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C-S cross-coupling reactions catalyzed by a non-symmetric phosphinito-thiophosphinito PSCOP-Ni(II) pincer complex

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ABSTRACT

A new non-symmetric phosphinito-thiophosphinito POCSP-Ni(II) pincer compound was synthetized and characterized. The molecular structure of [NiCl{C_6H_3-2-($OPPh_2$)-6-($SPPh_2$)}] (**1**) was unequivocally determined by single crystal X-ray diffraction analysis, showing the Ni center to be located into a slightly distorted square planar geometry. This compound was used as efficient catalyst in C-S couplings of disulfides with iodobenzenes, exhibiting good activity and selectivity as well as tolerance to different functional groups.

Introduction

Pincer complexes have played a protagonist role in catalysis for the last two decades, this being greatly due to their high stability reactivity and easy functionalization. Thus, these compounds have been widely used as efficient catalysts in reactions where difficult to activate bonds are involved, standing out their use in C-H activation processes and cross coupling reactions, among many other applications [1–21]. In spite if this, their use as catalyst for C-S cross-coupling reactions has been little explored [22–24].

C-S cross-coupling is an important process for industry, because these reactions can provide access to simple procedures for the production of biological and medicinal relevant substances such as herbicides and drugs [25]. This catalytic reaction has been promoted by different transition metals like Co [26], Pd [27–29], Cu [30–32] and Ni [33–36]. In this line, our group has described some relevant examples of catalysts based on pincer complexes capable to promote C-S cross-coupling reactions. Fig. 1 shows some of them based on NNN [37,38], SNS [39], SPS [40] and POCOP [41] pincer complexes. However, in recent years a trend to use non-symmetric pincer compounds [16] as catalysts has become more popular since this species may provide enhanced reactivities compared to their symmetric counterparts, but their use has been often hampered by long and often low yield synthetic procedures to attain these species. Thus, following our continuous interest in the development of pincer complexes and their applications as efficient catalysts in different relevant transformations, here we described the facile, high yield synthesis and characterization of a new non-symmetric phosphinito-thiophosphinito POCSP-Ni(II) pincer compound and its use as efficient catalysts in C-S couplings of disulfides with iodobenzenes.

Results and discussion

Synthesis and characterization of [NiCl{C_6H_3-2-($OPPh_2$)-6-($SPPh_2$)}] (1) [42]

The synthesis of the phosphinito-thiophosphinito POCSP-Ni(II) pincer complex was performed in a single step starting from 3-mercaptophenol (Scheme 1) [43]. The reaction of 3-mercaptophenol with chlorodiphenylphosphine in the presence of triethylamine affords the pincer ligand precursor (A) which upon reaction with $NiCl_2$ under reflux conditions produced complex (**1**) in good yields. Complex (**1**) was characterized by different analytical techniques such as ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR, mass spectroscopy and elemental analyses. Besides this, the structure of compound

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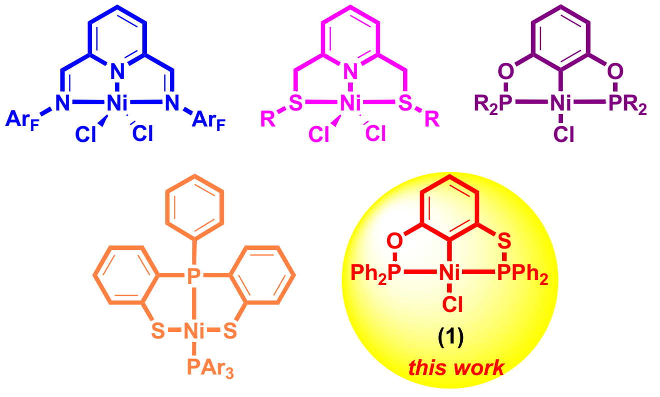
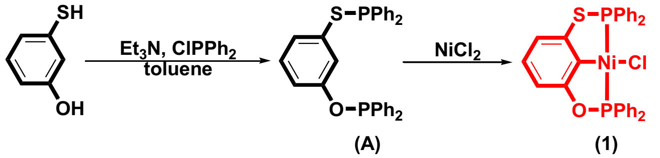


Fig. 1. Examples of pincer complexes used for C-S cross-coupling.



Scheme 1. Synthesis of [NiCl{C_6H_3-2-($OPPh_2$)-6-($SPPh_2$)}] (**1**).

(**1**) was unequivocally determined by single crystal X-Ray diffraction techniques.

Thus, the ^{1}H NMR spectrum of (**1**) is not very informative, as only shows signals due to the aromatic fragments in the typical region expected for aromatic hydrogen atoms. However, more informative results the ^{13}C{^{1}H} where the number of signals expected for the proposed structure are observed in the expected chemical shifts, being notable a characteristic signal due to the C-Ni bond that appears as a doublet of doublets at 142.7 ppm ($^2J_{CP}$ = 25.5, 16.7 Hz). Also, of interest the ^{31}P{^{1}H} NMR spectrum obtained, that displays two groups of signals as doublets. The first one being located at 137.9 ppm ($^2J_{PP}$ = 367 Hz) corresponding to the phosphinito moiety, while the signal due to the thiophosphinito moiety is observed at higher field at 66.4 ppm ($^2J_{PP}$ = 367 Hz), signals which are also in agreement with the non-symmetric nature of the phosphinito-thiophosphinito PSCOP-Ni(II) pincer compound (**1**). Completing this characterization, the analysis by mass spectrometry produced a spectrum showing a peak due to the molecular ion at 586 *m*/*z*. All these results and those of the elemental analysis agree with the proposed structure.

