8** (2.5)	DBT (100)	MeMgBr (300)	toluene	MePh-PhMe (16%); DBT (84%)
10	**1** (1)	**8** (10)	DBT (100)	MeMgBr (300)	toluene	DBT (100%)

[a] All reactions were carried out under solvent reflux for 5 days, typically using 0.012 mmol of the corresponding palladium nanoparticle precursor. All yields were determined by GC-MS, after work up.

Scheme 1. Stabilizers Used for the Catalytic Desulfurization of DBT Employing Palladium Nanoparticles
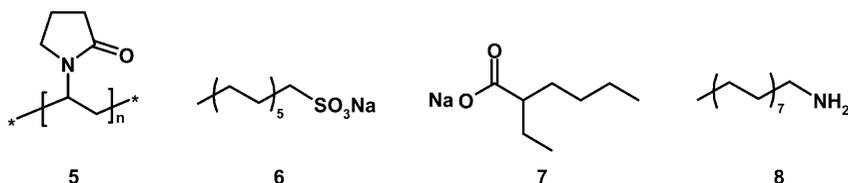
improvement (entry 6). In terms of the nature of the particular Grignard used, it is worth noting that with the more bulky the ones, EtMgBr and ^{i}PrMgCl, no desulfurization was observed (entries 7−8). Assessment of different nanoparticle precursors to **1**, such as **2**, **3**, or **4** (mentioned above), did not result in any desulfurization activity (entries 9−11), thereby confirming compound **1** as the best choice of catalyst precursor. All suspensions produced from desulfurization experiments were centrifuged (10 min at 5000 cycles/min) in order to recover the corresponding palladium precipitates and analyze them by TEM, the supernatant solutions were tested in desulfurization experiments, but no activity was observed. The TEM determinations were done with the aim of obtaining proof of the formation of palladium nanoparticles as the likely catalysts for the desulfurization reactions. The results obtained are discussed further in the text (vide infra).

Desulfurization of DBT Using Palladium Nanoparticles and Stabilizer Agents. Considering the fact that stabilizer agents have permitted notable improvements in activity whenever metal nanoparticles have been used as catalysts, this precedent encouraged us to use a number of commercially available stabilizing agents in the catalytic desulfurization of DBT using palladium nanoparticles. In principle, the improvement in activity is mostly due to the coordination of these stabilizers to the nanoparticles, which inhibit agglomeration and prevent their precipitation from the reaction media.[13−15] Scheme 1 illustrates the structures of the stabilizers that were used and Table 2 summarizes the catalytic desulfurization experiments undertaken in their presence.

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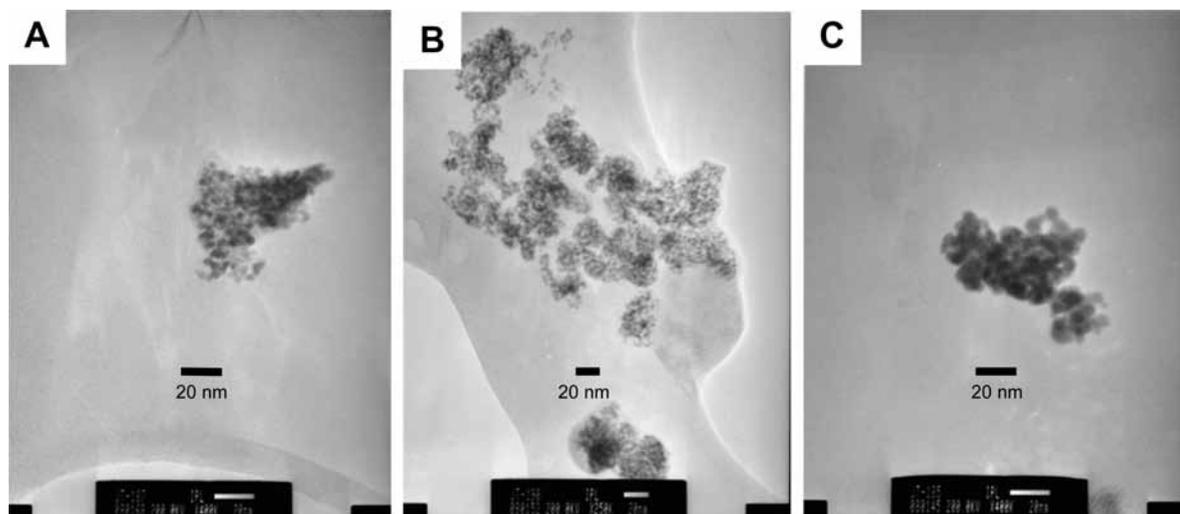
Figure 1. TEM images (20 nm scale) of palladium nanoparticles recovered from desulfurization processes undergone in the absence of a stabilizing agent. Nanoparticles formed: (A) from **1**, (B) from **2**, and (C) from **3**.

