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Ni(II)–POCOP pincer compound [NiCl{ $C_{10}H_5$ -2,10-(OPPh₂)₂}] an efficient and robust nickel catalyst for the Suzuki–Miyaura coupling reactions

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ABSTRACT

The Ni(II)–POCOP pincer complex $[NiCl{C_{10}H_5-2,10-(OPPh_2)_2}]$ (2) based on a naphthoresorcinol frame has been synthesized in a very simple and facile manner and efficiently used in the Suzuki–Miyaura cross-coupling of different *para*-substituted bromobenzenes producing high yields of the corresponding biphenyl derivatives.

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1. Introduction

Pincer compounds have had a preponderant importance in chemistry in the last decade, this being specially important in areas such as homogeneous catalysis, organometallic chemistry, the activation of un-reactive or difficult to activate bonds and the activation of small molecules [1]. The success of these species lying in part on their high thermal stability, as these complexes are in most of the cases able to withstand continuous heating at temperatures averaging 200 °C or higher without any apparent decomposition. However, the attractiveness of these species on occasions has been hampered by the sometimes, difficulty on their attaining, being the synthesis of some of these compounds difficult or requiring multi-step reaction paths with the undesirable combination of low yields. Thus, the discovery of POCOP phosphinite palladium pincer complexes, offered an answer to this problem, providing a synthetic procedure based on resorcinols and chlorophosphines to produce the corresponding phosphinito pincer derivatives in a simple manner [2].

On the other hand, the Suzuki–Miyaura cross coupling reaction [3] has been recognized as a true power tool in organic synthesis and although palladium species are widely accepted as suitable catalysts, cost still continues to be one of the main issues for their employment [4], leading the research involving Pd-based catalysts to the potential recycling or recovering of the catalysts [5]. Thus, it would be desirable to have the same catalytic activity by

employing catalysts based on cheaper and safer metals. In this point nickel could be the answer, as nickel catalysts have been already used successfully in other cross coupling reactions such as the formation of C–S bonds, the thioetherification reaction [6]. In spite of these, the reports employing Ni compounds for the Suzuki–Miyaura reaction are limited or the activities reported poor [7]. Thus, following our continuous interest in the synthesis of novel pincer complexes and their potential application on industrial relevant transformations [8] we would like to report on this opportunity the synthesis and successful application of the phosphinito POCOP pincer complex [NiCl{C₁₀H₅-2,10-(OPPh₂)₂]] (**2**) on Suzuki-Miyaura couplings.

2. Experimental

2.1. Material and methods

Unless stated otherwise, all reactions were carried out under an atmosphere of dinitrogen using conventional Schlenk glassware, solvents were dried using established procedures and distilled under dinitrogen immediately prior to use. The ¹H NMR spectra were recorded on a JEOL GX300 spectrometer. Chemical shifts are reported in ppm down field of TMS using the residual signals in the solvent (CDCl₃, δ 7.27) as internal standard. ³¹P{¹H} NMR spectra were recorded with complete proton decoupling and are reported in ppm using 85% H₃PO₄ as external standards. Elemental analyses were determined on a Perkin Elmer 240. Positive-ion FAB mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer





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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. GC–MS analyses were performed on a Agilent 6890N GC with a 30.0 m DB-1MS capillary column coupled to an Agilent 5973 Inert Mass Selective detector. The NiCl₂·6H₂O, naphthoresorcinol (1,3-dihydroxynaphthalene), ClPPh₂ and NEt₃ were commercially obtained from Aldrich Chemical Co. All compounds were used as received without further purification.

