FULL PAPERS

Alkyl- and Arylthiolation of Aryl Halides Catalyzed by Fluorinated Bis-Imino-Nickel NNN Pincer Complexes [NiCl$_2${C$_5$H$_3$N-2,6-(CHNAr$_f$)$_2$}]

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Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: The synthesis of bis-imino nickel(II) NNN pincer complexes of the type [NiCl$_2${C$_5$H$_3$N-2,6-(CHNAr$_f$)$_2$}]; Ar$_f$=C$_6$H$_3$-2,3-F$_2$ (**1**), C$_6$H$_3$-2,5-F$_2$ (**2**), C$_6$H$_3$-3,4-F$_2$ (**3**), C$_6$H$_3$-3,5-F$_2$ (**4**), C$_6$H$_2$-2,3,4-F$_3$ (**5**), C$_6$H$_2$-2,3,6-F$_3$ (**6**), C$_6$H$_2$-2,4,5-F$_3$ (**7**), C$_6$H$_2$-2,4,6-F$_3$ (**8**), has been achieved and their reactivity in alkyl- and arylthiolation reactions of halobenzenes examined. The use of fluorinated substituents Ar$_f$ on the imines has allowed the tuning of the electronics in these complexes and the influence of these substituents and those of the disulfides in the thiolation reactions have been analyzed.

Keywords: C−S cross-coupling; fluorinated ligands; homogeneous catalysis; nickel; pincer complexes; thiolation

Introduction

Recently, there has been an increasing demand for efficient, high-yield methods for the synthesis of diaryl thioethers and alkyl aryl thioethers owing to their importance as structural motifs in a wide range of molecules with numerous and important applications.[1] In addition, the scope and application of organosulfur chemistry in organic synthetic reactions has increased tremendously since sulfur-containing groups serve as important auxiliary functions in synthetic sequences,[2] for instance, in the reversal of the polarity (Umpolung), the enhancement of the acidity of C−H bonds, and the transfer of chirality from sulfur to carbon.[3] Furthermore, aryl sulfides are a common functionality found in numerous pharmaceutically active compounds.[4] In fact, a number of drugs in therapeutic areas such as diabetes and anti-inflammatory, immune, Alzheimer's and Parkinson's diseases contain the aryl sulfide functionality.[5] On the other hand, transition metal complex-catalyzed reactions have made a great contribution to the recent growth of organic synthesis.[6] Considerable attention has also been focused on sulfur-containing transition metal complexes as models of active sites of natural enzymes[7] and catalytic metal surfaces.[8] However, transition metal complex-catalyzed synthetic reactions using sulfur-containing compounds remain open to study, since sulfur compounds have long been known to act as catalyst poisons, often rendering the catalytic reaction to be totally ineffective.[9] Thus, recently several useful transformations of sulfur-containing compounds using transition metal catalysts have been developed.[10] The metal-catalyzed synthesis of aryl sulfides has included the cross-coupling of thiols with aryl halides using copper or palladium catalyst under basic conditions,[11] however, the metal-catalyzed thiolation of aryl halides with disulfides has rarely been done, despite the fact that the efficient use of (RS)$_2$ in the catalytic thiolation of alkyl halides has been reported.[12]

We believe that a robust complex used as catalyst may render a better performance in the alkyl- and arylthiolation of halobenzenes. Thus, following our continuous interest in the use of pincer type-compounds[13] for novel organic transformations and the use of aromatic fluorinated substituents[13] for the tuning of steric and electronic properties, we report our findings in the use of fluorinated bis-iminonickel(II) NNN pincer complexes [NiCl$_2${C$_5$H$_3$N-2,6-(CHNAr$_f$)$_2$}] as efficient catalysts for the cross-coupling of (RS)$_2$ and halobenzenes.

