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Catalytic Desulfurization of Dibenzothiophene and Its Hindered Analogues with Nickel and Platinum Compounds

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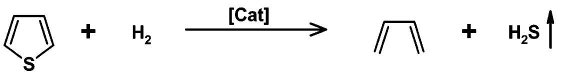
Catalytic amounts (1−0.1 mol %) of nickel and platinum compounds in 0, I, and II oxidation states containing mono- and diphosphines ligands, in conjunction with alkyl Grignard reagents, promoted the desulfurization of dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MeDBT), and 4,6-dimethyldibenzothiophene (4,6-Me_2DBT), to produce the corresponding substituted and unsubstituted biphenyls. It was also observed that the use of polar solvents such as THF yielded thiols, while the use of nonpolar solvents allowed the complete desulfurization of these substrates.

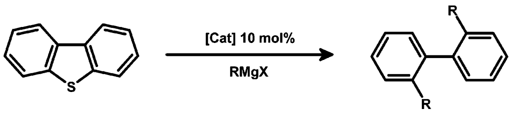
Introduction

The removal of organosulfur compounds from fuels is a mandatory issue in the goal of succeeding in diminishing the extent of atmospheric pollution caused from the emission of sulfur oxides, resulting from combustion processes.[1] As such, increasingly more stringent regulations regarding the limits of permissible sulfur content in fuels have been constantly raised in a number of countries.[2] Industrially, the process that is used for the removal of sulfur is known as *catalytic hydrodesulfurization* (HDS).[3] The commercial HDS process typically uses cobalt- or nickel-doped molybdenum sulfide catalysts over alumina. The latter is noteworthy, given that in fact the platinum group metals are the ones that exhibit the highest HDS activity, as has been shown by model reactor studies, the latter metals not being used commercially, probably because of their higher cost.[4] In addition to these facts, a variety of organometallic compounds—mostly in solution—containing different transition metals have also been tested in a number of HDS reactions with thiophenes: the latter compounds, particularly the more hindered dibenzothiophene derivatives 4-methyldibenzothiophene (4-MeDBT) and 4,6-dimethyldibenzothiophene (4,6-Me_2DBT), are particularly responsible for the poor sulfur removal achieved by commercial HDS processes.[5] An equation that exhibits the HDS process assisted by the presence of metal-supported or organometallic catalysts is presented in eq 1.



(1)

Implicit in eq 1, the metal catalyst undergoes a number of reaction intermediates to yield the corresponding HDS products and a stoichiometric amount of H_2S; the oxidative addition reaction of the C−S bond of the thiophene to the metal catalyst has been found to take place particularly in low oxidation state catalysts such as platinum(0) and nickel(0).[5] In addition, it has been reported that the use of nucleophiles such as Grignard reagents yields sulfur-free cross-coupling products such as 2,2′-dimethyl-1,1′-biphenyl from DBT in the presence of nickel(II) halide phosphine precursor complexes (10 mol %).[6] In this instance, a closely related report has recently appeared that describes the use of several Ni(0) catalysts (3 mol %) that yield chiral 1,1′-binaphthyls in the asymmetric cross-coupling reaction of dinaphtho[2,1-*b*:1′,2′-*d*]thiophene and 1,9-disubstituted dibenzothiophenes, in the presence of Grignard reagents (eq 2).[7]



(**2**)

It is worth noting that the use of organometallic nickel and platinum complexes in desulfurization reactions of DBTs has also been reported to occur in the presence of other nucleophiles besides Grignard reagents under stoichiometric conditions;[8] only a small number of compounds have been known to ring open 4,6-Me_2DBT to yield the corresponding desulfurization products.[9] In the case of our group, a preliminary report that describes the reactivity of a number of nickel complexes that yield the catalytic desulfurization reaction of DBT, 4-MeDBT, and 4,6-Me_2DBT under homogeneous conditions in the presence of alkyl Grignards has been recently published.[10] In all three cases, the

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[1] See for instance: Angelici, R. J. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: New York, 1994; p 1433.