2.2. Synthesis of $[C_{10}H_5-1,9-(OPPh_2)_2]$ (1)

The title compound was synthesized by a slight modification of the procedure described for compound $[C_6H_4\{1,3-(OPPr^i_2)_2\}]$ [9]. A Schlenk flask was charged with naphthoresorcinol (109 mg, 0.68 mmol), 30 mL of freshly distilled toluene and 0.2 mL of NEt₃ (1.43 mmol). The resulting mixture is stirred for 15 min and after this time chlorodiphenylphosphine (0.18 mL, 1.36 mmol) is added dropwise under stirring. The mixture is set to reflux overnight and then allowed to reach room temperature and filtered via canula. The filtered solution is evaporated under vacuum to afford ligand (1) as a colorless viscous oil, (88% yield). This compound was used in the next step without any further purification. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.46-7.72$ (m, 26H, Ar). ³¹P{¹H} NMR (121.379 MHz, CDCl₃): $\delta = 111.47$ (d, P_{ab}, ²J_{PaPb} = 75.52 Hz). EI-MS [M]⁺ = 528 (100%) *m/z. Anal.* Calc. for C₃₄H₂₆O₂P₂ (*M*_r = 528.52): C, 77.27; H, 4.96. Found: C, 77.34; H, 4.84%.

2.3. Synthesis of $[NiCl{C_{10}H_5-2, 10-(OPPh_2)_2}]$ (2)

A solution of ligand (1) (465 mg, 0.72 mmol) in toluene (20 mL) was added dropwise to a suspension of NiCl₂ (171 mg, 0.72 mmol) in toluene (30 mL) and set up to reflux overnight. The solution was then filtered over a short pad of silica gel, washed with diethyl ether and pumped off to dryness. The resulting oily product was extracted with CH₂Cl₂ (2 × 5 mL) and then the solvent removed under vacuum to afford complex (**2**) as a viscous amber oil which is recrystallized from a CH₂Cl₂/hexane solvent system producing emerald green crystals, (83%). ¹H NMR (300 MHz, CDCl₃): $\delta = 6.66-7.77$ (m, 22H, Ar). ³¹P{¹H} NMR (121.379 MHz, CDCl₃): $\delta = 141.69$ (d, ²*J*_{PaPb} = 8.5 Hz, P). FAB⁺-MS [M]⁺ = 621 (12%) *m/z*, [M–Cl]⁺ = 586 (88%) *m/z. Anal.* Calc. for C₃₄H₂₅Cl₁Ni₁O₂P₂ (*M*_r = 621.66): C, 65.69; H, 4.05. Found: C, 65.65; H, 4.03%.

2.4. General method for the Suzuki-Miyaura couplings

A DMF solution (4 ml) of 1.0 mmol of halobenzene, 1.3 mmol of phenyl boronic acid, and the prescribed amount of catalyst (3.0 mg, 4.8 mmol, 1.0% mol) was introduced into a Schlenk tube in the open air. The tube was charged with a magnetic stir bar and an equimolar amount of base (Na₂CO₃, 2.6 mmol), and sealed, and fully immersed in a 110 °C silicon oil bath. After the prescribed reaction time (15 h), the mixture was cooled to room temperature and the organic phase analyzed by gas chromatography (GC–MS) by duplicate.

2.5. Mercury drop experiments [10]

Following the above described procedures; additionally adding two drops of elemental Hg to the reaction mixture. After the prescribed reaction times, the solution was filtered and analyzed by GC–MS: no significant difference in conversion between these experiments and those in the absence of mercury was observed, indicating that heterogeneous Ni(0) is not involved. This experiment was performed under the optimized conditions for entry 6 (*e.g.* with bromobenzene).

