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Single Step, High Yield Synthesis of *para*-Hydroxy Functionalized POCOP Ligands and their Ni(II) Pincer Derivatives.

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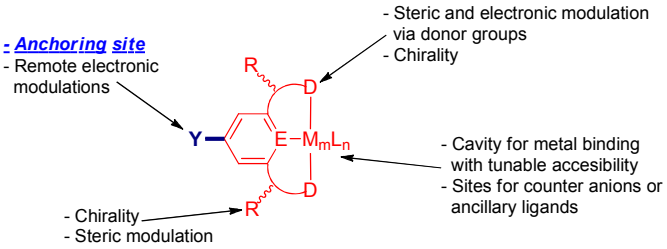
The stoichiometric control of the reaction of phloroglucinol and different chlorophosphines $ClPR_2$; R= *i*Pr (1), *t*Bu (2) or Ph (3), gives place to the direct and high yield synthesis of the *p*-hydroxy functionalized POCOP ligands [C_6H_3-5-OH-1,3-$(OPR_2)_2$]. Typical reactions of these compounds with $NiCl_2{\cdot}6H_2O$ provides a facile access to the corresponding POCOP pincer derivatives [NiCl{C_6H_2-4-OH-2,6-$(OPR_2)_2$]; R= *i*Pr (4), *t*Bu (5) or Ph (6).

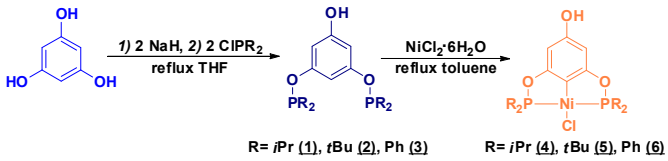
Since their renaissance some two decades ago, pincer compounds have had a tremendous evolution, both in the development of new pincer species and on the potential applications that their metallic derivatives have found in many areas of chemistry, biology, medicine and materials.[1] This being particularly true for the case of catalysis. Where the structural versatility and diversity of the pincer compounds has only been matched by the wide number of processes and organic transformations they catalyze, in part due to their well-known thermal stability. However, in many cases the utility of these compounds has been limited due to problems with the recyclability of the catalyst and separation of the products. Thus, authors have envision the possibility of heterogenize these compounds.[2,3] One of the most common solutions has been to functionalize these species at the *para* position of the aromatic ring of the main pincer backbone. Functionalization on this position should maintain the integrity of the pincer compounds both in structure and on their chemical reactivity and only serve as anchorage point to a given support or substrate. Thus, mimicking the potential activities of these catalysts in the homogeneous phase but acquiring the convenient properties of the heterogeneous catalyst hence greening the catalytic process. Thus, NCN,[4] SCS and PCP[5] *para*-functionalized pincer compounds including -OH, $-NH_2$ and $-OSiR_3$ groups have been synthesized (Scheme 1). However, functionalization of these species involve long and tedious synthetic routes accompanied by final low yields. On the other hand, about a decade ago the chemistry of pincer compounds welcomed the phosphinito POCOP pincer compounds. These species resulted very interesting given the fact that they exhibited the same thermal stability and chemical reactivities as their phosphino analogs, but with the convenience of their synthesis to be more facile. Thus, POCOP pincer complexes became popular and now a days complexes of a number of transition metals have been synthesized, being relevant their platinum group metal derivatives[1b-c,6,7,8], iridium[9], rhodium and rutenium[10]. These compounds exhibit excellent catalytic activities in a variety of processes including C-Halogen bond activation, alkane dehydrogenation[11] and more recently on the glucose reduction to hexane.[12]



Scheme 1. Versatility of the pincer backbone and potential sites for modification.

As expected efforts to functionalize these kind of ligands or their complexes, particularly those derivatives of iridium,[13,14] have also been reported using analogous methodologies to those already described for the phosphine counterparts.

Based on the above, we believe that a facile, high yield, straightforward synthetic method for the production of *para*-hydroxy functionalized POCOP ligands and their complexes, would be highly desirable and welcome by the chemistry community. Thus contributing to the potential and already remarkable impact of the chemistry of pincer complexes. With this idea on mind, in a single step we have achieved the synthesis of a series of *p*-hydroxy functionalized POCOP ligands [C_6H_3-5-OH-1,3-$(OPR_2)_2$] by stoichiometric control of the reaction of phloroglucinol and different chlorophosphines $ClPR_2$; R= *i*Pr (**1**), *t*Bu (**2**) or Ph (**3**). Further reactions of these ligands with $NiCl_2{\cdot}6H_2O$, cleanly provided in high yields, the corresponding Ni-POCOP pincer derivatives [NiCl{C_6H_2-4-OH-2,6-$(OPR_2)_2$] R= *i*Pr (**4**), *t*Bu (**5**) or Ph (**6**) (Scheme 2).



