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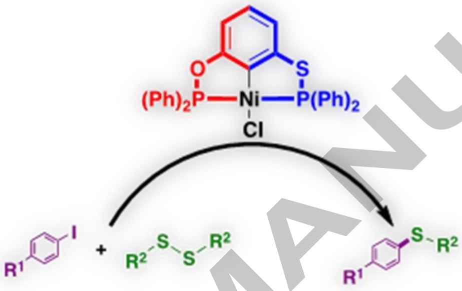

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ABSTRACT

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.

1. Introduction

Pincer complexes have played a protagonist role in catalysis for the last two decades, this being greatly due to their high stability and 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 some 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. Figure 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 the long and 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 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.

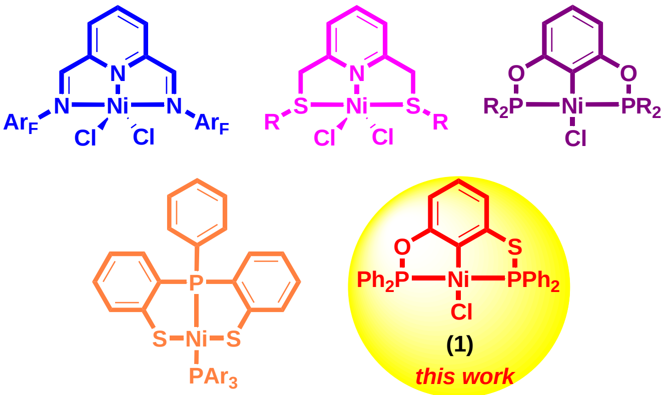
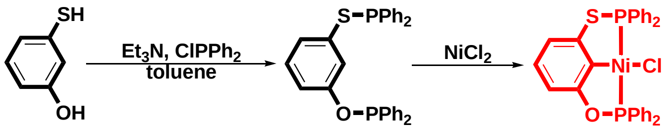


Figure 1. Examples of pincer complexes used for C-S cross-coupling.

2. Results and discussion

*2.1 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 (**1**) was unequivocally determined by single crystal X-Ray diffraction techniques.



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

Thus, the ^1H 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 $^{13}C\{^1H\}$ 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 doublet of doublets at 142.7 ppm ($^2J_{CP}$ = 25.5, 16.7 Hz). Also, of interest the $^{31}P\{^1H\}$ 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 Figure 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.

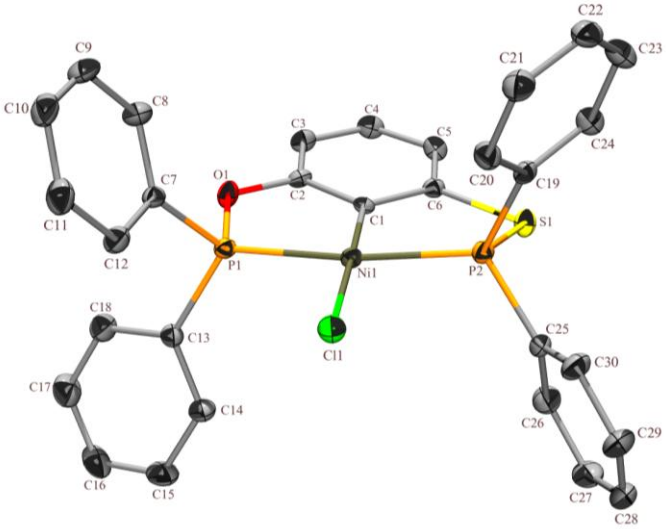


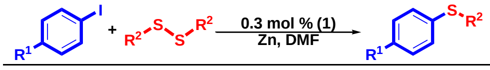
Figure 2. Molecular structure of (1). Selected bond lengths (Å): Ni–C1A 1.913(7), Ni–C1B 1.867(11), Ni–Cl 2.198(1), Ni–P1 2.160(1), Ni–P2 2.163(1), P1–O1A 1.649(8), P1–S1B 2.054(5), P2–S1A 2.149(2), P2–O1B 1.534(9). Selected bond angles (º): C1A–Ni–Cl 177.4(9), C1B–Ni–Cl 177.6(8), C1A–Ni–P1 83.6(5), C1B–Ni–P1 88.6(8), P1–Ni–P2 170.8(1), P1–Ni–Cl 94.8(1), P2–Ni–Cl 94.1(1).