Results and Discussion

The reaction of one equivalent of the potentially tridentate pincer NNN ligands with one equivalent of $NiCl_2 \cdot 6\,H_2O$, affords the corresponding complexes $[NiCl_2\{C_5H_3N\text{-}2,6\text{-}(CHNAr_f)_2\}]$; $Ar_f = C_6H_3\text{-}2,3\text{-}F_2$ (**1**), $C_6H_3\text{-}2,5\text{-}F_2$ (**2**), $C_6H_3\text{-}3,4\text{-}F_2$ (**3**), $C_6H_3\text{-}3,5\text{-}F_2$ (**4**), $C_6H_2\text{-}2,3,4\text{-}F_3$ (**5**), $C6H_2\text{-}2,3,6\text{-}F_3$ (**6**), $C_6H_2\text{-}2,4,5\text{-}F_3$ (**7**), $C_6H_2\text{-}2,4,6\text{-}F_3$ (**8**) in high yields. Analysis by NMR reveal these compounds to be paramagnetic, exhibiting broad signals in all cases. The magnetic moments for all complexes at room temperature (297 K) are in the range of 2.8–3.4 B. M. as expected for high-spin five-coordinate nickel-(II) complexes, these values are in good agreement with those reported in the literature.[14] Analysis of the pincer compounds by FAB+-MS spectrometry affords in most of the cases the molecular ion minus one chloride $[M - Cl]^+$, other important peaks include the consecutive loss of the remaining chlorides. In all cases elemental analysis are consistent with the proposed formulations.

Crystals suitable for single crystal X-ray diffraction analyses (Table S1 in the Supporting Information) were obtained for complexes **4** and **7**, the two structures share a number of common features, the only difference being the fluorinated substituent. In both complexes the nickel centers are pentacoordinated in a distorted trigonal bypiramidal geometry (TBP), with the two chlorides occupying the equatorial plane. The three nitrogens of the NNN pincer ligands occupy the remaining coordination sites. The average Ni−N bond distances of the NNN pincer ligand are of 2.109 Å (**4**) and 2.1207 Å (**7**), respectively. For both compounds the terminal Ni−N bond distances are somewhat longer than the central Ni(1)−N(1) bond distances being 1.964(3) Å (**4**) and 1.952(2) Å (**7**), respectively. The variation of these distances can be related to the packing of the molecules in the crystal lattice.

As in previous cases, we have focused on the use of pincer-type ligands and their complexes for novel organic transformations, and the selection of these ligands has been done on the basis of the robustness that they confer to the transition metal complexes they form.[15] Given the importance that cross-coupling reactions using palladium complexes have gained, we decided to attempt cross-coupling reactions, using nickel complexes, for an important process in organic chemistry, namely the synthesis of mixed alkyl aryl sulfides. This reaction has been previously reported using palladium or copper catalysts as in the Ullmann process, however, in most of the cases this reaction requires the use of the free thiol and basic conditions with prolonged reaction times. We believe that given the robustness that the present complexes offer, we may have a good chance to carry out similar catalysis using disulfides $(RS)_2$ instead of the free thiol. Thus, all the series of complexes were initially tested in the catalytic reaction of C_6H_5I with $(MeS)_2$ in the presence of zinc; the presence of zinc is fundamental because in its absence the catalytic reaction does not

proceed, neither in the absence of the nickel complex. From all the compounds tested (Table 1), complex $[NiCl_2\{C_5H_3N\text{-}2,6\text{-}(CHNC_6H_2\text{-}2,3,4\text{-}F_3)_2\}]$ (**5**) afforded the higher yields (90%), thus all the following experiments were carried out using this complex as catalyst.

Using the same reaction conditions employed for the methylthiolation of iodobenzene, the alkylthiolation of iodobenzene with different disulfides, using complex **5** as catalyst, was attempted (Table 2).

From Table 2 it is evident that the performance of the reaction has a clear dependence on the steric hindrance of the substituents in the disulfide, thus affording similar yields in the case of *iso*-propyl, *n*-butyl, *sec*-butyl and phenyl (an average of 75% yield) and affording only 60% yield in similar reaction times for the di-*tert*-butyl disulfide. These results can be rationalized in terms of steric hindrance at the nickel center since, as will be discussed further, activation of the $(RS)_2$ by the metal center is probably necessary first, this would probably give rise to a dithiolate nickel(II) complex which, in turn, must further react with iodobenzene. From these assumptions, it is clear that, as the size of the substituent in the $(RS)_2$ increases, the facility with which further addition of the halogenated compound could take place will decrease or even cease.

Attempts to carry out the same transformation using chloro- or bromobenzene were unsatisfactory, affording only 4% yield in the case of bromobenzene and only traces in the case of chlorobenzene (Table 3). These results were expected given the energy requirements for the cleavage of the C−Cl and C−Br bonds being higher in both cases that those required to break the C−I bond.

In an attempt to explore the effect of the substituents in the *para*-position for different bromobenzenes (Tables 4 and 5), we carried out some methylthiolation experiments, finding that indeed the presence of electron-withdrawing groups in the aromatic ring favors the cross-coupling process, the best results being obtained with $p\text{-HCO-}C_6H_4Br$ (35% yield).