Scheme 2. Synthesis of *p*-hydroxy substituted POCOP ligands **1-3** and Ni-POCOP pincer complexes **4-6**.

Thus, in a typical experiment (see experimental section for details) phloroglucinol was reacted with NaH (1:2 molar ratio) and the corresponding chlorophosphine (1:2 molar ratio) in dry THF to afford the POCOP ligands in good yields (79% (**1**), 84% (**2**) and 84% (**3**)). Analysis of the compounds obtained by $^{31}P\{^{1}H\}$ NMR (121.6 MHz, $CDCl_3$) reveal the ligands to be the only products, exhibiting unique signals at δ: 148.57 ppm (**1**); 146.57 ppm (**2**) and 111.59 ppm (**3**) respectively. These chemical shifts being similar to those reported for their analogous non-*para*-hydroxylated POCOP free ligands.[9,15] Thus, the ligands were used without further purification for their direct metallation with $NiCl_2.6H_2O$ in refluxing toluene. The Ni-POCOP pincer complexes [NiCl{C_6H_2-4-OH-2,6-$(OPR_2)_2$] R= *i*Pr (**4**), *t*Bu (**5**) or Ph (**6**). complexes obtained are all air stable and were fully characterized by common spectroscopic techniques. Exhibiting in the FT-IR spectra broad bands at *c.a.* 3219-3424 cm^{-1} (stretching) evidencing the presence of the free–OH on the complexes. As is the case for the free ligands, more informative resulted the analyses by $^{31}P\{^{1}H\}$-NMR. Affording spectra from the three complexes exhibiting a sole singlet at δ: 187.34 ppm (**4**); 189.81 ppm (**5**) and 147.7 ppm (**6**) in each case. These results accounting for both phosphorus nuclei to be magnetically equivalent in all cases. FAB^{+}-Mass Spectra were also recorded. The samples were amenable to this technique providing clean spectra showing the molecular ions m/z= 452 (**4**), 508 (**5**), 588 (**6**). All these results being consistent with the proposed formulations. In addition, crystals suitable for single crystal X-ray diffraction analysis were obtained (Figure 1), unequivocally proving the identity of the series of Ni-POCOP complexes (complex **5** crystallized as a solvate with a disordered CH_2Cl_2 solvent molecule).

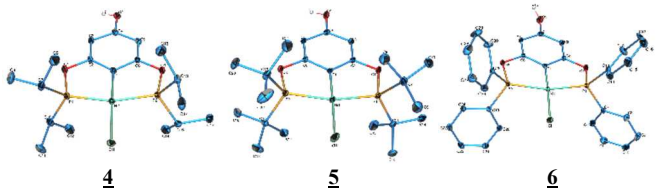
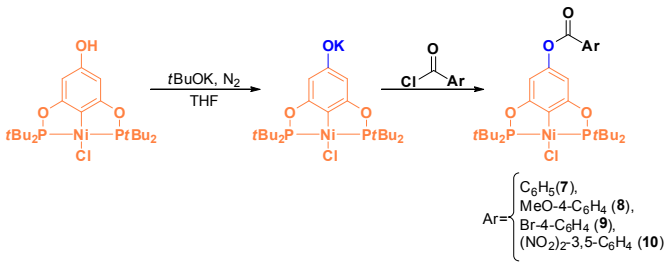


Figure 1. POV-Ray renditions[16] of the ORTEP[17] of Ni-POCOP complexes **4, 5** (CH_2Cl_2 solvent molecule has been omitted for comparison purposes) and **6** (50% thermal ellipsoids).

As a proof of concept, we have further easily functionalized the *para*-hydroxy group of complex [NiCl{C_6H_2-4-OH-2,6-$(OPtBu_2)_2$] (**5**) to their corresponding ester derivatives(see supporting information for details). Thus reaction of (**5**) with *t*BuOK in THF affords immediately the corresponding deprotonated phenoxide salt [NiCl{C_6H_2-4-***OK***-2,6-$(OPtBu_2)_2$] (**7**). Fact that it is noticeable by the change in color of the solution originally yellow to deep red (**Scheme 3**).The red color was discarded upon addition of the acyl chlorides to produce a yellow solution. Purification of the products was performed using column chromatography, to afford the Ni-POCOP ester derivatives [NiCl{C_6H_2-4-***O(CO)R***-2,6-$(OPtBu_2)_2$]; R= C_6H_5(**7**), MeO-4-C_6H_4 (**8**), Br-4-C_6H_4 (**9**) and $(NO_2)_2$-3,5-C_6H_4 (**10**) as yellow solids in good yields (see supporting information for details).