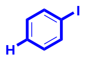
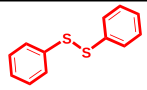
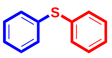
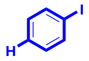
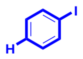
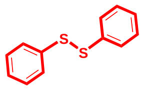
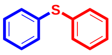
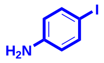
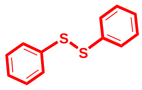
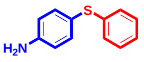
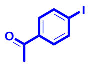
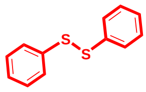
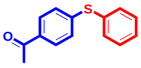
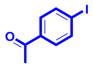
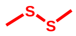
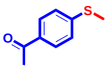
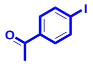
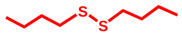
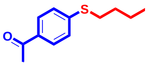
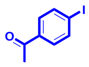
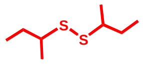
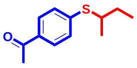
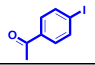
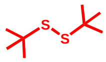
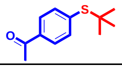
The Ni-P distances are very similar among them, 2.160(1) Å for Ni-P1 and 2.163(1) Å for Ni-P2. Because the molecular structure is disordered, some lengths and angles are slightly different. In all other senses the bond distances and angles are similar to those reported for analogous compounds (however 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]

*2.2 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 ºC for 4h. 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 ºC for 16.5 h (Entry 2, Table 1), while at 130 ºC for 22h a 60 % of conversion was produced.

Table 1. C-S cross-couplings catalysed by [NiCl{C_6H_3-2-($OPPh_2$)-6-($SPPh_2$)}] (**1**)[a]



Entry	R^1	R^2	Product	Yield[d] %
1[b]				26
2[c]				99
3[a]				60 (58)[e]
4[a]				70 (69)[e]
5[a]				92 (89)[e]
6[a]				91 (89)[e]
7[a]				72 (71)[e]
8[a]				50 (50)[e]
9[a]				10 (8)[e]

[a]Reaction conditions: 2 mmol of the corresponding iodobenzene, 1 mmol of the dialkyl or diaryl disulphide, 2 mmol of Zn, 3 mL of DMF, 0.3 mol % of catalyst (**1**), 130 ºC for 22h. [b]110 ºC for 4h. [c]140 ºC for 16.5h. [d]Conversions obtained by GC-MS are based on residual iodobenzene and are the average of two runs. [e]Isolated Yield.

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, 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.

3. Conclusions

We have synthesized a new non-symmetric Ni(II) phosphinito-thiophosphinito PSCOP pincer compound. Complex (**1**) was fully characterized, including the elucidation of its molecular structure by single crystal X-ray diffraction techniques. Complex (**1**) showed a good catalytic activity in C-S couplings of iodobenzene with different disulfides. The catalytic reaction was sensitive to the steric nature of the substrates (disulfides), showing higher conversions with those having the less sterically than with the more sterically hindered substituents.

