



Deoxydesulfurization of sulfones derived from dibenzothiophene using nickel compounds

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ABSTRACT

Catalytic amounts (1 mol%) of $[\text{Ni}(\text{dippe})\text{H}]_2$ (**1**), $[\text{Ni}(\text{dcype})\text{H}]_2$ (**2**), $[\text{Ni}(\text{dtbpe})\text{H}]_2$ (**3**), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (**4**) and $[\text{Ni}(\text{dippe})(\text{Me})_2]$ (**5**) reacted with MeMgBr to yield the straightforward deoxydesulfurization of sulfones of dibenzothiophene (DBTO_2), 4-methyl-dibenzothiophene (MeDBTO_2) and 4,6-dimethyldibenzothiophene (Me_2DBTO_2), thereof producing the corresponding sulfur-free biphenyls (85–100% yield) when using a solvent mixture of toluene–THF, 10:2 v/v. The formation of key intermediates of the type $[(\text{dippe})\text{Ni}(\kappa^2\text{-}(\text{O},\text{O})(\text{sulfone}))]$ play an important role in the activation of the C–S bond in the sulfone as they participate in the ultimate deoxygenation step, even with the more hindered substrates. The formation of MgO and MgS from the catalytic process is envisioned as the driving force for the whole reaction.

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1. Introduction

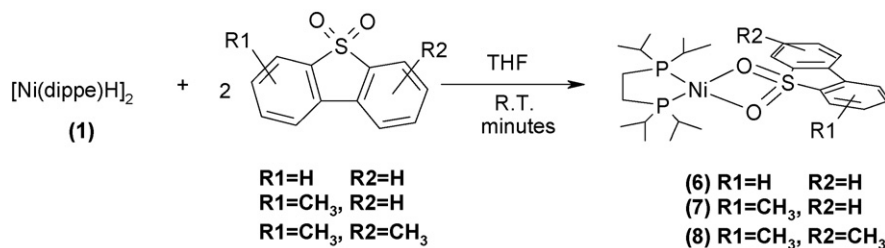
The use of heavy crude oils which contain major quantities of hetero-atoms such as N, O, and S has become necessary in the past few decades, as a result of due to the increasing demand of fuels. Sulfur-containing compounds are normally the most abundant impurities in such crude oils, present in the form of thiols, thiophenes (T's), benzothiophenes (BT's) and dibenzothiophenes (DBT's) [1] all of which are oxidized and emitted as SO_x gases when subjected to combustion processes in engines; thereby turning into major air contaminants that are responsible for the formation of acid rain. In that regard, the removal of sulfur-containing compounds from oils has thus been long performed by the industry indeed succeeding in removing most thiol-impurities by the use of heterogeneous catalysts (*vide infra*), the insufficiency to do so for the more refractory aromatic components, DBT's – particularly dramatic in the case of the more hindered derivatives such as the 4-methyldibenzothiophene (MeDBT), or the 4,6-dimethyldibenzothiophene (Me_2DBT) – turning into a considerably pressing circumstance when taken in context with the current environmental restrictions that establish smaller limits for acceptable sulfur contents in dispensed gasolines and diesels both

in the USA (<30 ppm, 2006) [2] and in Europe (<10 ppm, 2008) [3].

DBT's are the most refractory compounds in the traditional hydrotreatment process commonly known as hydrodesulfurization or HDS, which typically uses Co, Mo, W and Ni sulfides as heterogeneous catalysts in the petrochemical industry. High pressures (150–300 psi) and temperatures (500–800 °C) are usually required for the process, the latter conditions additionally involving a large consumption of hydrogen-gas (H_2), ultimately leading to a significant increase in operating expenses. [4] In particular, HDS does not allow a complete removal of DBT's, due to a combination of factors including enhanced stability of these compounds due to aromaticity of the thiophenic ring and inaccessibility to cleave the C–S bonds due to steric constraints; a feature that is dramatically illustrated by the more hindered derivatives, MeDBT and even more so, Me_2DBT .

The oxidative desulfurization process (ODS) emerges as a technological alternative to the HDS process, the former operating under milder conditions without hydrogen requirement. It involves the oxidation of the sulfur moiety in the thiophenic substrate with the aid of numerous oxidizing agents producing the corresponding sulfoxides and sulfones; the latter being removed later on by extraction or adsorption. The resulting products of this process, namely the corresponding sulfones, all they have relatively high melting and boiling points and are relatively chemically inert [5], the latter normally considered industrial waste.

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Scheme 1. Formation of complexes type $[(\text{dippe})\text{Ni}(\kappa^2-(\text{O},\text{O})-(\text{sulfone}))]$.

