Polyhedron 29 (2010) 592–600

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Group 10 phosphinite POCOP pincer complexes derived from 4-*n*-dodecylresorcinol: An alternative way to produce non-symmetric pincer compounds

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ARTICLE INFO

Article history:
Available online 24 July 2009

Keywords:
PCP pincer compounds
POCOP pincer compounds
Cross coupling reactions
Heck reaction
Suzuki-Miyaura reaction
Catalysis

ABSTRACT

Phosphinite POCOP pincer compounds [4-(n-$C_{12}H_{25}$)-C_6H_3-1,3-(OPR_2)$_2$] R=Ph (**1**), Pr^i (**2**) derived from 4-*n*-dodecylresorcinol and their group 10 derivatives [MCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-(OPR_2)$_2$}] M(R) = Ni(Ph) (**3**), Ni(Pr^i) (**6**), Pd(Ph) (**4**), Pd(Pr^i) (**7**) and Pt(Ph) (**5**), Pt(Pr^i) (**8**) were synthesized and the catalytic activity of the palladium species explored in the Mizoroki-Heck and Suzuki-Miyaura cross coupling reactions.

1. Introduction

Pincer compounds represent a group of species with very particular and interesting properties among which, their high thermal stability and unusual reactivities that confer to the metal complexes they form stand out. It is due, to these characteristics of robustness and thermal stability that pincer compounds have attracted the continuous attention of the chemistry community for multiple applications, this being particularly true in the case of homogeneous catalysis [1]. In the beginning, the very simple backbone exhibited by these compounds did not anticipate the wide variety of possible functionalizations in the main frame of the complex (Scheme 1). Thus, as up today, these ligands have been modified to include different donor groups such as NHC's heterocyclic carbenes [2], phosphines [3], thioethers [4], oxazolines [5], phosphinites [6], amines and imines [7], and so forth. Moreover, the very same system can be modified to include functional groups that enable these species to be anchored to solid supports [8] or allowing further functionalization to afford dendrimeric or nanostructured systems [9]. In many cases, these complexes have been successfully modified to include chiral motifs that have allowed the synthesis of enantiomerically pure systems which have been employed successfully in asymmetric synthesis and enantioselective catalysis.

In addition, the bare inclusion of different metals in the cavity of the ligands offers an endless possibility of a very diverse chemistry according to the metal selected. Hence, nowadays pincer compounds of many elements are known and their chemistries are motif of continuous and numerous studies. In this sense, phosphinite POCOP pincer compounds have been an answer for the easy synthesis of pincer compounds, maintaining the same characteristics of thermal robustness and in many occasions enhanced reactivity when compared to their phosphine counterparts. Moreover, the number of examples of complexes including non-symmetric pincer type ligands is limited in comparison with those of their symmetric analogs [10]. This is partly because their preparation is a considerable challenge, being laborious and requiring a series of steps to introduce different groups or donors. Moreover complexes bearing non-symmetric pincer ligands have shown enhanced and in many cases markedly different reactivities, such as hemilability [11].

Thus, following our continuous interest in the development on pincer chemistry [12], the present report describes an alternative way for the synthesis of non-symmetric POCOP pincer compounds their characterization and catalytic evaluation in relevant cross coupling reactions.

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 ^{1}H 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 ($CDCl_3$, δ 7.27) as internal standard. $^{31}P\{^1H\}$ NMR

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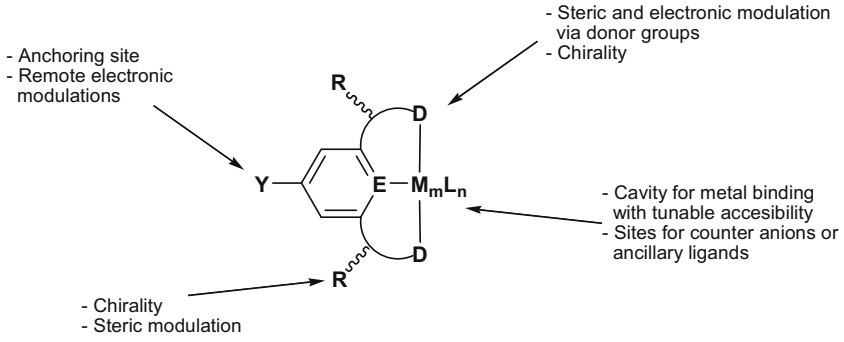
doi:10.1016/j.poly.2009.07.038