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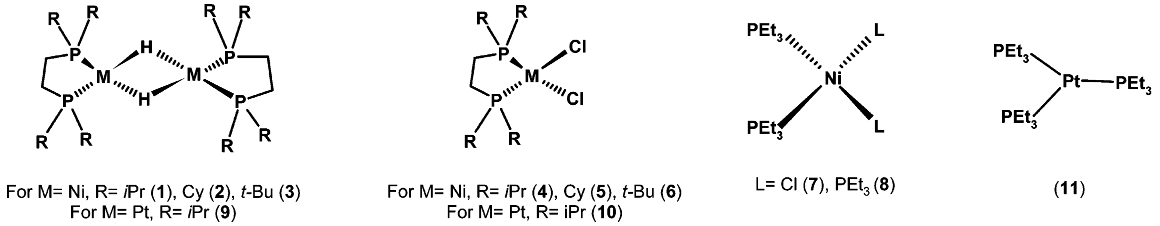

Figure 1. Catalytic precursors of Ni and Pt used to desulfurize DBT and its hindered analogues.

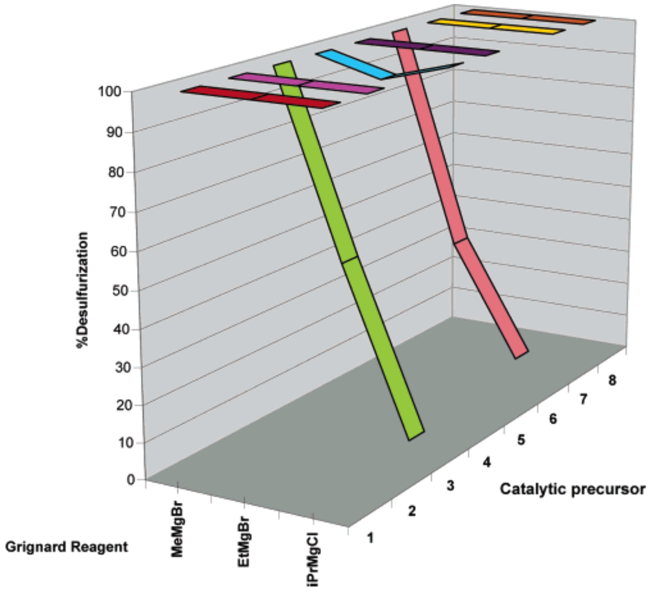

Figure 2. Catalytic desulfurization of DBT with nickel compounds. All reactions were carried out under toluene reflux using 1 mol % of the corresponding nickel catalyst. All yields were quantified by GC-MS, after workup.

reaction yielded the corresponding substituted biphenyls: the latter report is the first clear example of a catalytic desulfurization process for 4,6-Me$_2$DBT, which is largely unreactive. A mechanistic proposal that provides insight into these reactions, in which the formation of nickel thiametallacycles was proposed to take place after an initial oxidative addition reaction of the respective thiophene, was also addressed in the same work.[10] Herein, we report our findings after that initial report, including an extensive study of the catalytic desulfurization process for the same three dibenzothiophenic substrates in the presence of both nickel and platinum complexes, in different oxidation states and bearing different phosphine ligands (see Figure 1).

Results and Discussion

Catalytic Desulfurization of DBT with Nickel Compounds. The desulfurization reaction of DBT in the presence of two additional equivalents of MeMgBr and complexes **1**−**8** as catalyst precursors (1 mol %) under toluene reflux yielded in all cases only the cross-coupling product 2,2′-dimethyl-1,1′-biphenyl in 100%. In the case of EtMgBr and *i*-PrMgCl, both substituted and unsubstituted biphenyls were observed. A complete chart that summarizes the results obtained with all three Grignards with respect to the nickel complex used in each case for the desulfurization of DBT is presented in Figure 2.

As shown in Figure 2, the reactivity of all nickel compounds was optimal in the presence of MeMgBr, probably because of the small steric hindrance presented by this Grignard reagent. In the case of EtMgBr and *i*-PrMgCl, which present increasing steric bulk, the results obtained showed that a drastic decrease of the catalytic desulfurization activity was observed when either of these was used in the presence of the otherwise more impeded catalysts precursors **3** and **6**, both of which contain bis(ditertbutylphosphine)ethane as ancillary ligand.

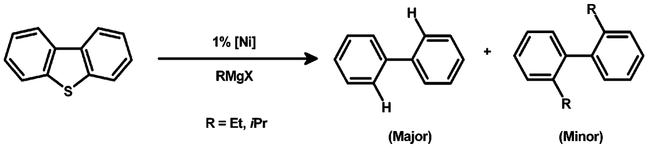

Figure 3. Products obtained when the Grignard reagents contain β-hydrogens.