It has been proposed that these sorts of reactions with nickel must proceed through Ni(0)/Ni(II) intermediates,[16] and it is possible that a similar mechanism may be working in the present case. Supporting proof for this assumption is that the analogous Ni(II) complex (**9**) undergoes reversible redox processes from Ni(I)-Ni(II)-Ni(III).[17]
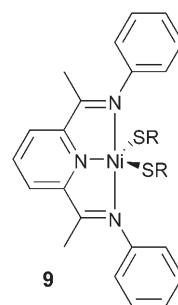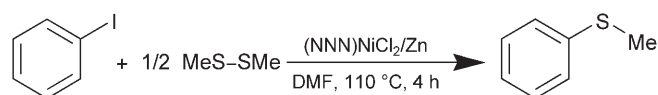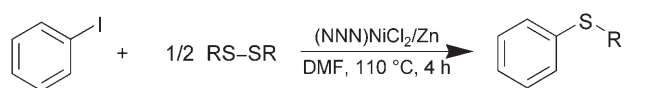

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Table 1. Methylthiolation of iodobenzene by [NiCl₂{C₅H₃N-2,6-(CHNAr_f)₂}] complexes.

Complex	Ni(II) complexes	Yield [%][a]
1		70
2		57
3		85
4		68
5		90
6		70
7		73
8		75%

[a] Yields obtained by GC-MS are based on haloarene.

Table 2. Alkyl- and arylthiolation of iodobenzene by [NiCl₂{C₅H₃N-2,6-(CHNC₆H₂-2,3,4-F₃)₂}] (**5**).

Entry	RS—SR	Yield [%][a]
1		90%
2		74%
3		75%
4		73%
5		60%
6		75%

[a] Yields were determined by GC-MS and are based on C₆H₅I.

Table 3. Methylthiolation of aryl halides by [NiCl₂{C₅H₃N-2,6-(CHNC₆H₂-2,3,4-F₃)₂}] (**5**).
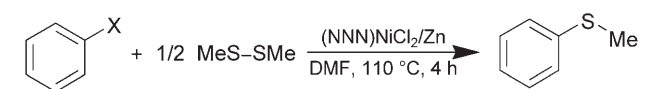
X= Cl, Br, I

Entry	Ph—X	Yield [%][a]
1	Cl	Traces
2	Br	4%
3	I	90%

[a] Yields obtained by GC-MS are based on haloarene.

Table 4. Nickel-catalyzed coupling of dimethyl disulfide with 4-bromoaryl compounds by [NiCl$_2$[C$_5$H$_3$N-2,6-(CHNC$_6$H$_2$-2,3,4-F$_3$)$_2$]] (**5**).
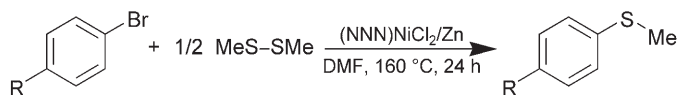
Entry	p-R−C$_6$H$_4$Br	Yield [%][a]
1		13%
2		5%
3		35%
4		4%
5		traces
6		6%
7		3%

[a] Yields obtained by GC-MS are based on haloarene.

Table 5. Nickel-catalyzed coupling of dialkyl and diaryl disulfides with 4-bromoaryl compounds by [NiCl$_2$[C$_5$H$_3$N-2,6-(CHNC$_6$H$_2$-2,3,4-F$_3$)$_2$]] (**5**).
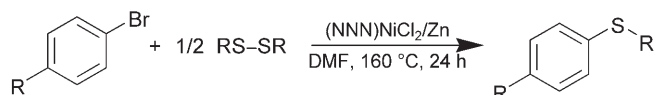
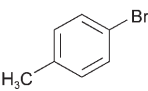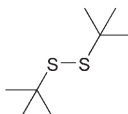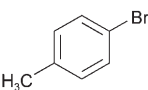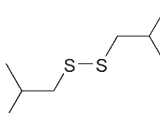| Entry	Bromides	RS-SR	Yield [%][a]
1			11
2			10
3			22
4			Traces
5			20
6			23
7			26
8			19
9			Traces
10			24
11			6
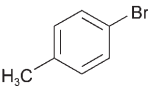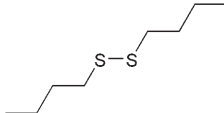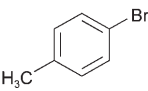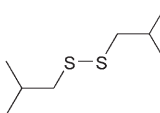
It is also known that nickel complexes rapidly insert into a disulfide bond to afford (RS)$_2$Ni complexes.[18] Thus, it would be logical to think that one of the first steps in the catalytic process would be the reduction of the Ni(II) complex by metallic zinc, further activation by this new Ni(0) complex of the disulfide RS−SR would lead to the cleavage of the S−S bond to afford a dithiolate Ni(II) species. At this point it is important to mention that as the size of the substituent in the thiolate increases the (RS)$_2$Ni complex becomes more stable;[19] this fact would explain why the reaction with sterically hindered disulfides affords lower yields, since the resulting intermediate would prefer to stay as a dithiolate species rather than react further.