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

spectra were recorded with complete proton decoupling and are reported in ppm using 85% H_3PO_4 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. GC–MS analyses were performed on a Agilent 6890 N GC with a 30.0 m DB-1MS capillary column coupled to an Agilent 5973 Inert Mass Selective detector. The $PdCl_2$, $PtCl_2$ were purchased from Pressure Chemical Co., 4-*n*-dodecylresorcinol was purchased from Acros Organics, and $ClPPh_2$, $ClPPr^i_2$, $NiCl_2{\cdot}6H_2O$, and NEt_3 were commercially obtained from Aldrich Chemical Co. All compounds were used as received without further purification. The starting materials $[(COD)PdCl_2]$ [13], *cis*-$[(SMe_2)_2PtCl_2]$ [14], were prepared according to published procedures.

2.2. Synthesis of [4-(n-$C_{12}H_{25}$)-C_6H_3-1,3-($OPPh_2$)$_2$] (**1**)

The title compound was synthesized by a slight modification of the procedure described for compound $[C_6H_4\{1,3\text{-}(OPPr^i_2)_2\}]$ [3a]. A Schlenk flask was charged with 4-*n*-dodecylresorcinol (400 mg, 1.436 mmol), 30 mL of freshly distilled toluene and 0.4 mL of NEt_3 (2.873 mmol). The resulting mixture is stirred for 15 min and after this time chlorodiphenylphosphine (0.51 mL, 2.873 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 filtrated is evaporated under vacuum to afford ligand (**1**) as a colorless viscous oil, (0.794 g, 1.228 mmol, 85.4%). This compound was used in the next step without any further purification. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (bs, 3H, $-CH_3$, *n*-dodecyl), 1.20 (bs, 18H, $-CH_2(CH_2)_7CH_2-$, *n*-dodecyl), 1.44 (bs, 2H, $-CH_2-$, *n*-dodecyl), 2.50 (bs, 2H, $-CH_2-$Ar, *n*-dodecyl), 6.46–7.72 (m, 23H, Ar). $^{31}P\{^1H\}$ NMR (121.379 MHz, $CDCl_3$): δ = 110.35 (s, P_a), 111.28 (s, P_b). EI-MS $[M]^+$ = 646 (100%) *m*/*z*. *Anal.* Calc. for $C_{42}H_{48}O_2P_2$ (M_r = 646.78): C, 77.99; H, 7.48. Found: C, 78.04; H, 7.46%.

2.3. Synthesis of [4-(n-$C_{12}H_{25}$)-C_6H_3-1,3-($OPPr^i_2$)$_2$] (**2**)

The title compound was synthesized by a similar procedure as that described for ligand (**1**) from 4-*n*-dodecylresorcinol (400 mg, 1.436 mmol), 30 mL of freshly distilled toluene, 0.4 mL of NEt_3 (2.873 mmol) and chlorodiisopropylphosphine (0.45 mL, 2.873 mmol). Ligand (**2**) was obtained as a colorless viscous oil, (0.68 g, 1.331 mmol, 92.6%). This compound was used in the next step without further purification. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (bs, 3H, $-CH_3$, *n*-dodecyl), 1.05–1.17 (bm, 24H, $-CH(CH_3)_2$, PPr^i_2), 1.25 (bs, 18H, $-CH_2(CH_2)_7CH_2-$, *n*-dodecyl), 1.44 (bs, 2H, $-CH_2-$, *n*-dodecyl), 1.84–1.91 (bm, 4H, $-CH(CH_3)_2$, PPr^i_2), 2.50 (bs, 2H, $-CH_2-$Ar, *n*-dodecyl), 6.56–7.26 (m, 3H, Ar). $^{31}P\{^1H\}$ NMR (121.379 MHz, $CDCl_3$): δ = 142.38 (s, P_a), 149.42 (s, P_b). EI-MS $[M]^+$ = 510 (100%) *m*/*z*. *Anal.* Calc. for $C_{30}H_{56}O_2P_2$ (M_r = 510.71): C, 70.55; H, 11.05. Found: C, 70.43; H, 10.96%.