As presented in Table 2, the desulfurization of DBT using polyvinylpyrrolidone (PVP, **5**) and sodium dodecylsulfate (**6**) as the stabilizing agents did not show any enhancement in the reaction yield. In fact, the two reactions presented a severe decrease in the catalytic activity when compared with the nonstabilized system (entries 1−2). The result in turn was attributed to the presence of reactive groups in the stabilizers, which may be subject to nucleophilic attack by MeMgBr, ultimately leading to poorly active nanoparticles. The use of 5 equiv of sodium 2-ethylhexanoate (**7**) resulted in an improved catalytic system when compared to the nonstabilized ones (entries 3−4). A 90% desulfurization of DBT was achieved when using this agent. The use of a smaller amount of **7** (2.5 equiv) resulted in a dramatic decrease in desulfurization (entry 5), which was also observed when concentrating it, instead (10 equiv; entry 6). As a result, these experiments showed that the relative ratio by which stabilizers are used with respect to the palladium nanoparticle precursor may severely affect the final outcome of catalysis. The use of hexadecylamine (**8**) showed results very similar to those of **7** (entries 7−10). An improvement in the desulfurization was achieved with the use of 5 equiv of this compound, which also exhibited a decrease in catalytic activity when modifying its concentration (2.5 or 10 equiv, likewise; entries 9 and 10). All the palladium nanoparticles that were formed during these reactions were also analyzed by TEM, following the procedure described in the previous section. Their micrographs are depicted later in the text (vide infra).

Analysis of Palladium Nanoparticles Formed during Desulfurization Processes. Precipitates formed during desulfurization reactions were analyzed at the end of these processes with the use of TEM, which allowed confirmation of the presence of palladium nanoparticles as the actual catalysts. Figure 1 illustrates the TEM images of palladium nanoparticles recovered from a series of experiments undertaken in the absence of stabilizing agents.

According to the micrographs shown in Figure 1, a conclusion that follows is that there are not important differences between palladium nanoparticles generated from either precursor **1** or **2** (labeled as A and B in the figure), as they exhibit diameter averages of 4 nm and in general, a very similar shape, even though the catalytic activity that is ultimately displayed from these was in fact different (see entries 5 and 9 of Table 1). It is therefore thought that the difference in catalytic activity among these two systems may be adduced to important differences in the degree of stabilization that is afforded over the nanoparticle-related catalytic intermediates, probably affected by the basicity of the particular phosphine that was present in the catalyst precursor.[15] Only the precursor containing the more basic phosphine (PEt₃) exhibited any catalytic activity. In the case of compound **3**, the nanoparticles that were formed exhibited a larger average size of 6 nm and may be the probable cause for the null activity encountered with this system. To note, all the catalytically active systems exhibited nanoparticles with an average diameter of 4 nm or less. Related to this observation, samples recovered from reactions assessed at different reaction times permitted the observation of nanoparticle-agglomeration, which may also be reflected in a decrease in catalytic activity. Figure 2 illustrates a series of micrographs which depict the appearance of aggregates of nanoparticles after 1, 3, and 5 days.