As mentioned above, whenever EtMgBr and *i*-PrMgCl were used, both substituted and unsubstituted biphenyl products were observed. One possible explanation for this may be that an initial attack of the nucleophile takes place over the metal center bearing the organic moiety, followed by a β-elimination step (*vide infra*).[11] Such combination might act as an *in situ* source of nickel hydride intermediates that allow the release of unsubstituted biphenyls via a hydride migration, which can be envisaged as an HDS product, instead of a cross-coupling product. To note, when this reaction was followed by NMR using a sealed tube, the free alkene formed as a result of the β-elimination step was detected. In this instance, when EtMgBr was used, ethylene was detected, while in the case of *i*-PrMgCl, 1-propene was found. The proportion of substituted and unsubstituted biphenyls indicates that the β-elimination step is favored over cross-coupling, provided that the amount of unsubstituted biphenyl was greater in most of the experiments carried out with those reagents (see Figure 3).

In addition to the systems mentioned above using 1 mol % of catalyst precursor, some other experiments were assessed using complexes **1**, **7**, and **8** at the lower concentration of 0.1 mol %. These results are shown in the Table 1. Entries 1−3 show that the desulfurization reaction is highly efficient: a total conversion of DBT has been observed to occur in all cases.

As indicated in Table 1, whenever the experiments were carried out using THF as solvent (entries 4 and 5), the general outcome was the production of 2,2′-dimethyl-1,1′-biphenyl and a quantity of the corresponding thiol (MePh−PhSH), which results from the occurrence of only one cross-coupling step. We propose that the production of the thiol is a consequence of the coordination of THF molecules, which disrupt the completion of the overall desulfurization process, provided that the use of a noncoordinating solvent such as toluene already confirmed the formation of disubstituted biphenyls as the only products (see entries 1−3).

The use of solvents with a higher boiling point than toluene, such as *o*-xylene and mesitylene (entries 6 and 7 of Table 1), resulted in a slight decrease of the catalytic activity, which was probably due to catalyst decomposition. The same kind of temperature effect over thiaplatinacycles used in the HDS

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Table 1. Nickel-Catalyzed Desulfurization of DBT with Grignard Reagents[a]

entry	complex (equiv)	thiophene (equiv)	grignard (equiv)	solvent	organics (%)
1	**1** (1)	DBT (1000)	MeMgBr (2000)	toluene	MePh−PhMe (100)
2	**7** (1)	DBT (1000)	MeMgBr (2000)	toluene	MePh−PhMe (100)
3	**8** (1)	DBT (1000)	MeMgBr (2000)	toluene	MePh−PhMe (100)
4	**1** (1)	DBT (100)	MeMgBr (200)	THF	MePh−PhMe (60), MePh−PhSH (25), DBT (15)
5	**8** (1)	DBT (100)	MeMgBr (200)	THF	MePh−PhMe (73), MePh−PhSH (27)
6	**1** (1)	DBT (100)	MeMgBr (200)	*o*-xylene	MePh−PhMe (95), DBT (5)
7	**1** (1)	DBT (100)	MeMgBr (200)	mesitylene	MePh−PhMe (90), DBT (10)
8	**12** (1)	DBT (100)	MeMgBr (200)	toluene	MePh−PhMe (91), DBT (9)
9	**13** (1)	DBT (100)	MeMgBr (200)	toluene	MePh−PhMe (100)

[a] All reactions were carried out under reflux of their corresponding solvent for 5 days, typically using 0.012 mmol of the corresponding nickel catalyst. All yields were quantified by GC-MS, after workup.

process of substituted thiophenes was also observed by our group and has already been reported.[12]