2.4. Synthesis of [NiCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**3**)

A solution of (**1**) (465 mg, 0.72 mmol) in toluene (20 mL) was added dropwise to a suspension of $NiCl_2$ (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 CH_2Cl_2 (2 × 5 mL) and then the solvent removed under vacuum. The solvent is taken off under vacuum to afford complex (**3**) as a viscous amber oil, (0.442 g, 0.597 mmol, 83.1%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (bs, 3H, $-CH_3$, *n*-dodecyl), 1.24 (bs, 18H, $-CH_2(CH_2)_7CH_2-$, *n*-dodecyl), 1.57 (bs, 2H, $-CH_2-$, *n*-dodecyl), 2.45 (bs, 2H, $-CH_2-$Ar, *n*-dodecyl), 6.66–7.77 (m, 22H, Ar). $^{31}P\{^1H\}$ NMR (121.379 MHz, $CDCl_3$): δ = 138.76, 142.67 (s, $^2J_{PaPb}$ = 474.88 Hz, P_a) and 143.18, 147.08 (s, $^2J_{PaPb}$ = 474.88 Hz, P_b). FAB^+-MS $[M]^+$ = 738 (50%) *m*/*z*, $[M-Cl]^+$ = 703 (88%) *m*/*z*. *Anal.* Calc. for $C_{42}H_{47}ClNiO_2P_2$ (M_r = 739.92): C, 68.18; H, 6.40. Found: C, 68.05; H, 6.43%.

2.5. Synthesis of [NiCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPr^i_2$)$_2$}] (**4**)

Complex (**4**) was synthesized by an analogous method as that described for the phenyl derivative (**3**), from ligand (**2**) (367 mg, 0.72 mmol) in toluene (20 mL) and $NiCl_2$ (171 mg, 0.72 mmol) in toluene (30 mL). Complex (**4**) was obtained as a viscous amber oil, (0.397 g, 0.657 mmol, 91.4%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (bs, 3H, $-CH_3$, *n*-dodecyl), 1.24 (bs, 18H, $-CH_2(CH_2)_7CH_2-$, *n*-dodecyl), 1.18–1.40 (bm, 24H, $-CH(CH_3)_2$, PPr^i_2) 1.51 (bs, 2H, $-CH_2-$, *n*-dodecyl), 1.99–2.03 (bm, 4H, $-CH(CH_3)_2$, PPr^i_2), 2.48 (bs, 2H, $-CH_2-$Ar, *n*-dodecyl), 6.33–6.90 (m, 2H, Ar). $^{31}P\{^1H\}$ NMR (121.379 MHz, $CDCl_3$): δ = 180.79, 183.46 (s, $^2J_{PaPb}$ = 324.53 Hz, P_a) and 184.21, 186.88 (s, $^2J_{PaPb}$ = 324.53 Hz, P_b). FAB^+-MS $[M]^+$ = 602 (12%) *m*/*z*, $[M-Cl]^+$ = 567 (10%) *m*/*z*. *Anal.* Calc. for $C_{30}H_{55}ClNiO_2P_2$ (M_r = 603.85): C, 59.67; H, 9.18. Found: C, 58.96; H, 9.16%.

2.6. Synthesis of [PdCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**5**)

Complex (**5**) was synthesized by an analogous method as that described for complex (**3**), from ligand (**1**) (465 mg, 0.72 mmol) in toluene (20 mL) and $[CODPdCl_2]$ (205 mg, 0.72 mmol) in toluene

(30 mL). Complex (**5**) was obtained as a viscous amber oil, (0.508 g, 0.645 mmol, 89.7%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (bs, 3H, –CH_3, *n*-dodecyl), 1.23 (bs, 18H, –$CH_2(CH_2)_7CH_2$–, *n*-dodecyl), 1.59 (bs, 2H, –CH_2–, *n*-dodecyl), 2.66 (bs, 2H, –CH_2–Ar, *n*-dodecyl), 6.67–7.98 (m, 22H, Ar). $^{31}P\{^1H\}$ NMR (121.379 MHz, $CDCl_3$): δ = 138.75, 142.65 (s, $^2J_{PaPb}$ = 473.06 Hz, P_a) and 143.17, 147.09 (s, $^2J_{PaPb}$ = 473.06 Hz, P_b). FAB$^+$-MS [M]$^+$ = 787 (8%) *m*/*z*, [M−Cl]$^+$ = 751 (100%) *m*/*z*. *Anal.* Calc. for $C_{42}H_{47}ClO_2P_2Pd$ (M_r = 787.64): C, 64.05; H, 6.01. Found: C, 64.08; H, 6.03%.