Currently, R&D targeting ODS mainly focuses on the improvement of the process for the petrochemical industry [6–10]. However, to the best of our knowledge there are relatively few examples addressing the reactivity afforded by ODS-products. The oxidesulfurization of sulfoxides or the closely related sulfones as is the case of the dibenzothiophene sulfone (DBTO₂) has only been achieved under harsh conditions, either by the use of sodium metal and liquid ammonia [11] or by the use of NiCRA's [12]. Other diphenyl sulfones have also been reacted in the presence of Mg–MeOH; [13] the DBTO₂, the benzothiophene sulfone (BTO₂) [14], benzonaphthothiophene sulfone (BNTO₂) [15] and other closely related sulfones [16] been also reduced by the use of strongly reductive media employing metallic Zn or LiAlH₄. The use of activated metals [17] and di-iodobutylaluminium hydride (Dibal-H) for the reduction of sulfones has also been reported [18]. The use of other methodologies for the reduction of aromatic and heterocyclic sulfones, such as using supercritical water (scH₂O) [19], or the radiolytic [20] and photochemically assisted decompositions of DBT's sulfones [21] have also been informed; the latter method being effective for the desulfurization of methyl-substituted DBT's-sulfones dissolved in 2-propanol, even though the photo-irradiation of BT-sulfones was not found to yield sulfur-free aromatics, producing only acetylated or polymerized products. In the case of alkyl- and aryl-sulfoxides (*vide supra*), their deoxygenation or reduction using Grignard [22], organolithium reagents [23], nickel boride [24] and tin chloride [25] have also been informed.

For several years, our group has been involved in the study of HDS model reactions with different late-transition metals such as platinum [26] and lately, it has also undertaken the study of reactivity of a number of different nickel compounds that yield the catalytic desulfurizations of DBT, MeDBT and Me₂DBT under homogeneous conditions, in the presence of alkyl Grignards [27]. The reactions yielded the corresponding substituted biphenyls; the latter studies rendering the first clear examples of a catalytic desulfurization process for Me₂DBT. A mechanistic proposal providing insight for these reactions, in which the formation of a nickel thiametallacycle was proposed to take place after an initial oxidative addition reaction of the respective thiophene, also addressed in such reports. This encouraged us to study the reactivity of sulfones derived from DBT and its more hindered derivatives with electron-rich nickel complexes; a first series of results derived from such study being disclosed herein.

2. Results and discussion

2.1. Activation of dibenzothiophene sulfones (DBTO₂)

The reaction of $[\text{Ni}(\text{dippe})\text{H}]_2$ (**1**, dippe = 1,2-bis-(di-*iso*-propylphosphino)ethane) with DBTO₂ yielded the compound $[(\text{dippe})\text{Ni}(\kappa^2-(\text{O},\text{O})-(\text{DBTO}_2))]$ (**6**), which depicts the sulfone ligand as coordinated to nickel by the two oxygen atoms (Scheme 1). The same reactivity was observed for all the other sulfones that were used (MeDBTO₂, Me₂DBTO₂). Compound **6** was character-

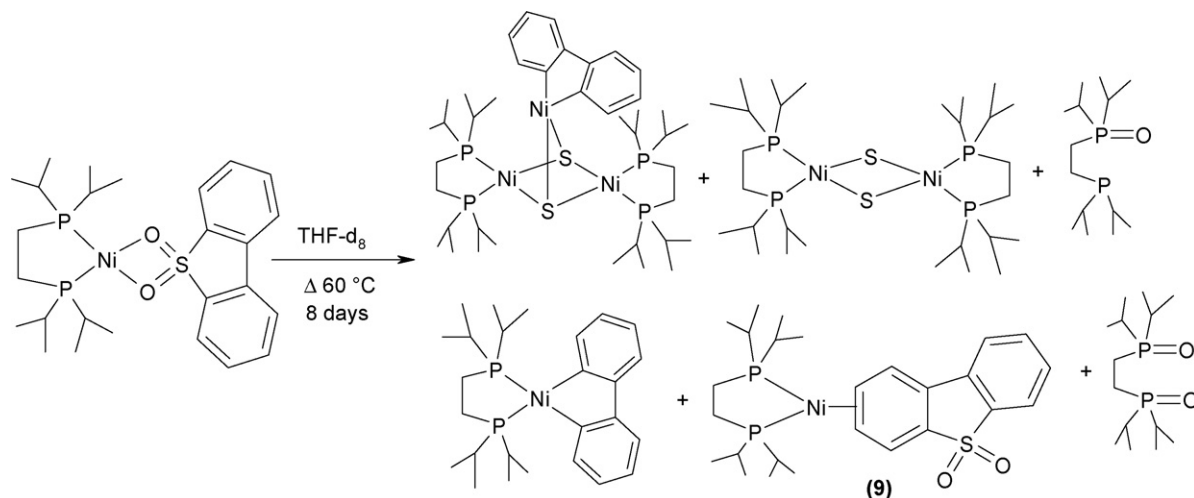
ized by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy in THF-*d*₈ solution at room temperature, the latter showing a singlet at 63.3 ppm, consistent with a symmetric phosphorous environment around the nickel center. The ^1H NMR spectrum displayed all the aromatic protons in the bound sulfone ligand to shield as a result of coordination, appearing in the range of 7.09–6.51 ppm vs. those of the free sulfone (7.96–7.83 ppm); the latter data along with those of all remaining complexes of the type $[(\text{dippe})\text{Ni}(\kappa^2-(\text{O},\text{O})-(\text{sulfone}))]$ (**6–8**), being summarized in Table 1.