2.6. Data collection and refinement for $[NiCl{C_{10}H_5-2,10-(OPPh_2)_2}]$ (2)

Crystalline green-yellow prisms of $[NiCl{C_{10}H_5-2,10-(OPPh_2)_2}]$ (2) were grown by slow evaporation from a CH_2Cl_2/n -hexane solvent system, and mounted in random orientation on glass fibers. In all cases, the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD-based three-circle X-ray diffractometer system using graphite mono-chromated Mo K α (λ = 0.71073 Å) radiation. The detector was placed at a distance of 4.837 cm from the crystals in all cases. A total of 1800 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package [11] using a narrow-frame integration algorithm. The integration of the data was done using a monoclinic unit cell to yield a total of 24154 reflections to a maximum 2θ angle of 50.00° (0.93 Å resolution), of which 5278 were independent. Analysis of the data showed in all cases negligible decays during data collections. The structures were solved by Patterson method using SHELXS-97 [12] program. The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps, using a $P2_1/n$ space group, with Z = 4. 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 with $U_{iso}(H) = 1.2 U_{eq}$ of the parent atom in all cases. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [13] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determinations are given in Table 1. The numbering of the atoms is shown in Fig. 1 (ORTEP) [14].

3. Results and discussion

The phosphinito POCOP pincer ligand $[C_{10}H_5-1,9-(OPPh_2)_2]$ (1) was synthesized in a similar manner as that described by our group for $[C_6H_4-1,3-(OPPr_2)_2]$ [9]. Thus, the reaction of 1,3-dihydroxy-naphthalene with ClPPh₂ in a 1:2 M ratio in the presence of a slight excess of NEt₃ under reflux in toluene (Scheme 1) affords ligand (1) in good yields and pure enough, as shown by ³¹P{¹H} NMR to be used for the synthesis of the corresponding nickel metal complexes.

Analysis of the ligand by ¹H NMR spectroscopy only displays signals due to the presence of the phenyl rings, between δ 6.46 and 7.72 ppm. However, more informative results were obtained from the analysis by ³¹P{¹H} NMR. In this instance the spectra obtained shows a doublet centered at δ 111.47 ppm [111.78 (P_a) and 111.15 (P_b) ppm]. The later results are in agreement with the two phosphorus being in a slightly different chemical and magnetic environments, as expected for a non-symmetric pincer ligand (the two P donor atoms are different by symmetry). Analysis of compound (1) by mass spectrometry affords the molecular ion. Elemental analysis was also in agreement with the proposed formulations.

The synthesis of the Ni(II) complex was carried out in a similar manner as we have reported before by direct C–H activation [6c,15] according to Scheme 2.

Thus, the reaction of ligand (**1**) with NiCl₂·6H₂O under reflux conditions in toluene affords complex [NiCl{C₁₀H₅-2,10-(OPPh₂)₂]] (**2**) as an emerald green crystalline product in good yields. Analysis by proton NMR spectroscopy of this product yields a similar spectrum as that determined for the free ligand, with the signals just been shifted slightly to higher field (δ 7.24–8.05 ppm). Further

Table 1

 $(e Å^{-3})$

	Crystal data and structure	parameters for	[NiCl{C10H5-2,10-	(OPPh ₂) ₂] (2).
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Identification code	(2)	
Empirical formula	$C_{34}H_{25}Cl_1O_2P_2Ni_1$	
Formula weight	621.64	
T (K)	298(2)	
λ (Å)	0.71073	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions		
a (Å)	8.8952(7)	
α (°)	90	
b (Å)	27.561(2)	
β (°)	104.723(2)	
c (Å)	12.1216(10)	
γ (°)	90	
$V(Å^3)$	2874.2(4)	
Z	4	
D_{calc} (Mg/m ³)	1.437	
Absorption coefficient (mm ⁻¹)	0.910	
F(000)	1280	
Crystal size (mm)	$0.26 \times 0.06 \times 0.05$	
θ Range for data collection (°)	1.48-25.38	
Index ranges	$-10 \le h \le 10, -33 \le k \le 33,$	
	$-14 \le l \le 14$	
Reflections collected	24154	
Independent reflections	5278 [R(int) = 0.0969]	
Absorption correction	empirical	
Maximum and minimum transmission	0.9559 and 0.7978	
Refinement method	full-matrix least-squares on F^2	
Data/restraints/parameters	5278/0/361	
Goodness-of-fit (GOF) on F^2	1.010	
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0633, wR_2 = 0.1255$	
R indices (all data)	$R_1 = 0.1091, wR_2 = 0.1416$	
Largest difference in peak and hole	0.467 and -0.284	



Scheme 1. Synthesis of the POCOP phosphinite ligand $[C_{10}H_5-1,9-(OPPh_2)_2]$ (1).