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References and notes

1. D. Morales-Morales, Ed., *Pincer Compounds. Chemistry and Applications*, Elsevier, 2018.
2. J. Serrano-Becerra and D. Morales-Morales, *Curr. Org. Synth.*, 2009, 6, 169–192.
3. D. Morales-Morales, *Mini-Rev. Org. Chem.*, 2008, 5, 141–152.
4. W. Kuriyama, T. Matsumoto, O. Ogata, Y. Ino, K. Aoki, S. Tanaka, K. Ishida, T. Kobayashi, N. Sayo and T. Saito, *Org. Process Res. Dev.*, 2012, 16, 166–171.
5. N. Selander and K. J Szabó, *Chem. Rev.*, 2011, 111, 2048–2076.
6. D. Morales-Morales and C. M. Jensen, Eds., *The Chemistry of Pincer Compounds*, Elsevier, 2007.
7. D. F. Brayton, P. R. Beaumont, E. Y. Fukushima, H. T. Sartain, D. Morales-Morales and C. M. Jensen, *Organometallics*, 2014, 33, 5198−5202.
8. S. Chakraborty, P. Bhattacharya, H. Dai and H. Guan, *Acc. Chem. Res*., 2015, 48, 1995–2003.
9. G. van Koten and R. A. Gossage, Eds., *The Privileged Pincer-Metal Platform: Coordination Chemistry & Applications*, Springer International Publishing, Cham, 2016, vol. 54.
10. D. Morales-Morales, H. Valdes, M. A. García-Eleno and D. Canseco-Gonzalez, *ChemCatChem*, DOI: 10.1002/cctc.201702019, in press.
11. D. Srimani, A. Mukherjee, A. F. G. Goldberg, G. Leitus, Y. Diskin Posner, L. J. W. Shimon, Y. Ben David and D. Milstein, *Angew. Chem.*, 2015, 127, 12534–12537.
12. J. R. Khusnutdinova, J. A. Garg and D. Milstein, *ACS Catal*., 2015, 5, 2416–2422.
13. C. Gunanathan and D. Milstein, *Chem. Rev.*, 2014, 114, 12024–12087.
14. T. Zell, Y. Ben David and D. Milstein, *Angew. Chem. Int. Ed. Engl*., 2014, 53, 4685–4689.
15. E. Balaraman, E. Khaskin, G. Leitus and D. Milstein, *Nat. Chem.*, 2013, 5, 122–125.
16. M. Asay and D. Morales-Morales, *Dalton Trans.*, 2015, 44, 17432–17447.
17. M. Asay and D. Morales-Morales, *Top. Organomet. Chem*., 2016, 54, 239–268.
18. M. Albrecht and G. van Koten, *Angew. Chem. Int. Ed. Engl.*, 2001, 40, 3750–3781.
19. M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, 103, 1759–1792.
20. H. Valdés, L. González-Sebastián and D. Morales-Morales, *J. Organomet. Chem.*, 2017, 845, 229–257.
21. D. Morales-Morales, *Revista de la Sociedad Química de México*, 2004, 48, 338–346.
22. G. T. Venkanna, H. D. Arman and Z. J. Tonzetich, *ACS Catal*., 2014, 4, 2941–2950.
23. P. Gogoi, S. Hazarika, M. J. Sarma, K. Sarma and P. Barman, *Tetrahedron*, 2014, 70, 7484–7489.
24. J. Zhang, C. M. Medley, J. A. Krause and H. Guan, *Organometallics*, 2010, 29, 6393–6401.
25. C. C. Eichman and J. P. Stambuli, *Molecules*, 2011, 16, 590–608.
26. Y.-C. Wong, T. T. Jayanth and C. H. Cheng, *Org. Lett.*, 2006, 8, 5613–5616.
27. A. Byeun, K. Baek, M. S. Han and S. Lee, *Tetrahedron Lett*., 2013, 54, 6712–6715.
28. C. F. Fu, Y.-H. Liu, S. M. Peng and S. T. Liu, *Tetrahedron*, 2010, 66, 2119–2122.
29. M. Platon, N. Wijaya, V. Rampazzi, L. Cui, Y. Rousselin, M. Saeys and J.-C. Hierso, *Chem. Eur. J*., 2014, 20, 12584–12594.
30. H. Wang, L. Jiang, T. Chen and Y. Li, *Eur. J. Org. Chem.*, 2010, 2010, 2324–2329.
31. S. Jammi, S. Sakthivel, L. Rout, T. Mukherjee, S. Mandal, R. Mitra, P. Saha and T. Punniyamurthy, *J. Org. Chem.*, 2009, 74, 1971–1976.
32. S. Zhang, P. Qian, M. Zhang, M. Hu and J. Cheng, *J. Org. Chem.*, 2010, 75, 6732–6735.
33. P. Guan, C. Cao, Y. Liu, Y. Li, P. He, Q. Chen, G. Liu and Y. Shi, *Tetrahedron Lett.*, 2012, 53, 5987–5992.
34. S. Jammi, P. Barua, L. Rout, P. Saha and T. Punniyamurthy, *Tetrahedron Lett.*, 2008, 49, 1484–1487.
35. R. Singh, B. K. Allam, N. Singh, K. Kumari, S. K. Singh and K. N. Singh, *Adv. Synt. Catal.*, 2015, 357, 1181–1186.
36. Y. Zhang, K. C. Ngeow and J. Y. Ying, *Org. Lett.*, 2007, 9, 3495–3498.
37. O. Baldovino-Pantaleón, S. Hernández Ortega and D. Morales-Morales, *Inorg. Chem. Commun.*, 2005, 8, 955–959.
38. O. Baldovino-Pantaleón, S. Hernández Ortega and D. Morales-Morales, *Adv. Synt. Catal.*, 2006, 348, 236–242.
39. M. Basauri Molina, S. Hernández Ortega and D. Morales-Morales, *Eur. J. Inorg. Chem.*, 2014, 4619–4625.