Mechanistic Insights for the Catalytic Desulfurization of DBTs Using Nickel Compounds. As indicated in our former communication,[10] the feasibility of the intermediacy of the corresponding thianickelacycles and nickelacycles during desulfurization was also addressed. To do so, complexes [(dippe)Ni(η^2-*C,S*-$C_{12}H_8$)] (**12**) ($^{31}P\{^1H\}$ NMR in toluene-d_8 δ 74.39, d, $^2J_{P-P} = 10$ Hz; 75.55, d, $^2J_{P-P} = 10$ Hz) and [(dippe)Ni(η^2-*C,C′*-$C_{12}H_8$)] (**13**) ($^{31}P\{^1H\}$ NMR in toluene-d_8 δ 70, s) were prepared and tested as catalyst precursors in a 1 mol % catalytic proportion; the outcome of these experiments is the formation of the corresponding cross-coupling products in yields higher than 90% (see entries 8 and 9 of Table 1). Thiametallacycle **12** reacts at room temperature upon addition of MeMgBr and is re-formed under reflux within the reaction time: a persistent concentration of this compound, together with **13** and [(dippe)$_2$Ni] ($^{31}P\{^1H\}$ NMR in toluene-d_8 δ 54.5, s), has been detected to take place after 90% conversion of the starting DBT, implying partial decomposition of the catalyst, as has been mentioned above. An improved mechanistic proposal based on the generally accepted catalytic cycle for the nickel-catalyzed cross-coupling reactions,[7,13] along with our previous findings on this subject[10] and the additional ones concluded from this work, is depicted in Scheme 1. As shown in the scheme, it is likely that the first active intermediate within the catalytic cycle is the thiametallacycle **12**. These kinds of compounds have already been proposed as important intermediates in HDS reactions, and as mentioned in the case of **12**, experiments using this complex as starting material yielded the desulfurization process: the latter complex was found to exhibit a high activity (*vide supra*). Intermediate **A** is produced by the nucleophilic attack of the Grignard reagent to the metal center in **12**. This species may evolve by two different routes: the first one is the reductive elimination of the alkyl and biphenyl groups (the latter one still bearing the sulfur moiety), to form the thiolate **B**; the second route is the β-elimination reaction, which is restricted exclusively to those Grignards that hold protons in the β-position and is, thus, the route for unsubstituted biphenyls that was mentioned earlier (*vide supra*). Intermediate **B** is proposed to be responsible for the formation of the thiol compounds that were also mentioned before (entries 4 and 5, Table 1): the coordination of THF molecules to this intermediate is likely to lead to the release of the corresponding magnesium thiolates, thereof producing thiols once the reaction mixture had been subjected to workup. Under noncoordinating solvents such as toluene (entries 1−3, Table 1), **B** is likely to evolve into intermediate **C**, once a second C−S bond activation step—this time over the thiolate moiety—had occurred. The second nucleophilic attack over the metal center, promoted by another equivalent of Grignard, would drive the release of the magnesium salts (MgS and $MgBr_2$)[14] and the formation of the alkyl-substituted nickel(II) complex, that is, **C**. This intermediate can evolve by two routes, as was also the case of **A**, either by undergoing the cross-coupling reaction promoting the disubstituted biphenyl or by performing a second β-elimination step, in which case the final unsubstituted biphenyl would be formed instead. Finally, after either of these steps had taken place, the resulting 14-electron "[(dippe)Ni]" intermediate would regenerate the thiametallacycle **12** in the presence of additional thiophene and, thus, complete the desulfurization cycle.

Catalytic Desulfurization of 4-MeDBT with Nickel Compounds. As in the case of DBT, the reactivity of 4-MeDBT, which is one of the most refractory organosulfur compounds in fuels, was also addressed. To do so, complexes **1** and **8**, which had shown the highest activity in the desulfurization of DBT, were tried; the results obtained showed that these complexes were also very active with this substrate (Table 2).

As can be seen in Table 2, the complete desulfurization of 4-MeDBT using 1 mol % of **1** and 0.1 mol % of **8** was observed. The fact that this reaction was achieved under such conditions constitutes a very important result; it effectively confirms the usefulness of these nickel compounds for the generation of efficient systems for the desulfurization of organosulfur compounds as stable as 4-MeDBT: the complete conversion of it into the cross-coupling product 2,2′,3-trimethyl-1,1′-biphenyl has been found to take place in both cases.

Catalytic Desulfurization of 4,6-Me$_2$DBT with Nickel Compounds. Compounds **1**−**8** (2 mol %) were tested in the catalytic desulfurization of the more hindered 4,6-Me$_2$DBT using alkyl Grignards. As in the case of 4-MeDBT, the reaction with 4,6-Me$_2$DBT is a very important one, provided that this substrate is considered to be by far the most refractory organosulfur compound of its family. To the best of our knowledge, the results obtained herein represent the first clear examples of homogeneously catalyzed desulfurization reactions of 4,6-Me$_2$DBT using organometallic compounds. A chart that summarizes the results obtained thus far is presented in Figure 4. As illustrated in this figure, the reactivity of the nickel complexes used presented an optimal behavior in the desulfurization of 4,6-Me$_2$DBT whenever MeMgBr was used as the Grignard reagent, the selectivity of the process being exclusive to the cross-coupling product 2,2′,3,3′-tetramethyl-1,1′-biphenyl. As in the case of DBT, the reactions performed over 4,6-Me$_2$DBT showed a strong dependence on the overall steric hindrance displayed by the reagents: the monophosphine-containing compounds **7** and **8** were found to exhibit the highest activity

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(13) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Manato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958.