Thermolysis of compound **6** at 60 °C was also monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR, using THF-*d*₈ [28]. Several species were detected in solution over the course of 8 d, namely $[(\text{dippe})\text{Ni}(\eta^2-(\text{C},\text{C})-(\text{DBTO}_2))]$ (**9**), $[(\text{dippe})\text{Ni}(\eta^1, \eta^1-(\text{C},\text{C})-(2,2'-\text{C}_{12}\text{H}_8))]$, $\{[(\text{dippe})\text{Ni}(\mu\text{-S})]_2 \cdot [\text{Ni}(\mu\text{-S})(\eta^1, \eta^1-(\text{C},\text{C})-(2,2'-\text{C}_{12}\text{H}_8))]\}$, $[(\text{dippe})\text{Ni}(\mu\text{-S})]_2$, $[(\text{dippe})_2\text{Ni}]$, dippeO and dippeO₂; the reactivity encountered being very similar to the one reported for the thermolysis of thianickelacycles by Jones and Vicic [29,30]. In summary, the formation of these species is regarded as if derived from the cleavage of S–O and C–S bonds of the originally bound sulfone; a feature that is illustrated further in Scheme 2.

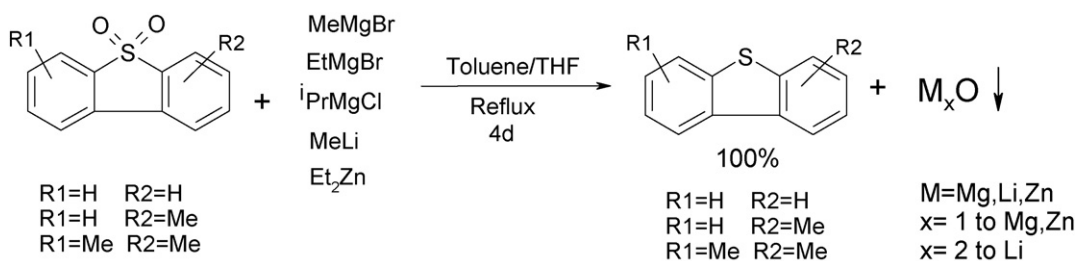
The potential formation of the nickel(0) compound **9** is proposed by the gradual apparition of two doublets at 73.81 and 69.92 ppm, with $^2J_{\text{P-P}} = 71.45$ Hz – typical of nickel(0) – [31] during $^{31}\text{P}\{^1\text{H}\}$ NMR spectra follow-ups, along with two broad multiplets at 6.05 and 5.32 ppm in the corresponding ^1H NMR. In principle, formation of **9** is proposed as a shunt of the desulfurization process as one of the benzene rings of DBTO₂ ultimately coordinates to the $[(\text{dippe})\text{Ni}]$ moiety. The formulation for this compound is inspired on previous observations by our group that showed a quinoline analogue to coordinate in a similar way, the presence of dissimilar chemical shifts for the two phosphorus atoms in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **9**, consistent with the un-equivalence of these two, as expected for such compound. The same follow up was performed over Me- and Me₂-DBTO₂, resulted in a general reactivity; the corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[(\text{dippe})\text{Ni}(\eta^2-(\text{C},\text{C})-(\text{MeDBTO}_2))]$ (**10**) and $[(\text{dippe})\text{Ni}(\eta^2-(\text{C},\text{C})-(\text{Me}_2\text{DBTO}_2))]$ (**11**) analogues, summarized in Table 3 of the SI section.

Table 1
Spectroscopy data for complexes of the type, $[(\text{dippe})\text{Ni}(\kappa^2-(\text{O},\text{O})-(\text{sulfone}))]$

Complex	$^{31}\text{P}\{^1\text{H}\}$	^1H
$[(\text{dippe})\text{Ni}(\kappa^2-(\text{O},\text{O})-(\text{DBTO}_2))]$ (6)	63.33 (s)	7.07 (d, 1H) $^3J_{\text{H-H}} = 7.5$ Hz 6.84 (t, 1H) $^3J_{\text{H-H}} = 7.2$ Hz 6.70 (t, 1H) $^3J_{\text{H-H}} = 7.5$ Hz 6.51 (d, 1H) $^3J_{\text{H-H}} = 6.9$ Hz
$[(\text{dippe})\text{Ni}(\kappa^2-(\text{O},\text{O})-(\text{MeDBTO}_2))]$ (7)	63.16 (s)	7.07 (d, 1H) $^3J_{\text{H-H}} = 7.5$ Hz 6.84 (t, 1H) $^3J_{\text{H-H}} = 7.2$ Hz 6.70 (t, 1H) $^3J_{\text{H-H}} = 7.5$ Hz 6.51 (d, 1H) $^3J_{\text{H-H}} = 6.9$ Hz
$[(\text{dippe})\text{Ni}(\kappa^2-(\text{O},\text{O})-(\text{Me}_2\text{DBTO}_2))]$ (8)	63.19 (s)	7.07 (d, 1H) $^3J_{\text{H-H}} = 7.5$ Hz 6.22 (t, 1H) $^3J_{\text{H-H}} = 7.5$ Hz 5.94 (d, 1H) $^3J_{\text{H-H}} = 7.5$ Hz 2.46 (s, 3H) $^3J_{\text{H-H}} = 6.9$ Hz



Scheme 2. Thermolysis of $[(\text{dippe})\text{Ni}(\kappa^2\text{-}(O,O)\text{-DBTO}_2)]$, at 60 °C.