Scheme 2. Synthesis of POCOP pincer complex [NiCl{C10H5-2,10-(OPPh2)2}] (2).





Fig. 1. An ORTEP representation of the structure of $[NiCl\{C_{10}H_5-2,10-(OPPh_2)_2\}]$ (**2**) at 50% of probability showing the atom labeling scheme. Selected bond lengths (Å): Ni(1)–C(2) 1.885(4), Ni(1)–P(2) 2.1487(14), Ni(1)–P(1) 2.1544(13), Ni(1)–Cl(1) 2.2000(13). Selected bond angles (°): C(2)–Ni(1)–P(2) 82.12(15), C(2)–Ni(1)–P(1) 81.39(15), P(2)–Ni(1)–P(1) 162.50(5), C(2)–Ni(1)–Cl(1) 177.47(14), P(2)–Ni(1)–Cl(1) 98.34(5).

analysis of this sample by ³¹P{¹H} NMR spectroscopy reveals once more the non-symmetric nature of the ligand, by displaying a spectrum for a second order AB system, with a doublet (corresponding to two different *P* nuclei) centered at δ 141.69 ppm [141.72 (*P*_a) and 141.65 (*P*_b) ppm], having a ²*J*_{PaPb} coupling constant of 8.5 Hz.

Analysis by FAB⁺-MS showed the presence of the molecular ion at $[M]^+$ = 621 (12%) *m/z*. Other important peaks arose from the loss

Fig. 2. π - π interactions observed in complex [NiCl{C₁₀H₅-2,10-(OPPh₂)₂]] (**2**).

of the Cl in the fragmentation process to afford peaks at $[M-Cl]^+ = 586 (88\%) m/z$. Results obtained from elemental analysis are also in agreement with the proposed formulation.

Attempts to crystallize [NiCl{ $C_{10}H_5$ -2,10-(OPPh₂)₂}] (**2**) from a CH₂Cl₂/hexane solvent system furnished crystals suitable for single crystal X-ray diffraction analysis. This analysis confirmed unequivoally the proposed structure and the non-symmetric nature of the pincer compound (**2**) (Fig. 1).

The structure shows the nickel center into a slightly distorted square planar environment, two of the coordination sites being occupied by the phosphorus donor ligands in a mutually *trans* conformation, and completing the coordination sphere the organometallic Ni–C bond and the chloride ligand *trans* to the organometallic carbon. From Fig. 1, it is clear that by symmetry both phosphorus are different, this observation being in agreement with the results observed in the ³¹P{¹H} NMR spectrum, the fact that the value of the coupling constant is just ²*J*_{PaPb} = 8.5 Hz, reflects the close similarity (closely isochronous nuclei) both chemically and magnetically of the two *P* donor nuclei. A similar phenomenon has been recently observed by our group in other similar pincer systems [15,16]. Additionally, analysis of the structure reveals weak π – π interactions (4.436 Å) among the naphthalene aromatic system (Fig. 2), this interactions defining the array in the unit cell.

The longstanding search for efficient catalytic systems in transition metal-catalyzed coupling reactions remains an active subject



R= NH₂, OMe, Me, H, CI, CHO, COMe, CN, NO₂

Scheme 3. Evaluation of the catalytic Activity of Complex $[NiCl{C_{10}H_5-2,10-(OPPh_2)_2}]$ (2).