Once the nickel dithiolate complex has been formed, the metallic zinc would reduce this Ni(II) species to a Ni(I) thiolate complex of the type [Ni(I)(NNN)(SR)]. After this, the oxidative addition of iodobenzene may produce a Ni(III) complex of the type [Ni(III)-(NNN)(SR)(C$_6$H$_5$)(I)], elimination of the desired prod-

Table 5 (cont.)

Entry	Bromides	RS-SR	Yield [%][a]
12			4
13			18
14			Traces
15			5

[a] Yields obtained by GC-MS are based on haloarene.

uct Ar−SR would yield an unsaturated [Ni(II)-(NNN)(SR)] species that, after a new reduction with more metallic zinc, would restart the catalytic cycle all over again (Scheme 1). However, the present mechanistic proposal may have other logical variations that cannot be ruled out at this point; hence experiments aimed to validate the proposed mechanism are currently under process and will be disclosed elsewhere.

Conclusion

In conclusion, we have designed a high-yield one-pot synthesis for asymmetrical alkyl aryl thioethers from disulfides and iodobenzene in the presence of metallic zinc as an indispensable reducing agent, this method can efficiently use (RS)$_2$ as a thiol source under neutral conditions. Experiments changing iodo- for bromo- and chlorobenzene suggest that the system probably has to be more robust to carry out the reaction at the higher temperatures required to provide the necessary energy to activate the more robust C−Br and C−Cl bonds. Based on the models we have employed successfully for the Heck reaction, we are currently employing Ni(II)-phosphine and phosphinite pincer complexes of the type [PCPNiCl], these results will be reported elsewhere.

Experimental Section

Materials and Methods

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glass-ware. Solvents were dried using standard procedures and distilled under dinitrogen immediately prior to use. The IR spectra were recorded on a Nicolet-Magna 750 FT-IR spectrometer as nujol mulls. The ^{1}H NMR (300 MHz) spectra were recorded on a JEOL GX300 spectrometer. Chemical shifts are reported in ppm downfield of TMS using the residual solvent (CDCl$_3$, δ = 7.27) as internal standard. ^{19}F{^{1}H} spectra were recorded with complete proton decoupling and are reported in ppm using C$_6$F$_6$ as external standard. Elemental analyses were determined on a Perkin-Elmer 240. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operated at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol (NOBA) matrix using 3 keV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material or, alternatively, by electric field scans with the sample peak bracketed by two (polyethylene glycol or cesium iodide) reference ions. Melting points were determined in a MEL-TEMP capillary melting point apparatus and are reported without correction. GC-MS analyses were performed on an Agilent 6890N GC with a 30.0 m DB-1MS capillary column coupled to an Agilent 5973 Inert Mass Selective detector.

Dialkyl and diaryl disulfides and halobenzenes were obtained commercially from Aldrich Chem. Co. and used as received without further purification. The bis-imino NNN pincer ligands {C$_5$H$_3$N-2,6-(CHNAr$_f$)$_2$} were synthesized according to the published procedures.[20]

### General Procedure for the Synthesis of Complexes [NiCl$_2${C$_5$H$_3$N-2,6-(CHNAr$_f$)$_2$}]

All complexes were synthesized by the following method illustrated for the synthesis of [NiCl$_2${C$_5$H$_3$N-2,6-(CHNC$_6$H$_3$-2,3-F$_2$)$_2$}] (**1**).

Synthesis of [NiCl$_2${C$_5$H$_3$N-2,6-(CHNC$_6$H$_3$-2,3-F$_2$)$_2$}] (1)

A solution of the ligand {C$_5$H$_3$N-2,6-(CHNC$_6$H$_3$-2,3-F$_2$)$_2$} (120 mg, 0.33 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL) was added to a stirred solution of NiCl$_2$·6 H$_2$O (0.078 g, 0.33 mmol) in absolute methanol (10 mL). The resulting green solution was stirred at room temperature for 2 h. After this time an orange suspension is noted and the solvent evaporated under vacuum. The product was purified by recrystallization from MeOH; the resulting precipitated was filtered and washed with hexane (3 × 5 mL) and dried under vacuum. Crystals suitable for single crystal X-ray diffraction studies were obtained from a dichloromethane/methanol (4:1) solution. An orange solid was obtained; yield: 142 mg (88%); mp: 240 °C (dec.).