Scheme 3. Deoxygenation of sulfones with nucleophilic reagents.

2.2. Deoxygenation of sulfones employing nucleophilic reagents

As was mentioned above, the deoxygenation of sulfones employing Grignard reagents has been undertaken over alkyl- and aryl-sulfones [22], the cases derived from DBT and its methyl-substituted analogues been scarcely studied, in contrast. The latter was deemed particularly relevant for the purpose of the current work and thus, the study of such reactivity using a variety of nucleophilic reagents such as MeMgBr, EtMgBr, *i*-PrMgCl, MeLi and Et₂Zn, with the aim of achieving desulfurization was assessed over DBTO₂, 4-MeDBTO₂ and 4,6-Me₂DBTO₂, a quantitative yield (100%)

of the corresponding deoxygenated compounds, DBT, MeDBT and Me₂DBT, obtained for these substrates (see Scheme 3).

The precipitation of the corresponding magnesium, lithium and zinc oxides in these reactions were envisaged as the driving forces for each, the formation of the metal oxides corroborated by powder X-ray diffraction studies. Some additional by-products were also detected in the crude reaction residues depending of the nucleophile source used, the formation of MgBr₂ and CH₃-CH₃ been confirmed on using MeMgBr.

A mechanistic proposal for the deoxygenation of sulfones illustrated for DBTO₂, based on a sulfurane transition state is depicted

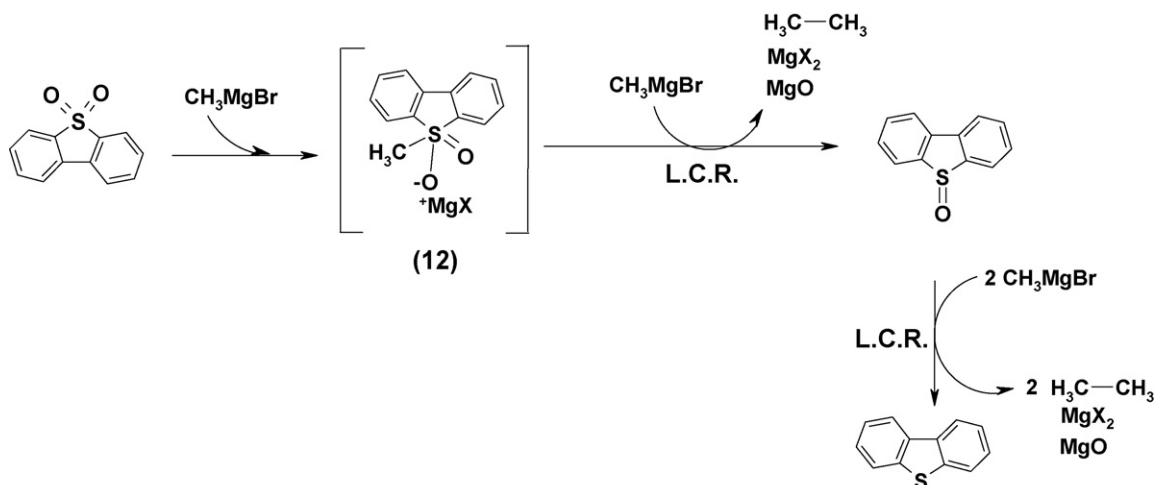


Fig. 1. Mechanistic proposal for the deoxygenation of DBTO₂.

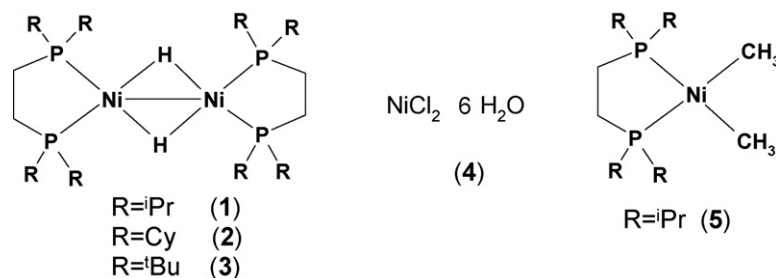
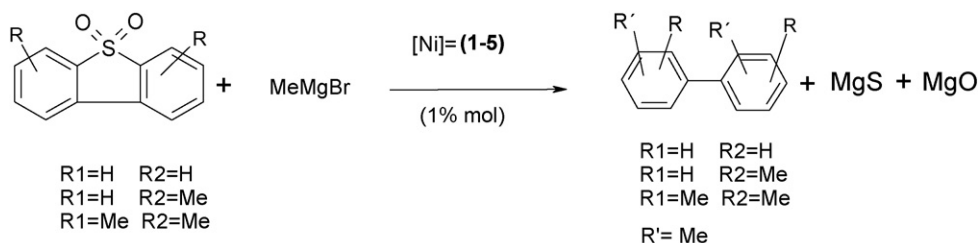


Fig. 2. Nickel catalyst-precursors used for deoxydesulfurization of sulfones.