(14) MgS was identified by X-ray powder diffraction.[10]

Scheme 1. Mechanistic Proposal for the Desulfurization of DBT

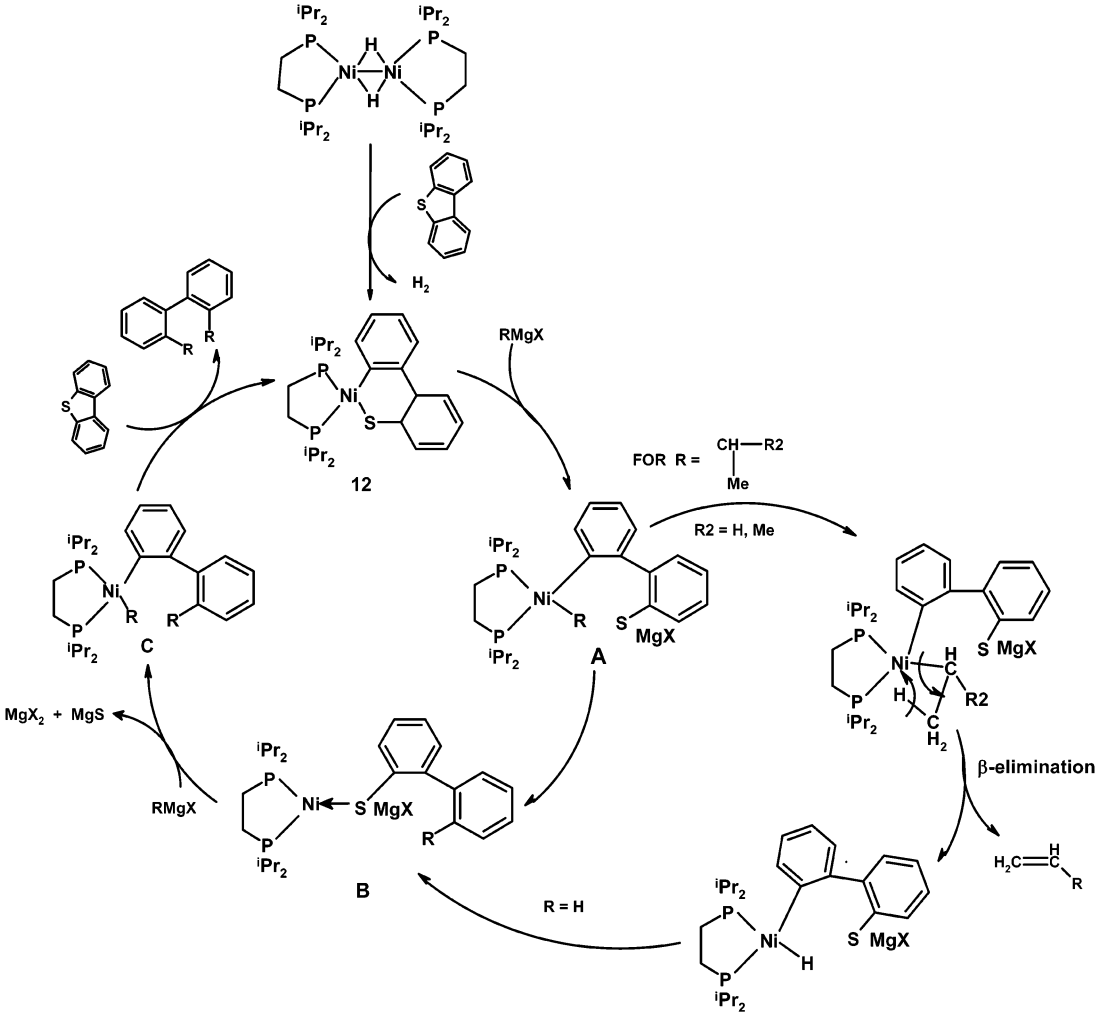

Table 2. Nickel-Catalyzed Desulfurization of 4-MeDBT with Grignard Reagents[a]

entry	complex (equiv)	thiophene (equiv)	grignard (equiv)	solvent	organics (%)
1	**1** (1)	4-MeDBT (100)	MeMgBr (200)	toluene	MePh−PhMe$_2$ (100)
2	**8** (1)	4-MeDBT (1000)	MeMgBr (2000)	toluene	MePh−PhMe$_2$ (100)