in organic synthesis. Metallacycles possessing the pincer ligand framework could be an efficient system because of their considerable thermal and oxidative stabilities. Various types (e.g., PCP, NCN, CNC) of pincer complexes of transition metals have been reported to date; among them, palladium–pincer complexes have been widely investigated and employed as catalysts for cross-coupling reactions [1,2,8,17]. Much less attention has been paid to the nickel–pincer complexes, although the use of nickel catalysts instead of palladium catalysts may offer interesting advantages, such as cost effectiveness and distinct catalytic abilities. Thus in an attempt to probe the theory that a robust Ni(II)–POCOP pincer complex would perform well as catalyst we decided to test the air and moisture stable [NiCl{ $C_{10}H_5$ -2,10-(OPPh₂)₂]] (2) pincer complex and explore its reactivity on the Suzuki–Miyaura C–C cross coupling reactions (Scheme 3), of different *p*-substituted bromobenzenes and phenylboronic acid. The results of these experiments are presented in Table 2.

The results obtained are notable, particularly for the activated bromobenzenes attaining quantitative conversions.

Besides, from this table a clear trend can be observed, which is dependant upon the kind of substituent in the bromobenzene, thus the more electro-withdrawing is the group the higher the

Table 2

Suzuki-Miyaura couplings using [NiCl{ $C_{10}H_5$ -2,10-(OPPh₂)₂}] (2) as catalyst.



Table 2 (continued)

Entry	Hammet parameter (σ)	p-Bromobenzene	% Conversion ^a
5	0.23	CI	CI
6	0.00	H	84.5 H
7	-0.17	Br	77.6
8	-0.27	Br	58.6
9	-0.66	H ₂ N Br	54.1
			н ₂ N ~ 42.4

^a Yields obtained by GC are based on bromobenzene and are the average of two runs.

Suzuki-Miyaura Cross-Couplings



Graphic 1. Conversion (%) vs. Hammett parameter (σ).

conversion to the biphenyl product. This trend can be better observed when the percentage of conversion is plotted against the Hammett parameter [18] (Graphic 1) where a near linear behavior can be clearly noted.

As with so many other analogous metallocycle examples, it is possible that the reaction may proceed through the formation of soluble nickel nanoparticles. Hence, in order to rule out this possibility a mercury drop experiment [10] (see Section 2) was performed with no appreciable difference in the performance of the catalyst with or without the presence of Hg(0). It is noteworthy the fact that the presence the Cl substituent at the Ni center does not have to be substituted by a labile group in order to make this catalysts reactive as has been the case for some palladium pincer complexes in Heck couplings where silver additives are necessary. It is possible that the enhanced reactivity observed may be related to the more versatile redox behavior of the nickel center as has been the case when similar systems are employed for the thioetherification reaction (C-S cross coupling). Efforts aiming to shed further light on the mechanism through which this catalyst proceeds in this process are currently under investigation in our labs.

In summary, we have successfully synthesized in high yields a non-symmetric POCOP pincer ligand and its Ni(II) derivatives. The non-symmetric nature of ligand (1) and its complex (2) is clearly demonstrated by the ³¹P{¹H} NMR experiments and unequivocally exposed by single crystal X-ray diffraction experiments. Preliminary catalytic evaluation of the Ni(II) derivative (2), shows this species to be a very efficient and robust Ni(II) catalyst which exhibits a comparable performance in the Suzuki-Miyaura cross coupling reactions as that of similar Pd(II) pincer systems such as [PdCl{3-(*n*-C₁₂H₂₅)-C₆H₂-2,6-(OPPh₂)₂}] [15] albeit with longer reaction periods (compare 15 versus 8 h) and larger, however still catalytic amounts of catalysts (compare 1% Ni versus 0.1% Pd). Another attractive characteristic of the present system is the easy synthesis from cheap commercially available starting materials and the use of considerable cheaper and biocompatible Ni(II), thus making this system attractive for its potential application in organic synthesis. Efforts aimed to extend the studies of the reactivity of the species presented in this work in other cross coupling reactions are currently under study in our laboratories.

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Appendix A. Supplementary material

CCDC 862571 contains the supplementary crystallographic data for complex **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.12.052.

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