Scheme 4. Deoxydesulfurization of sulfones using MeMgBr in the presence of nickel compounds.

in Fig. 1 [22,23,32,33]. The mechanistic proposal suggests consecutive nucleophilic attacks by MeMgBr over the sulfur atom of the sulfone, that eventually produce intermediate (**12**); the consecutive nucleophilic attacks by a second equiv. of MeMgBr over this intermediate promoting precipitation of MgBr₂ and MgO and allowing a concomitant ligand coupling reaction that produces ethane. The transient formation of a sulfoxide intermediate is presumed to be formed through this pathway, the consecutive nucleophilic attack by 2 equiv. of MeMgBr to this intermediate resulting in the formation of DBT.

2.3. Catalytic deoxydesulfurization of DBTO₂ with nickel compounds

The catalytic deoxydesulfurization reaction of DBTO₂ was attempted further on, complementary to the previous experiments by our group in the context of desulfurization of DBT's; [27] the reactivity of DBTO₂, 4-MeDBTO₂ and 4,6-Me₂DBTO₂ initially with MeMgBr and a variety

of nickel catalytic precursors (compounds **1–5** in Fig. 2; dcype = 1,2-bis-(dicyclohexylphosphino)ethane, dtbpe = 1,2-bis-(di-*tert*-butylphosphino)ethane), addressed thereof. Scheme 4 illustrates our general findings in this study; a complete table with results included in Table 2.

As indicated in Scheme 4 and in Table 2, the main products of deoxydesulfurization were the methyl-substituted biphenyls derived from cross-coupling with MeMgBr, similarly to the reaction scheme found when starting from the thiophenes directly [27]. A 100% conversion to the mentioned biphenyls (complete deoxydesulfurization) of all the sulfones was encountered when using **1–3** and **5** as catalyst precursors. From these, compounds **1–3** exhibited a particularly high reactivity towards the deoxydesulfurization of 4,6-Me₂DBTO₂ (entries 11–13, Table 2), the use of **4** giving the lowest yields in that instance (entries 14–16); a confirmation of the importance that the ancillary ligands (*i.e.*, alkyl-diphosphines) have over activity and selectivity. In the case of **5**, the fact that complete deoxydesulfurization of DBTO₂ could be achieved while starting from a Ni(II) precursor (entry 17, Table 2), suggests that catalysis

Table 2
Nickel-catalyzed deoxydesulfurization with MeMgBr^a

Entry	Complex (equiv.)	Sulfone (equiv.)	MeMgBr (equiv.)	Solvent	Organic (yield %)
1	1 (1)	DBTO ₂ (100)	(600)	Tol/THF	MePh–Ph (3%) MePh–PhMe (97%)
2	2 (1)	DBTO ₂ (100)	(600)	Tol/THF	MePh–Ph (8%) MePh–PhMe (76%) DBT (16%)
3	3 (1)	DBTO ₂ (100)	(600)	Tol/THF	Ph–Ph (1%) MePh–Ph (7%) MePh–PhMe (77%) DBT (15%)
4	1 (1)	DBTO ₂ (1000)	(6000)	Tol/THF	MePh–PhMe (100%)
5	2 (1)	DBTO ₂ (1000)	(6000)	Tol/THF	MePh–PhMe (100%)
6	3 (1)	DBTO ₂ (1000)	(6000)	Tol/THF	MePh–PhMe (100%)
7	1 (1)	DBTO ₂ (100)	(600)	THF	Ph–Ph (1%) MePh–Ph (44%) MePh–PhMe (24%) Ph–PhSH (2%) MePh–PhSH (14%) DBT (14%)
8	1 (1)	MeDBTO ₂ (100)	(600)	Tol/THF	MePh–PhMe ₂ (4%), Me ₂ Ph–PhMe ₂ (86%) MeDBT (10%)
9	2 (1)	MeDBTO ₂ (100)	(600)	Tol/THF	MePh–PhMe ₂ (99%) MeDBT (1%)
10	3 (1)	MeDBTO ₂ (100)	(600)	Tol/THF	MePh–PhMe (10%) MePh–PhMe ₂ (90%)
11	1 (1)	Me ₂ DBTO ₂ (100)	(600)	Tol/THF	Me ₂ Ph–PhMe ₂ (88%) Me ₂ DBT (12%)
12	2 (1)	Me ₂ DBTO ₂ (100)	(600)	Tol/THF	Me ₂ Ph–PhMe ₂ (99%) Me ₂ DBT (1%)
13	3 (1)	Me ₂ DBTO ₂ (100)	(600)	Tol/THF	Me ₂ Ph–PhMe ₂ (99%) Me ₂ DBT (1%)
14	4 (1)	DBTO ₂ (100)	(600)	Tol/THF	MePh–Ph (3%) MePh–PhMe (87%) DBT (10%)
15	4 (1)	MeDBTO ₂ (100)	(600)	Tol/THF	MePh–PhMe (28%) MePh–PhMe ₂ (36%) MeDBT (37%)
16	4 (1)	Me ₂ DBTO ₂ (100)	(600)	Tol/THF	Me ₂ Ph–PhMe ₂ (8%) Me ₂ Ph–PhMe ₂ SH (2%) Me ₂ DBT (90%)
17	5 (1)	DBTO ₂ (100)	(600)	Tol/THF	MePh–Ph (2%) MePh–PhMe (98%)

^a The reactions were carried out under reflux for 4 d, using 1 mol% of the corresponding nickel precursor. All yields were quantified by GC–MS, after workup.