The agglomeration of palladium nanoparticles takes place as a function of time and a considerably larger size of the total entity may be found after 5 days of reaction (C). The latter is consistent with a less active system over time, confirmed by the presence of unreacted DBT in all the experiments in which no stabilizer was used. Complementary to this conclusion, the same type of TEM analysis performed over nanoparticles produced from **1** in the presence of stabilizing agents confirmed the extent of agglomeration to be smaller, accompanied by a better catalytic performance of the catalysts in the desulfurization process overall

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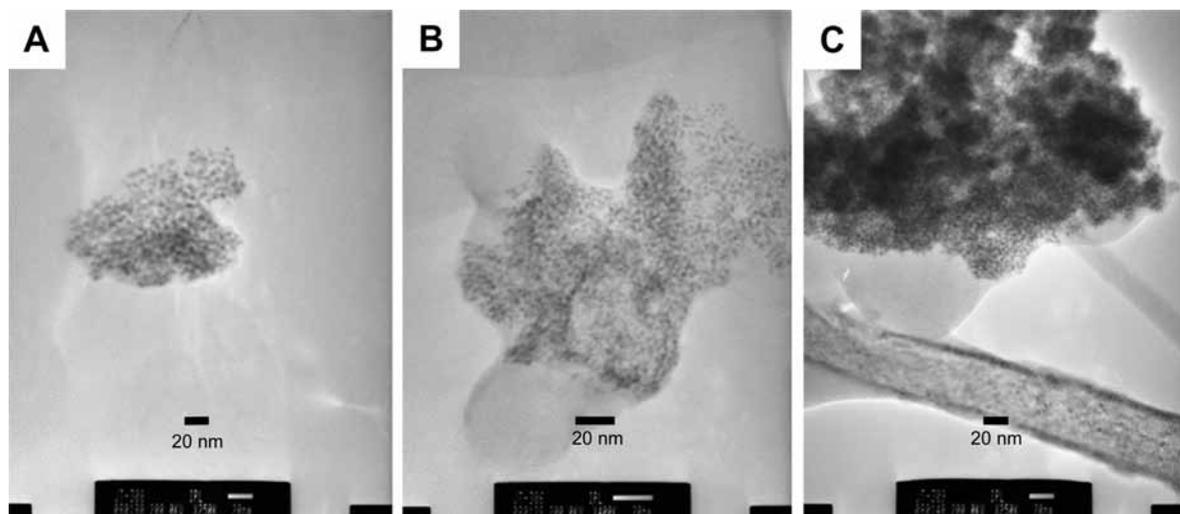
Figure 2. TEM images (20 nm scale) of palladium nanoparticles produced from **1**, taken at different reaction times: (A) 1 day, (B) 3 days, (C) 5 days.
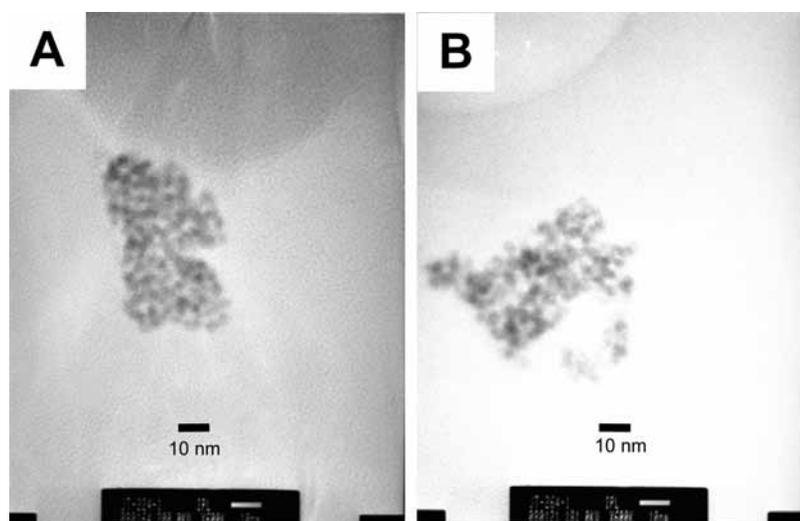
Figure 3. TEM images of palladium nanoparticles produced from **1** after the desulfurization process, in the presence of a stabilizer. (A) Sodium 2-ethylhexanoate and (B) hexadecylamine.

(compare results in Table 2 with those in Table 1). Figure 3 illustrates two of the TEM images obtained from the systems in which a stabilizer was used, comparing between (A) sodium 2-ethylhexanoate with (B) hexadecylamine.