40. V. Gomez Benitez, H. Valdés, S. Hernández Ortega, J. Manuel Germán-Acacio and D. Morales-Morales, *Polyhedron*, 2018, 143, 144-148.
41. V. Gomez Benitez, O. Baldovino-Pantaleón, C. Herrera-Álvarez, R. A. Toscano and D. Morales-Morales, *Tetrahedron Lett.*, 2006, 47, 5059–5062.
42. **Synthesis of [NiCl{C_6H_3-2-(OPPh$_2$)-6-(SPPh$_2$)}] (1).** Under nitrogen atmosphere, a mixture of 3-mercaptophenol (6 mmol, 0.64 mL) and triethylamine (6.6 mmol, 1.8 mL) was stirred for 15 min. Then, 60 mL of toluene and chlorodiphenylphosphine (12 mmol, 2.25 mL) was added to the mixture. The reaction was heated at reflux for 18h. After this time, the solution was filtered through Celite® and $NiCl_2$ (6 mmol, 778 mg) was added. The solution was refluxed for 16 h. After this time, all the volatiles were removed under high vacuum. The crude product was purified by chromatographic column, using a 2:1 solution of dichloromethane/pentane. Yield: 3.21 g (91%). Melting point: 247 ºC (280 ºC decomposes). ^{1}H NMR (300 MHz, $CDCl_3$) 8.01 – 7.94 (m, 8H, P-CH_{Ar}), 7.53 – 7.43 (m, 12H, P-CH_{Ar}), 7.01 – 6.95 (m, 1H, CH_{Ar}), 6.90 – 6.88 (m, 1H, CH_{Ar}), 6.70 – 6.60 (m, 1H, CH_{Ar}). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 166.3 (dd, *C*-O, $^{2}J_{CP}$ = 15.6, 7.6 Hz), 154.8 (dd, *C*S, $^{2}J_{CP}$ = 22.2, 6.5 Hz), 142.7 (dd, *C*-Ni, $^{2}J_{CP}$ = 25.5, 16.7 Hz), 133.5 (d, OP-C_{Ar}, $^{2}J_{CP}$ = 12.1 Hz), 132.3 (d, SP-C_{Ar}, $^{2}J_{CP}$ = 12.6 Hz), 132.2 (dd, SP-C_{Ar}, $^{1,3}J_{CP}$ = 46.6, 4.6 Hz), 131.9 (d, OP-C_{Ar}, $^{4}J_{CP}$ = 2 Hz), 131.3 (dd, OP-C_{Ar}, $^{1,3}J_{CP}$ =36.7, 2Hz), 131.2 (d, SP-C_{Ar}, $^{4}J_{CP}$ = 2.3 Hz), 128.8 (d, SP-C_{Ar}, $^{3}J_{CP}$ = 10.8 Hz), 128.7 (C_{Ar}), 117.7 (d, S-CAr, $^{3}J_{CP}$ = 15.6 Hz), 109.6 (d, O-C_{Ar}, $^{3}J_{CP}$ = 14.4 Hz). ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$) 137.9 (d, O*P*, $^{2}J_{PP}$ = 367 Hz), 66.4 (d, SP, $^{2}J_{PP}$ = 367 Hz). EM-IE^{+}: m/z 586 (56) $[M]^{+}$, 550 (10) $[M\text{-}HCl]^{+}$, 493 (100) $[M\text{-}NiCl]^{+}$. Elem. Anal. Calcd. for $C_{30}H_{23}ClNiOP_2S$ (587.66): C, 61.33; H, 3.69; S, 5.04. Found: C, 61.38; H, 3.68; S, 4.99.
43. a) J. M. Serrano-Becerra. *In Catálisis homogénea mediada por complejos de Pd(II), Ni(II) y Au(I): algunas aplicaciones en síntesis orgánica*. Ph.D. Dissertation. Universidad Nacional Autónoma de México. Instituto de Química. 2010. México b) J. M. Serrano-Becerra, S. Hernández-Ortega, D. Morales-Morales. *Inorg. Chim. Acta*. 2010, 363, 1306–1310.