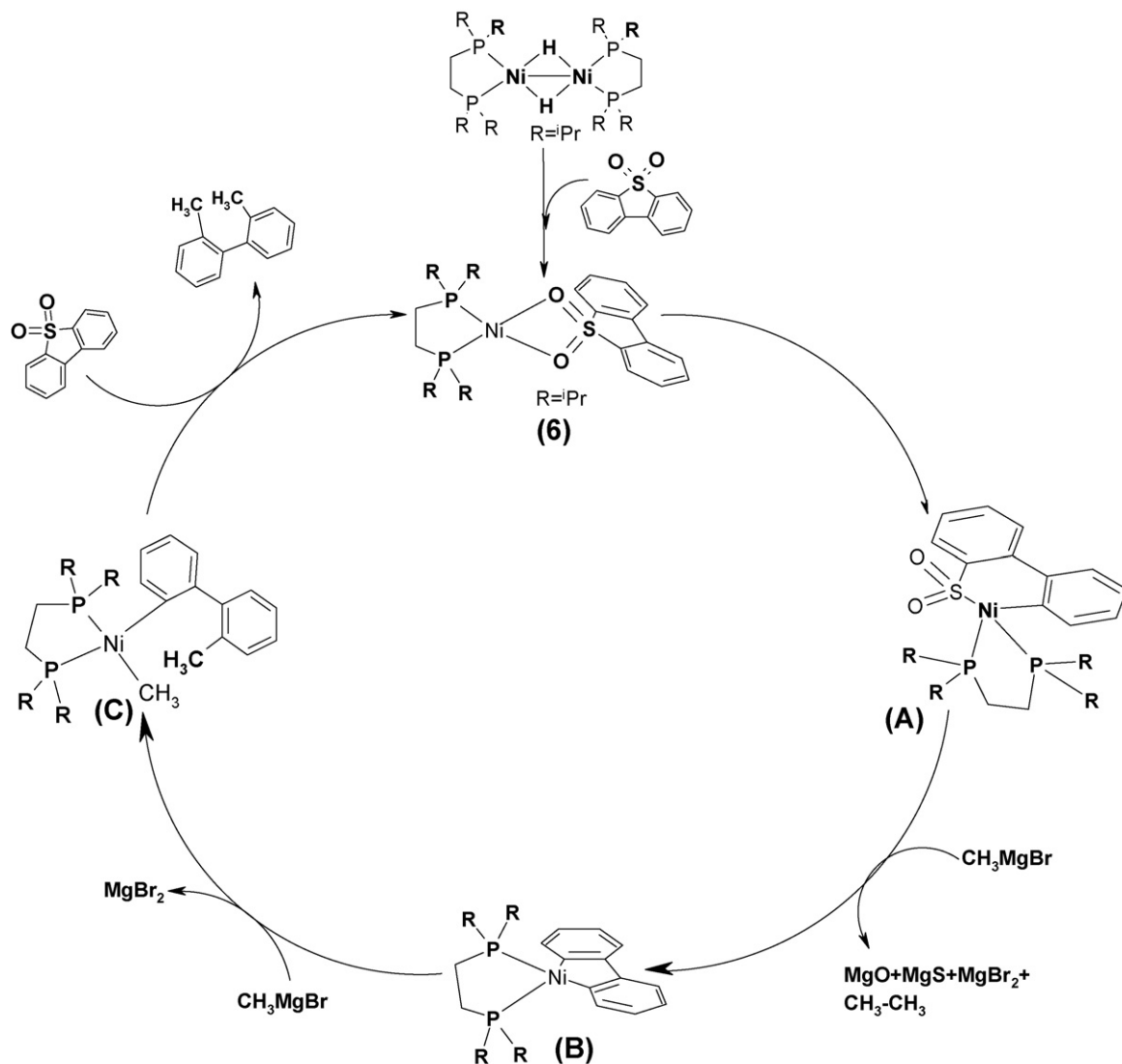


Fig. 3. Mechanistic proposal for the deoxydesulfurization of DBTO₂ using MeMgBr and nickel compounds.

probably involves the *in situ* formation of a Ni (0) intermediate as Pörschke and co-workers have already reported [34], the catalytic deoxydesulfurization of DBTO₂ undergone thereafter.