Scheme 3. Synthesis of *p*-ester substituted POCOP pincer compounds **7-10**.

The characterizations of these compounds shows diagnostic C=O vibration bands at *c.a.* ≈1750 cm^{-1} and no O-H stretching bands in the FT-IR spectra. In addition, ^{1}H-NMR analyses were consistent with the introduction of the corresponding aromatic groups (complexes **7-10**). Analyses by $^{13}C\{^{1}H\}$-NMR showed all expected signals including one in all spectra at δ ≈169 ppm characteristic for the presence of the C=O from the ester groups. While analyses by FAB^{+}-MS showed peaks congruent with the molecular ions of the ester products. Moreover, unequivocally determination of the structure by X-ray diffraction techniques were made for complexes (**7**) and (**8**).

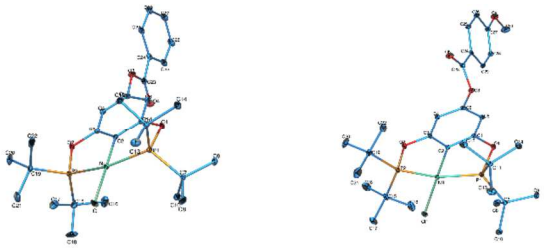


Figure 2. POV-Ray renditions[16] of the ORTEP[17] of Ni-POCOP complexes **7** and **8** (50% thermal ellipsoids).

In summary, we have provided a facile, straightforward, high yield, stoichiometrically-controlled procedure for the synthesis of *para*-hydroxy functionalized POCOP ligands and their Ni(II) complexes. We believe that this report will allow the further development of other areas of chemistry involving pincer compounds providing a simple method for the attaining of valuable building blocks that may impact in the synthesis of dendrimers, functionalization of solid supports to produce materials or heterogenized catalyst with pincer motifs as well as for the "decoration" of pincer species with a plethora of functional substituents that may impact areas as diverse as biological and medicinal chemistry or help in the production of compounds including more than one metal thus envisioning the rationalized design of tandem catalysis. Efforts to explore some of this ideas are currently under development in our laboratory.

Experimental

General procedure for the synthesis of ligands [C_6H_3-5-OH-1,3-$(OPR_2)_2$]: In a typical experiment, phloroglucinol (126 mg, 1 mmol) was added to a schlenk flask containing sodium hydride (54 mg, 2.25 mmol) and dry THF (20 mL) under nitrogen atmosphere. The resulting reaction mixture was stirred for 30 min. After this time the corresponding chlorophosphine $ClPR_2$ (2 mmol) was added and the reaction mixture set to reflux for 24 hours. After the prescribed reaction time, the mixture is evaporated under vacuum and the residue extracted with 20 mL of Toluene. The resulting solution is filtrated through cannula and the solvent evaporated under vacuum.

The crude products were obtained as colorless viscous oils that crystallize on time. The ligands were found to be pure enough to be used in the metallation reactions without further purification. **[C_6H_3-5-OH-1,3-(OP*i*Pr_2)$_2$] (1).** 126 mg of phloroglucinol, 54 mg of NaH and 304 mg of ClP*i*Pr_2 in toluene. The compound was obtained as a whitish viscous oil in 79% yield (284 mg). ^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ: 1.08 (m, 24H), 1.80 (m, 4H), 6.3 (d, 2H), 6.5 (s, 2H). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ: 148.57 ppm. **[C_6H_3-5-OH-1,3-(OP*t*Bu_2)$_2$] (2).** 126 mg of phloroglucinol, 54 mg of NaH and 360 mg of ClP*t*Bu_2 in toluene. The compound was obtained as a whitish viscous oil in 84% yield (347 mg). ^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ: 0.9(m, 36H), 6.44 (m, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ: 146.57 ppm. **[C_6H_3-5-OH-1,3-(OPPh_2)$_2$] (3).** 126 mg of phloroglucinol, 54 mg of NaH and 440 mg of ClPPh_2 in toluene. The compound was obtained as a whitish viscous oil in 84% yield (413 mg). ^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ: 7.03 (s, 2H), 7.45 (m, 21H). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ: 111.59 ppm.