As noted in Figure 3, the use of stabilizers promoted the formation of smaller diameter nanoparticles (average diameter, 3 nm), unlike to the agglomerates obtained over time in the case of unstabilized systems. The use of stabilizers prevented the agglomeration of the metal particles and as such the better performance of the catalytic systems that was encountered in the presence of the former is consistent with this fact.

Conclusions

The current work demonstrates an efficient palladium nanoparticle system that is useful for the catalytic desulfurization of DBT. The reaction allows the selective formation of 2,2′-dimethylbiphenyl by means of a cross-coupling reaction with MeMgBr. The use of stabilizing agents permits the onset of a greater catalytic performance of the nanoparticles as a result of a smaller diameter size, and a lesser extent

of nanoparticle agglomeration. Studies are underway to expand the scope of this reaction to closely related S- and N-containing substrates.

Experimental Section

All manipulations were carried out using standard Schlenk and glovebox techniques,[16] under argon (Praxair 99.998). THF (J. T. Baker) was dried and distilled from dark purple solutions of sodium/ benzophenone ketyl. Toluene, *o*-xylene and mesitylene (J. T. Baker) were dried and distilled from sodium. MeMgBr (3.0 M in diethyl ether solution) was purchased from Aldrich and was used as received. DBT, (COD)PdCl$_2$, PVP, sodium dodecylsulfate, sodium 2-ethylhexanoate and hexadecylamine were purchased from Aldrich, were dried in vacuo, and were used without further purification. PEt$_3$, PPh$_3$, and dppe were purchased from Aldrich and were also used without further purification. 1,2-Bis(diisopropylphosphino)et-hane (dippe) was prepared as reported.[17] Deuterated solvents were

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purchased from Cambridge Isotope Laboratories and were stored over 3 Å molecular sieves in an MBraun glovebox (<1 ppm H_2O and O_2). ^1H, and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature on a 300 MHz Varian Unity spectrometer in toluene-d_8. ^1H chemical shifts (δ) are reported relative to the residual proton resonances in the deuterated solvent. $^{31}P\{^1H\}$ NMR spectra were recorded relative to external 85% H_3PO_4. All NMR spectra were carried out using thin wall (0.38 cm) WILMAD NMR tubes with J. Young valves. GC-MS determinations were performed using a Varian Saturn 3 on a 30 m DB-5MS capillary column. All nanoparticles produced were characterized by TEM at 200 kV using a Jeol-2010 electron microscope.

Nanoparticle Precursors. Complexes $[(PEt_3)_2PdCl_2]$ (**1**), $[(PPh_3)_2PdCl_2]$ (**2**), $[(dippe)PdCl_2]$ (**3**), $[(dppe)PdCl_2]$ (**4**) were prepared following the procedures reported in the literature.[18] The methylated compounds were prepared in situ by reaction of chlorinated compounds with excess of MeMgBr.[19]

Catalytic Desulfurization Experiments. A 50 mL Schlenk flask was charged in a glovebox with the corresponding chlorinated catalytic precursor (0.012 mmol) dissolved in 8 mL of dry toluene and to it was added DBT (1.2 mmol) with constant stirring, during 30 min. After complete mixing, a solution of the Grignard reagent (2.4 mmol) was added. No changes in color were observed. The reaction mixture was heated to reflux under argon in a gas/vacuum line and constantly stirred during the whole time of reaction. A color change from yellow to brown was observed during the course of reaction, accompanied by formation of a beige precipitate. Heating was stopped and the sample hydrolyzed at room temperature using HCl (10 mL, 10% v). A strong effervescence was observed with the immediate release of H_2S (*caution poisonous gas!*), which was bubbled into a trap with 50 mL of an aqueous concentrated solution of $Pb(CH_3COO)_2$ inside a fume hood. After bubbling and venting all the gases, all organics proceeding from the reaction mixture were extracted using CH_2Cl_2 (3 × 5 mL) and the organic layer analyzed by GC-MS. The samples prepared for TEM analysis were not hydrolyzed but centrifuged at 5000 cycles/min for 10 min. After this time, the supernatant solution was removed leaving a grayish solid which was dried for 5 h in vacuo and then analyzed.

Supporting Information Available: Includes detailed tables for the desulfurization experiments, typical chromatographic plots, and bar graphs with the nanoparticle size distribution of representative experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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