In addition, suitable crystals of (**1**) for their analysis by single crystal X-ray diffraction techniques were obtained by slow diffusion of diethyl ether into a concentrated solution of (**1**) in dichloromethane. Allowing the unequivocal determination of the structure of (**1**) [44]. Complex (**1**) crystallizes in the monoclinic crystal system and $P2_1/n$ space group. The molecular structure exhibits a disorder in the central aromatic ring and bridge atoms (O, S). As can be seen in Fig. 2, the nickel atom is coordinated in a square-planar fashion, with the POCSP pincer ligand coordinated in a typical meridional tridentate manner and one chlorine ligand completing the coordination sphere about the nickel. Noteworthy the fact that the strain of one of the 5 membered metallocycles formed is partially alleviated by the larger size of the sulphur atom.

The Ni-P distances are very similar among them, 2.160(1) Å for Ni-*P*1 and 2.163(1) Å for Ni-*P*2. Because the molecular structure is disordered, some lengths and angles are slightly different. In all other senses the bond distances and angles are similar to those reported for analogous compounds (however no full comparison could be made due to the fact that values for some bond distances and bond angles of this complex were not given due to the strongly disordered POCSP ligand in the refereed compound) [46].

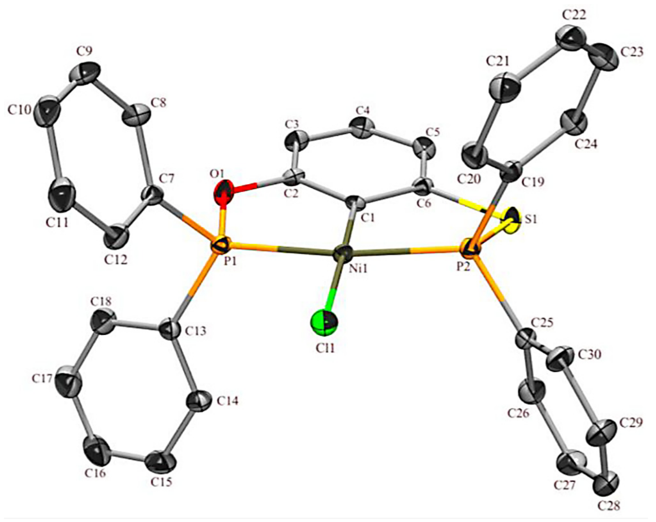


Fig. 2. Molecular structure of (**1**). Selected bond lengths (Å): Ni–C1A 1.913(7), Ni–C1B 1.867(11), Ni–Cl 2.198(1), Ni–*P*1 2.160(1), Ni–*P*2 2.163(1), *P*1–O1A 1.649(8), *P*1–S1B 2.054(5), *P*2–S1A 2.149(2), *P*2–O1B 1.534(9). Selected bond angles (°): C1A–Ni–Cl 177.4(9), C1B–Ni–Cl 177.6(8), C1A–Ni–*P*1 83.6(5), C1B–Ni–*P*1 88.6(8), *P*1–Ni–*P*2 170.8(1), *P*1–Ni–Cl 94.8(1), *P*2–Ni–Cl 94.1(1).

*Catalytic evaluation of [NiCl{C_6H_3-2-($OPPh_2$)-6-($SPPh_2$)}] (**1**) in C-S cross-couplings [47]*

The catalytic activity of complex (**1**) was evaluated in the C-S cross-coupling reaction (Table 1). First, we carried out the catalytic reaction using iodobenzene and diphenyl disulphide as substrates, using 0.3 mol % of catalyst at 110 °C for 4 h. Under these conditions a 26% of conversion (Entry 1, Table 1) was obtained. In order to improve this result, we decided to modify the reactions conditions and increase the temperature and the reaction time, attaining a 99% of conversion at 140 °C for 16.5 h (Entry 2, Table 1), while at 130 °C for 22 h a 60% of conversion was produced.

The latter conditions were chosen to better observe the potential effects of sterics and electronics on the yield of the reactions. In terms of electronic effects, we did not make an exhaustive comparison, however we compared three points having as *para* substituents —H (0.0), —NH_2 (−0.66) and —$COCH_3$ (0.05) in terms of the Hammett parameter [48], although the amino substrate was expected to show lower yields in comparison to —H and —$COCH_3$ we were glad to observe that even with this substrate that typically hinders the reaction we got good yields with the present catalytic system. Then, since the iodobenzene *para* substituted with —$COCH_3$ (4-Iodoacetophenone) produced the best conversions we further evaluated the steric effect of different substituents at the disulphide substrates on the C-S coupling reactions using this substrate. In this study, we chose functional groups with different size, namely phenyl, methyl, *n*-butyl, *sec*-butyl and *tert*-butyl (Table 1). We observed that using the substrate with less steric hindrance, *i.e.* dimethyl disulphide (Entry 6, Table 1), the conversion was up to 91%, while the conversion with a more sterically demanding substrate, such as di-*tert*-butyl disulphide, dramatically decreased to 10%. Thus, it is clear that the more steric hindrance of the disulphide substituents, the less conversion is obtained. This trend has been previously observed by our research group leading to the conclusion that this is due to the size of the cavity in the pincer catalyst [37–41]. And given the fact that no appreciable change in the size of the cavity is produced by changing from the POCOP to the POCSP system, a similar trend was expected.