General Procedure for the synthesis of the complexes [NiCl{C_6H_2-4-OH-2,6-(OPR_2)$_2$]: A rubber septum-capped Schlenk flask containing 1 equiv. of the corresponding ligand in 20 mL of dry toluene (previously dried and purged with nitrogen), was charged with 1 equiv. of $NiCl_2{\cdot}6H_2O$. The resulting reaction mixture was set to reflux for 12 hours. After this time the reaction mixture is allowed to cool down to room temperature and then filtered and the solvent evaporated under vacuum. The solid residue was passed through a short column of silica gel and eluted with CH_2Cl_2. Further elimination of the solvent under vacuum provides the pincer complexes as microcrystalline powders. **[NiCl{C_6H_2-4-OH-2,6-(OP*i*Pr_2)$_2$}] (4).** 284 ligand **1** (0.79 mmol) and 188 mg of $NiCl_2.6H_2O$ (0.79 mmol) in toluene were refluxed for 12 hours to produce 295 mg of complex **4** (0.65 mmol, 83% yield) as a yellow microcrystalline solid, mp 152°C.^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ:1.3 (m, 24H), 2.32 (m, 4H), 5.93 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 75.57 Hz) δ: 16.9, 17.6, 27.9, 94.0, 114.0, 157.9, 169.0. ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ: 187.34. EM (EI$^+$; m/z): 452 [M]$^+$ (25%), 391 [M-C_4H_{10}]$^+$ (60%), 149 [M-$C_{12}H_{28}ClO_2P_2$]$^+$ (100%). IR (KBr; νmax/cm-1): 3285, 2929, 2870, 1598, 805, 997. Anal. Calc. for $C_{18}H_{31}Cl_1Ni_1O_3P_2$: C, 47.88; H, 6.92. Found: C, 47.91, H, 6.95. **[NiCl{C_6H_2-4-OH-2,6-(OP*t*Bu_2)$_2$}] (5).** ligand **2** (347 mg, 0.84 mmol) and 201 mg $NiCl_2.6H_2O$ (0.85 mmol) were mixed in toluene and set to reflux for 12 hours to produce 374 mg of complex **5** (0.74 mmol, 89% yield) as a yellow microcrystalline solid, mp 265-267°C. ^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ: 1.4 (m, 36H), 5.9 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 75.57 Hz) δ: 27.8, 39.1, 93.7, 114.2, 157.9, 170.3. ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ: 189.81. EM (FAB$^+$; m/z): 508 [M]$^+$ (100%), 471 [M-Cl]$^+$ (40%). IR (KBr; νmax/cm-1): 3424, 2962, 2901, 2869, 999, 798. Anal. Calc. for $C_{22}H_{39}Cl_1Ni_1O_3P_2$: C, 52.05; H, 7.74. Found: C, 51.98, H, 7.79. **[NiCl{C_6H_2-4-OH-2,6-(OPPh_2)$_2$} (6).** ligand **3** (410 mg, 0.84 mmol) and 201 mg of $NiCl_2.6H_2O$ (0.85 mmol) in toluene were refluxed 12 hours to accomplish 359 mg of product **6** (0.61 mmol, 72% yield) as a yellow solid, mp 325-327°C. ^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ: 6.9 (s, 2H), 7.2 (m, 20H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 75.57 Hz) δ: 95.3, 128.3, 128.5, 128.9, 131.1, 131.6, 131.7, 132.5. ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ:147.7. EM (EI$^+$; m/z): 588 [M]$^+$ (100%), 551 [M-Cl]$^+$ (10%), 493 [M-NiCl]$^+$ (35%). IR (KBr; νmax/cm-1): 3293, 3051, 3074. Anal. Calc. for $C_{30}H_{23}Cl_1Ni_1O_3P_2$: C, 61.32; H, 3.95. Found: C, 61.27, H, 3.79.