The use of coordinating solvents such as THF (entry 7, Table 2) leads to the formation of thiols, Ph-PhSH and MePh-PhSh, possibly due to the involvement of a thiolate intermediate within the catalytic process, inducing decoordination of the latter from the nickel catalyst by action of the polar solvent; a feature already observed by our group when undertaking the desulfurization of DBT [27]. To avoid the thiol formation during the deoxydesulfurization process, catalysis was thereof undergone using a mixture of toluene and THF (10:2, v/v), which indeed was deemed to improve the corresponding desulfurization yields (compare for instance with entry 1, in the same table).

To note also, entries 4–6 indicate the results obtained when diluting the catalyst precursor in the reaction media going from 1 (entries 1–3) to 0.1 mol%, a total conversion of DBTO₂ into MePh-PhMe – representing a more active catalytic system for this transformation – confirmed thereof.

Two reaction pathways for the deoxydesulfurization reactions were envisaged on the basis of results obtained from the catalytic runs described above. The first one involves a deoxygenation of

the corresponding sulfone by Grignard reagents (*vide supra*) followed by a desulfurization reaction via cross-coupling reactions, very similar to the mechanistic proposal for the desulfurization of DBT's recently reported by our group [27]. However, given that conversion of the more hindered DBT's in such process were observed to be very low while using the same ancillary alkyl-diphosphine ligands (dippe, dcype or dtbpe), we therefore speculate that in the case of sulfones a second or parallel reaction pathway may be operating (see Fig. 3): the formation of an intermediate of the type [(dippe)Ni(κ²-(O,O)-(DBTO₂))] (6), followed by a C–S bond activation of the sulfone ring, producing a nickelacycle intermediate (A). Extrusion of the sulfur and oxygen atoms in this intermediate by action of the nucleophile (MeMgBr) is predicted to occur next, producing a second metalacycle of the type [(dippe)Ni(η¹,η¹-(C,C)-(2,2'-C₁₂H₈))] (B), in fact predicted from thermolysis follow up of compound 6, described earlier in the text, along with MgS, MgO, MgBr₂ and ethane. The metathesis reaction of intermediate B with 1 equiv. of MeMgBr is presumed to evolve into a methyl-bound nickel(II) intermediate [(dippe)Ni(η¹-Me){η¹-(2-C)-(2'-(Me)-C₁₂H₈)}] (C), from which the observed cross-coupling product 2,2'-(Me)Ph-Ph(Me) is ultimately obtained.

3. Conclusions

An efficient catalytic system for the deoxydesulfurization of DBTO₂, MeDBTO₂ and Me₂DBTO₂ using MeMgBr in the presence of nickel compounds has been developed, the systems studied exhibiting both a high activity and selectivity to the corresponding biphenyls; the latter products formed as a result of cross-coupling reactions with the Grignard reagent. The intermediacy of compounds of the type [(dippe)Ni(κ²-(O,O)-(sulfone))] are proposed as key intermediates of the catalytic cycle leading to the deoxydesulfurization of the corresponding sulfones; further experiments to elucidate the mechanistic pathway that operates for this process being currently underway.

4. Experimental

4.1. General considerations

All procedures were carried out using standard Schlenk and glove box techniques, using an MBraun glovebox (<1 ppm H₂O, O₂) under argon (Praxair, 99.998%). THF (J.T. Baker) was dried and distilled from dark purple solutions of sodium/benzophenone ketyl. Toluene (J.T. Baker) was dried over sodium and distilled under inert atmosphere. MeMgBr (3 M, in ether solution), EtMgBr (1 M, in THF solution), *i*-PrMgCl (2 M, in THF solution), MeLi (1.6 M, in ether solution) were purchased from Aldrich, Et₂Zn was purchased from Alpha and were used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves in the glove box for at least 24 h prior to its use. DBT, MeDBT, Me₂DBT were purchased from Aldrich and were also used as received. [(dippe)NiH]₂ (**1**) [29a] was prepared from Super-Hydride and [(dippe)NiCl₂] [35] suspended in hexane, similarly to the literature procedure; [(dcype)NiH]₂ (**2**), and [(dtbpe)NiH]₂ (**3**) were prepared analogously. The chelating bisphosphine ligand, dippe was synthesized from 1,2-bis(dichlorophosphino)ethane (Aldrich) [36], and the corresponding isopropylmagnesium chloride solution (2.0 M) in THF (Aldrich); dtbpe also prepared according to the published method [37] and dcype was purchased from Strem. [(dippe)Ni(Me)₂] (**5**) was prepared according to the published method [34]. Neutral alumina and silica were heated to 200 °C under vacuum for 2 days and stored in the glovebox. All other chemicals and filter aids were reagent grade and were used as received. Isolated complexes were purified by crystallization or column chromatography. The corresponding sulfones were prepared according to the reported method [38], always dried *in vacuo* prior to use. ¹H, ³¹P{¹H} NMR spectra were determined at room temperature in THF-*d*₈ (nickel compounds) and CDCl₃ (organics). ¹H chemical shifts (δ, ppm) are reported relative to the residual proton resonances in the corresponding deuterated solvent. ³¹P{¹H} NMR spectra were recorded relative to external 85% H₃PO₄. All spectra of molecular nickel compounds were carried out using thin-wall (0.38 cm) WILDMAD NMR tubes with J. Young's valves. GC-MS determinations were performed using a Varian Saturn 3, on a 30-m DB-5MS capillary column. Infrared spectra were obtained using a PerkinElmer 1600 Series FT-IR spectrometer. Analytical, mass spectrometric and powder X-ray determinations (Powder-XRD) were performed by USAI-UNAM. Analytical determinations were performed using an EA 1108 FISON Instruments analyzer. MS-EI⁺ analyses were performed using a Thermo-Electron DFS. Powder-XRD determinations were determined using graphite monochromatized Cu Kα radiation (λ = 1.5406 Å) in a Siemens D5000 diffractometer.