[a] All reactions were carried out under reflux of their corresponding solvent for 5 days, typically using 0.012 mmol of the corresponding nickel catalyst. All yields were quantified by GC-MS, after workup.

of all. In the case of the diphosphine-substituted nickel compounds, a decreasing trend in reactivity could be established depending on the bulkiness of the ancillary ligands, and as such, complexes **1**, **2**, **4**, and **5**, which bear the less bulky diphosphines, displayed moderate reactivity in the desulfurization reaction, while complexes **3** and **6**, with more bulky diphosphines, exhibited no reactivity at all. Noteworthy, the nature of the Grignard reagent was also found to be important in the final outcome of the catalysis: the use of the more bulky Grignards, EtMgBr or *i*-PrMgCl vs MeMgBr, was found to inhibit the desulfurization reaction in all cases.

Another important observation found for this process is that regarding the nature of the solvent used. Unlike DBT, the desulfurization of 4,6-Me$_2$DBT does not require the reaction to take place in a particular solvent: the reaction in either toluene or THF yielded the same result, every time. A possible explanation for this is that the THF molecules cannot coordinate to the formed metallacycles (and to the rest of the intermediaries) in any of these cases, as a result of the increased steric hindrance opposed by the proximity that the two methyl groups in 4,6-Me$_2$DBT likely hold toward the nickel center in all intermediates within the catalytic cycle. As in the case of DBT, the use of higher boiling point solvents such as *o*-xylene or mesitylene also diminished the catalytic activity, presumably due to catalyst decomposition (*vide supra*).

Catalytic Desulfurization of DBT with Platinum Compounds. It is well known that several platinum compounds can cleave the C−S bond of DBT, 4Me-DBT, and 4,6-Me$_2$DBT and that in the presence of a source of hydrogen they can carry out the HDS reaction.[8,9] However, in all those examples the reactions are stoichiometric. Thus, given the success in achieving catalytic HDS reactions with those substrates using the nickel complexes described above, we became interested in assessing the feasibility of a catalytic process using platinum compounds. To do so, a series of platinum complexes (**9**, **10**, and **11**; see Figure 1) analogous to those of nickel were prepared with the objective of making a comparison of both systems. The main desulfurization results are summarized in Figure 5. As shown in the figure, a drastic diminishment of the catalytic activity of the three platinum compounds was observed in all the desulfurization experiments attempted, on comparison with their corresponding nickel analogues, the highest activity within this

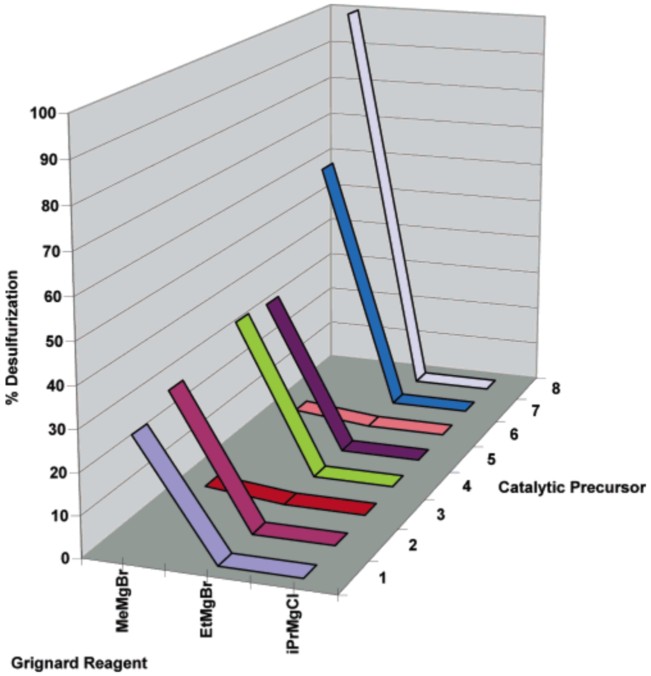

Figure 4. Catalytic desulfurization of 4,6-Me_2DBT with nickel compounds. All reactions were carried out under toluene reflux for 5 days using 2 mol % of the corresponding nickel catalyst. All yields were quantified by GC-MS, after workup.