General esterification procedure: In a typical experiment, To a solution of [NiCl{C_6H_2-4-OH-2,6-(OP*t*Bu_2)$_2$}] (**5**) (50 mg, 0.098 mmol) in dry THF (50 mL) *t*BuOK (11 mg, 0.1 mmol) was added under stirring at room temperature. The solution initially yellow turned red. Thus color is discharged when the corresponding acyl chloride was added turning the solution yellow. The solvent is then evaporated under vacuum and the solid residue purified by column chromatography using a hexane-ethyl acetate solvent system as eluent. Evaporation of the solvent produces the ester derivative as microcrystalline yellow solids. **[NiCl{C_6H_2-4-(OCOC_6H_5)-2,6-(OP*t*Bu_2)$_2$}] (7)**. Pincer compound **5**, base and benzoyl chloride (13.7 mg, 0.098mmol) was reacted. To produce 34 mg of a microcrystalline yellow solid (54%), mp 235°C. ^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ (ppm): 1.42 (m, 36H), 6.28 (s, 2H), 7.42 (m, 2H), 7.55 (m, 1H), 8.07 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 75.57 Hz) δ (ppm): 28.17, 39.53, 99.28, 121.53, 128.77, 129.80, 130.27, 133.77, 151.52, 165.12, 169.14. ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ (ppm): 189.7. EM (FAB$^+$; m/z): 610 [M]$^+$ (100%), 575 [M-Cl]$^+$ (50%), 518 [M-ClNi]$^+$ (20%). IR (KBr; νmax/cm-1): 1742. Anal. Calc. for $C_{29}H_{43}Cl_1Ni_1O_4P_2$: C, 56.94; H, 7.08. Found: C, 56.89, H, 7.13. **[NiCl{C_6H_2-4-(OCOC_6H_4-4-OCH_3)-2,6-(OP*t*Bu_2)$_2$}] (8)**. Pincer compound **5**, base and 4-Methoxybenzoyl chloride (16.7 mg, 0.098mmol) were reacted. To produce 37.7 mg of a microcrystalline yellow solid (60%), mp 236°C. ^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ (ppm): 1.42 (m, 36H), 3.81 (s, 3H), 6.27 (s, 2H), 6.89 (d, 2H), 8.03 (d, 2H). ^{13}C NMR ($CDCl_3$, 25°C, 75.57 Hz) δ (ppm): 27.76, 39.19, 77.23, 99.50, 114.26, 121.57, 122.37, 132.75, 152.18, 164.64, 165.45, 169.77. ^{31}P NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ (ppm): 188.62. EM (FAB$^+$; m/z): 640 [M]$^+$ (100%), 605 [M-Cl]$^+$ (50%), 548 [M-ClNi]$^+$ (20%). IR (KBr; νmax/cm-1): 1731, 1255. Anal. Calc. for $C_{30}H_{45}Cl_1Ni_1O_5P_2$: C, 56.14; H, 7.07. Found: C, 56.08, H, 6.98. **[NiCl{C_6H_2-4-(OCOC_6H_4-4-Br)-2,6-(OP*t*Bu_2)$_2$}] (9)**. Pincer compound **5**, base and 4-Bromobenzoyl chloride (21.5 mg, 0.098mmol) were reacted. To produce 64 mg of a yellow microcrystalline solid (95%), mp 210°C. ^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ (ppm): 1.46 (m, 36H), 6.31 (s, 2H), 7.61 (d, 2H), 7.98 (d, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 75.57 Hz) δ (ppm): 27.77, 39.22, 99.28, 122.09, 129.07, 129.33, 132.12, 132.53, 151.81, 165.01, 169.79. ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ (ppm): 189.01. EM (FAB$^+$; m/z): 690 [M]$^+$ (100), 655 [M-Cl]$^+$ (50%), 597 [M-Cl-Ni]$^+$ (100%). IR (KBr; νmax/cm-1): 1742, 1259. Anal. Calc. for $C_{29}H_{42}Br_1Cl_1Ni_1O_4P_2$: C, 50.43; H, 6.13. Found: C, 50.41, H, 6.21. **[NiCl{C_6H_2-4-(OCOC_6H_4-3,5-(NO_2)$_2$)-2,6-(OP*t*Bu_2)$_2$}] (10)**. Pincer compound **5,** base and 3,5-dinitrobenzoyl chloride (22.6 mg, 0.098mmol) were reacted. To produce 50.2 mg of a microcrystalline yellow solid (73%), mp. 259°C. ^{1}H NMR ($CDCl_3$, 25 °C, 300.52 Hz) δ (ppm): 1.44 (m, 36H), 6.34 (s, 2H), 9.22 (m, 1H), 9.24 (d, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 75.57 Hz) δ (ppm): 27.78, 39.33, 98.79, 123.39, 130.37, 134.07, 149.51, 151.09, 161.03, 169.89. ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 121.65 Hz) δ (ppm): 189.91. EM (FAB$^+$; m/z): 700 [M]$^+$ (100%) 665 [M-Cl]$^+$ (50%). IR (KBr; νmax/cm-1): 1752, 1546, 1263. Anal. Calc. for $C_{29}H_{41}Cl_1N_2Ni_1O_8P_2$: C, 49.64; H, 5.89, N, 3.99. Found: C, 49.71, H, 5.96, N, 3.94.

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Notes and references

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† Electronic Supplementary Information (ESI) available: NMR for the whole set of compounds 1-10. Crystallographic data for complexes **4-8**. CCDC 1017478-1017482. See DOI: 10.1039/c000000x/

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