4.2. Preparation of [(dippe)Ni(κ²-(O,O)-(DBTO₂))] (**6**)

A 50 mL Schlenk flask was charged with a THF (7 mL) solution of [(dippe)NiH]₂ (0.05 g, 0.776 mmol) and to it was added DBTO₂ (0.0335 g, 1.55 mmol). The mixture thoroughly stirred at room temperature for 3 h, the resulting red solution dried under high vacuum (*P* < 10⁻⁴ mmHg) in a Schlenk line. A red solid residue was obtained, the latter been re-dissolved in hexanes and filtered via cannula to a new Schlenk flask. Solvent was again removed under vacuum, the resulting product further dried *in vacuo* for at least 4 h. Yield: 85% of a red powder. Anal. Calcd. for C₂₆H₄₀SO₂P₂Ni: %C 58.11, %H 7.50, %S 5.96. Found: %C 58.2, %H 7.51, %S 6.0. MS-EI⁺ (*m/z*): {M⁺-DBT} = 355. FT-IR (cm⁻¹, in KBr disc) 2962 (w), 1261 (s), 1092 (vs), 1021 (vs), 799 (s). ¹H NMR (THF-*d*₈, 25 °C, 300 MHz): δ 7.07 (d, ³J_{H-H} = 7.5 Hz, 2H), 6.84 (d, ³J_{H-H} = 7.2 Hz, 2H), 6.70 (t, ³J_{H-H} = 7.5 Hz, 2H), 6.51 (t, ³J_{H-H} = 6.9 Hz, 2H), 2.06–1.88 (m), 1.52–1.42 (m), 1.80–0.85 (m). ¹³C{¹H} (THF-*d*₈, 25 °C, 75.4 MHz): δ 99.74 (s), 99.73 (s), 119.38 (s), 122.23 (s), 123.97 (s), 126.73 (s), 25.86 (s), 21.558 (pseudo t, ²J_{P-C} = 18.47 Hz), 18.814 (s). ³¹P{¹H} (THF-*d*₈, 25 °C, 121.32 MHz): δ 63.326 (s).

4.3. Reactivity of sulfones with MeMgBr

A representative experiment was made as follows: in the glove box, a 50-mL Schlenk flask was charged with a solution of MeMgBr (0.37 mL, 1.1 mmol, 3 M) and DBTO₂ (0.04 g, 0.184 mmol), dissolved in a mixture of Toluene/THF (10:2, v/v), with constant stirring giving a yellow solution. The reaction mixture was refluxed under argon in a Schlenk line, constantly stirred for 4 d. A white precipitate was observed to form gradually, heating was stopped and the mixture hydrolyzed once room temperature had been reached, using HCl (10 mL, 10%) in a well-vented fume hood. The remaining residue was then extracted using CH₂Cl₂ washings (3 × 10 mL), the organic layer separated from the aqueous one in a funnel and dried using anhydrous MgSO₄, collected and analyzed by GC-MS.

4.4. Catalytic deoxydesulfuration of sulfones

A typical experiment was made as follows: in the glove box, a 50-mL Schlenk flask was charged with [Ni(dippe)H]₂ (0.002 g, 0.0031 mmol) and DBTO₂ (0.067 g, 0.31 mmol), and to it was added a 10:2 v/v mixture of toluene (10 mL) and THF (2 mL), the resulting solution constantly stirred for 30 min, at room temperature. After complete mixing and venting all the released gases in the dry box, a 3.0-M solution of MeMgBr (0.62 mL, 1.86 mmol) was added to the mixture, the solution observed to change from red to orange. The reaction mixture was then heated to reflux for 4 d under argon atmosphere in a Schlenk line; during which time, a blend of precipitates (beige to brown) was observed to form gradually. Heating was stopped after the mentioned time, the mixture hydrolyzed at room temperature, following the procedure described above. A strong effervescence was observed upon addition of the mineral acid, consistent with release of H₂S (*caution poisonous gas!*), which was bubbled into a concentrated Pb(CH₃COO)₂ solution in water trap thereby precipitating PbS as a black solid. After the venting of all gases, the latter mixture was extracted with CH₂Cl₂ (3 × 7 mL), and the organic layers separated and dried as described above and then analyzed by GC-MS. To note, whenever the characterization of the solid was required, acid hydrolysis was avoided; the reaction mixture centrifuged and washed with hexanes and acetone. The solid was dried for 4 h under high vacuum and analyzed by Powder-XRD against MgO, MgBr₂ and MgS standards.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.06.015.

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