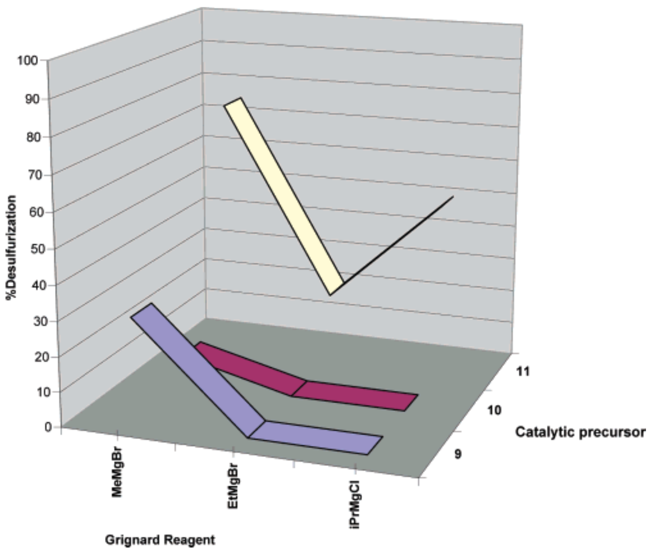

Figure 5. Catalytic desulfurization of DBT with platinum compounds. All reactions were carried out under toluene reflux for 5 days, using 1 mol % of the corresponding platinum catalyst. All yields were quantified by GC-MS, after workup.

series of complexes being depicted by the monophosphine platinum complex [Pt(PEt_3)$_3$] (**11**; 1 mol %), which in the presence of MeMgBr achieved up to 75% conversion of DBT into its cross-coupling product: the closely related nickel complex [Ni(PEt_3)$_4$] (**8**) was found to yield 100% conversion of this substrate at a much lower concentration of 0.1 mol % (entry 3, Table 1). In the case of the diphosphine complexes [(dippe)PtH]$_2$ (**9**) and [(dippe)$PtCl_2$] (**10**), the desulfurization of DBT gave much poorer results ($<$20%), even with MeMgBr. The results suggest an even greater contrast in activity than those exhibited by the platinum complex **11** or the nickel hydride dimer [(dippe)NiH]$_2$ (**1**), the latter displaying an excellent performance in the desulfurization reaction even at 0.1 mol % (entry 1, Table 1). It is worth noting that the use of the more bulky Grignards (EtMgBr and *i*-PrMgCl) has resulted in an even greater drop in activity. The use of complex **11** in the case of *i*PrMgCl produce a higher HDS yield, probably due to an increased number of β-hydrogens, while no activity was obtained when either complex **9** or **10** was used (see Table S3 in the Supporting Information). As a result of these trends in reactivity, the lesser activity of the platinum complexes might be due to the larger M−C bond strength that is typically shown by these, unlike those of nickel.[15] If this is so, then it is likely that the platinum intermediates within the overall desulfurization process would become more stable than the corresponding nickel analogues and, as such, behave as less reacting species, ultimately reducing the overall efficiency of catalysis. The attempt to increase conversion by using higher boiling point solvents such as *o*-xylene or mesitylene did not yield any improvement; the systems explored under such conditions showed no reactivity at all.

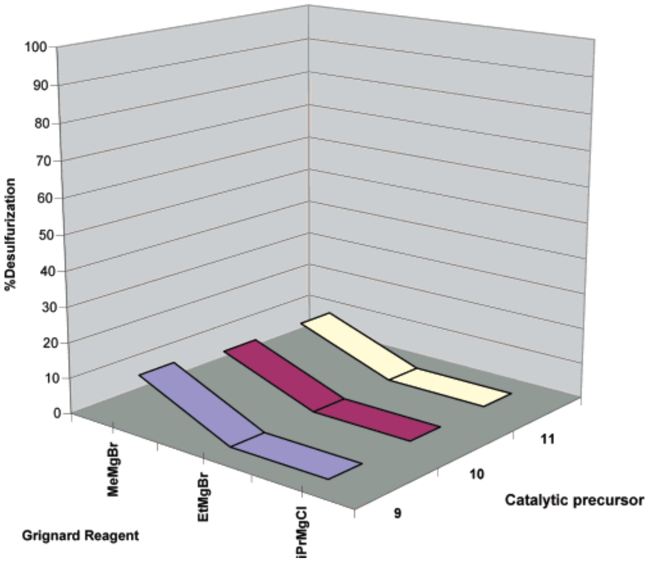

Figure 6. Catalytic desulfurization of 4,6-Me_2DBT with platinum compounds. All reactions were carried out under toluene reflux for 5 days, using 2 mol % of the corresponding platinum catalyst. All yields were quantified by GC-MS, after workup.