Alkyl- and Arylthiolation of Halobenzenes

Under an atmosphere of nitrogen, a solution of 4.9 mmol of halobenzene, 2.45 mmol of the corresponding dialkyl or diaryl disulfide, 0.0057 mmol of the corresponding catalyst and 202 mg (0.924 mmol) of diethylene glycol di-n-butyl ether (internal standard) in 3.0 mL of DMF, was introduced into a Schlenk tube containing a magnetic stir bar and charged with 4.9 mmol of zinc dust. The tube was sealed and fully immersed
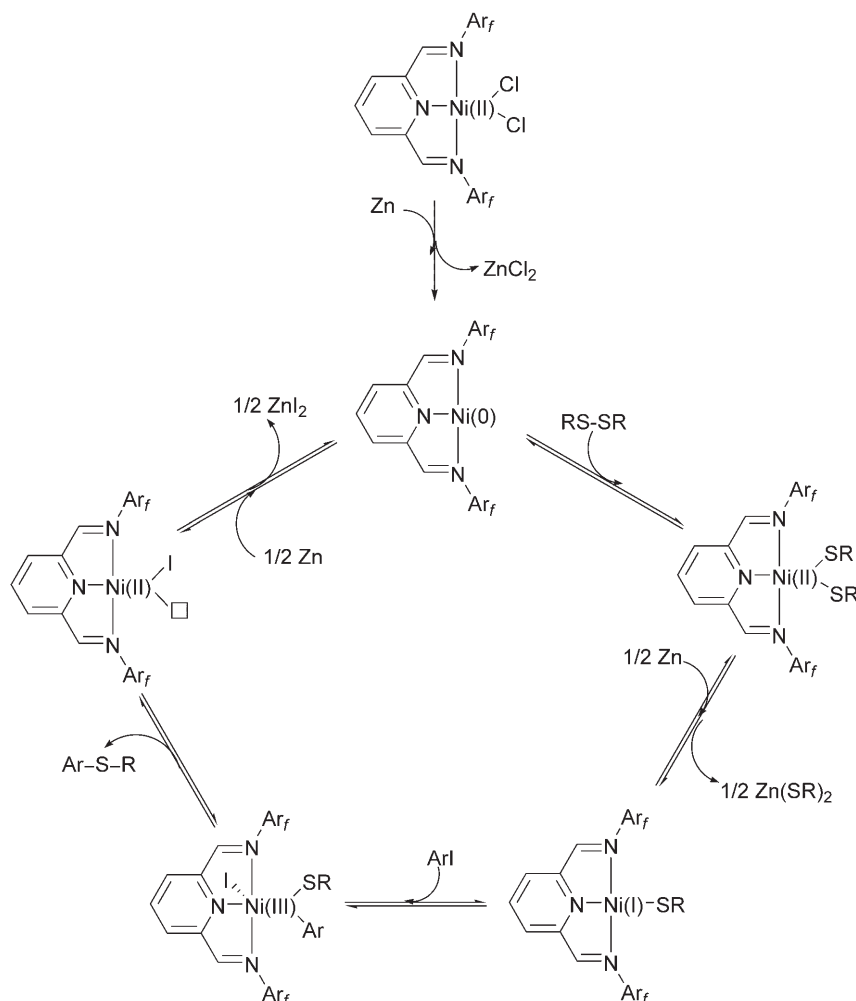
Scheme 1. A mechanistic proposal for the thiolation of halobenzenes using fluorinated bis-imino-nickel NNN pincer complexes [NiCl$_2${C$_5$H$_3$N-2,6-(CHNAr$_f$)$_2$}].

in a 110 °C or a 160 °C silicon oil bath. After 4 h or 24 h, the reaction mixture was cooled to room temperature and the organic phase analyzed by gas chromatography (GC-MS).

Crystallographic data for complex **4** and **7** have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the deposition numbers CCDC 267432 and CCDC 267433.

Supporting Information

Supporting information includes complete characterization data of complexes **1** to **8** and crystallographic data for complexes **4** and **7**.

Acknowledgements

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