44. **Data collection and refinement for [NiCl{C_6H_3-2-(OPPh$_2$)-6-(SPPh$_2$)}] (1).** A Yellow and laminar crystal of (**1**), was grown independently from CH_2Cl/Et_2O and mounted on glass fibres, then placed on a Bruker Smart Apex II diffractometer with a Mo-target X-ray source (λ = 0.71073Å). The detector was placed at a distance of 5.0 cm from the crystal frames were collected with a scan width of 0.5 in ω and an exposure time of 10 s/frame. Frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. Non-systematic absences and intensity statistics were used in monoclinic P2(1)/n space group. The structure was solved using Patterson methods using SHELXS-2014/7 program.[45] The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps. Hydrogen atoms were input at calculated positions and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups using a Ueq = 1.2 Å to precedent atom. The final cycle of refinement was carried out on all non-zero data using SHELXL-2014/7.[45] Absorption correction was applied using SADABS program. The fragment S-Ph-O, is disordered and was modelled and refined anisotropically in two positions using a variable site occupational factor (SOF). The ratio of SOF was 60/40 %. 294 restraints were applied at the refinement, 240 for SIMU, 36 for DELU and 18 for SAME instructions respectively. The ligand S-Ph-O is coplanar with metal center coordination, however the phenyl rings are rotated by 61.2(4)° (C7 to C12), 66.2(14° (C13 to C18), 74.5(3)° for C19 to C24 and 74.2(4)° for C25 to C30.
45. G. M. Sheldrick. *Acta Cryst.* 2015, C71, 3-8.
46. P. Hasche, M. Joksch, G. Vlachopoulou, H. Agarwuala, A. Spannenberg, T. Beweries. *Eur. J. Inorg. Chem.* 2018, 676-680.
47. **Alkyl- and Arylthiolation of Iodobenzenes.** Under an atmosphere of nitrogen, a solution of 2 mmol of halobenzene, 1 mmol of the corresponding alkyl- or aryldisulfide, 0.3 mol% of the catalyst in 3.0 mL of DMF, was introduced into a Schlenk tube containing a magnetic stir bar and charged with 2 mmol of zinc dust. The tube was sealed and fully immersed in a 130 ^{o}C silicon oil bath. After 22 h, the reaction mixture was cooled to room temperature and the organic phase analyzed by gas chromatography (GC-MS) (Quantitative 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).
48. C. Hansch, A. Leo, R. W. Taft. *Chem. Rev.* 1991, 91, 165-195.

Supplementary Material

Supplementary data for compound (**1**) has 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 1823658.

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Highlights

- A new Ni(II) phosphinito-thiophosphinito PSCOP pincer was synthesized.
- The PSCOP-Ni(II) pincer complex efficiently catalyses C-S couplings of disulfides and iodobenzene.
- The activity of the catalyst is strongly related with the steric demand of the substituent at the disulphide.