Catalytic Desulfurization of 4,6-Me_2DBT with Platinum Compounds. As was mentioned before, Me_2DBT displays the more refractory behavior of this family. Complexes **9**, **10**, and **11** were tried in its desulfurization, and as expected, on the basis of their smaller overall activity in the desulfurization of DBT, a much smaller activity was confirmed for this substrate. The results are summarized in Figure 6.

Conclusions

The current work demonstrates the use of mono- and diphosphino-containing nickel complexes in the homogeneous catalytic desulfurization of DBT, and its more hindered analogues 4-MeDBT and 4,6-Me_2DBT, in the presence of alkyl Grignard reagents. The percent of desulfurization is very high, and the conditions required to do so are very mild. The reactions yielded the corresponding substituted biphenyls via cross-coupling reactions if attempted in hydrocarbon solvents, and in the case of polar solvents, such as THF, led to the formation of thiols. The use of Grignard reagents bearing β-hydrogens

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[15] Ateşin, T. A.; Oster, S. S.; Skugrud, K.; Jones, W. D. *Inorg. Chim. Acta* **2006**, *359*, 2798.

(EtMgBr and *i*-PrMgCl) leads to the formation of unsubstituted biphenyls, and the increase in the steric hindrance of the ancillary ligands results in diminishing the percent of desulfurization of the starting thiophene. The use of platinum compounds has resulted in a smaller catalytic activity, and thus, it is likely that the greater M−C bond strength displayed by this metal affects the turnover rate of overall catalysis, therefore leading to smaller percents of desulfurization. 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 under argon (Praxair 99.998). THF (J. T. Baker) was dried and distillated from dark purple solutions of sodium/benzophenone ketyl. Toluene, *o*-xylene, and mesitylene (J. T. Baker) were dried and distilled from sodium. MeMgBr (1.4 M in toluene/THF, 75:25, solution), EtMgBr (1 M in THF solution), and *i*-PrMgCl (2 M, in THF solution) were purchased from Aldrich and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves in an MBraun glovebox (<1 ppm H_2O and O_2). DBT, 4-MeDBT, and 4,6-Me_2DBT were purchased from Aldrich, dried *in vacuo*, and used without further purification. ^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.

Catalytic Precursors. All complexes were prepared as reported in the literature: $[(dippe)NiH]_2$ (**1**), $[(dcpe)NiH]_2$ (**2**), $[(dtbpe)NiH]_2$ (**3**), $[(dippe)PtH]_2$ (**9**), [(dippe)Ni(η^2-*C*,*S*-$C_{12}H_8$)] (**12**), and [(dippe)Ni(η^2-*C*,*C′*-$C_{12}H_8$)] (**13**);[16] [(dippe)$NiCl_2$] (**4**), [(dcpe)$NiCl_2$] (**5**), [(dtbpe)$NiCl_2$] (**6**), and [$Ni(PEt_3)_2Cl_2$] (**7**);[17] [$Ni(PEt_3)_4$] (**8**);[18] [(dippe)$PtCl_2$] (**10**);[19] and [$Pt(PEt_3)_3$] (**11**).[20]

Catalytic Desulfurization Experiments. In the drybox a 50 mL Schlenk flask was charged with the corresponding catalytic precursor (0.012 mmol) and dissolved in 8 mL of dry toluene, adding the thiophene (1.2 mmol) with constant stirring during 30 min. After complete mixing and once the released gases had been vented in the box, a solution of the Grignard reagent (2.4 mmol) was added; the color changed to brown. The reaction mixture was heated to reflux under argon in a gas/vacuum line, constantly stirred during the time of reaction. During this time, a mixture of precipitates can be seen: a beige precipitate and a red-brown precipitate. After this time, the heating was stopped and the sample was hydrolyzed at room temperature with HCl (10 mL, 10% v). A strong effervescence was observed with the immediate release of H_2S, which was usually bubbled into a trap with 50 mL of an aqueous concentrated solution of $Pb(CH_3COO)_2$. After bubbling and venting all the gases, all organics produced from the reaction mixture were extracted using CH_2Cl_2 (3 × 5 mL), and the organic layer was analyzed by GC-MS.

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Supporting Information Available: Detailed tables of the desulfurization experiments, representative GC-MS traces, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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