2.7. Synthesis of [PdCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPr^i_2$)$_2$}] (**6**)

Complex (**6**) was synthesized by an analogous method as that described for the phenyl derivative (**3**), from ligand (**2**) (367 mg, 0.72 mmol) in toluene (20 mL) and [$CODPdCl_2$] (205 mg, 0.72 mmol) in toluene (30 mL). Complex (**6**) was obtained as a viscous amber oil, (0.452 g, 0.694 mmol, 96.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (bs, 3H, –CH_3, *n*-dodecyl), 1.24 (bs, 18H, –$CH_2(CH_2)_7CH_2$–, *n*-dodecyl), 1.27–1.41 (bm, 24H, –$CH(CH_3)_2$, PPr^i_2) 1.51 (bs, 2H, –CH_2–, *n*-dodecyl), 2.11–2.22 (bm, 4H, –$CH(CH_3)_2$, PPr^i_2), 2.48 (bs, 2H, –CH_2–Ar, *n*-dodecyl), 6.44–6.78 (m, 2H, Ar). $^{31}P\{^1H\}$ NMR (121.379 MHz, $CDCl_3$): δ = 182.71, 186.11 (s, $^2J_{PaPb}$ = 412.36 Hz, P_a) and 186.65, 190.03 (s, $^2J_{PaPb}$ = 412.36 Hz, P_b). FAB$^+$-MS [M]$^+$ = 651 (11%) *m*/*z*, [M−Cl]$^+$ = 615 (100%) *m*/*z*. *Anal.* Calc. for $C_{30}H_{55}ClO_2P_2Pd$ (M_r = 651.58): C, 55.30; H, 8.51. Found: C, 55.25; H, 8.49%.

2.8. Synthesis of [PtCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**7**)

Complex (**7**) was synthesized by an analogous method as that described for complex (**3**), from ligand (**1**) (465 mg, 0.72 mmol) in toluene (20 mL) and cis-[(Me_2S)$PtCl_2$] (280 mg, 0.72 mmol) in toluene (30 mL). Complex (**7**) was obtained as a viscous amber oil, (0.532 g, 0.608 mmol, 84.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (bs, 3H, –CH_3, *n*-dodecyl), 1.24 (bs, 18H, –$CH_2(CH_2)_7CH_2$–, *n*-dodecyl), 1.61 (bs, 2H, –CH_2–, *n*-dodecyl), 2.71 (bs, 2H, –CH_2–Ar, *n*-dodecyl), 6.68–7.99 (m, 22H, Ar). $^{31}P\{^1H\}$ NMR (121.379 MHz, $CDCl_3$): δ = 128.98, 132.88 (s, $^2J_{PaPb}$ = 473.39 Hz, P_a) and 133.48, 137.37 (s, $^2J_{PaPb}$ = 473.039 Hz, P_b); δ = 119.68, 146.08 and 120.29, 146.67 (s, $^1J_{PPt}$ = 3193 Hz). FAB$^+$-MS [M]$^+$ = 876 (45%) *m*/*z*, [M−Cl]$^+$ = 841 (100%) *m*/*z*. *Anal.* Calc. for $C_{42}H_{47}ClO_2P_2Pt$ (M_r = 876.30): C, 57.57; H, 5.41. Found: C, 57.58; H, 5.43%.

2.9. Synthesis of [PtCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPr^i_2$)$_2$}] (**8**)

Complex (**8**) was synthesized by an analogous method as that described for the phenyl derivative (**3**), from ligand (**2**) (367 mg, 0.72 mmol) in toluene (20 mL) and cis-[(Me_2S)$PtCl_2$] (280 mg, 0.72 mmol) in toluene (30 mL). Complex (**8**) was obtained as a viscous amber oil, (0.432 g, 0.584 mmol, 81.2%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (bs, 3H, -CH_3, *n*-dodecyl), 1.24 (bs, 18H, –$CH_2(CH_2)_7CH_2$–, *n*-dodecyl), 1.27–1.45 (bm, 24H, -$CH(CH_3)_2$, PPr^i_2) 1.53 (bs, 2H, –CH_2–, *n*-dodecyl), 2.17–2.24 (bm, 4H, -$CH(CH_3)_2$, PPr^i_2), 2.51 (bs, 2H, –CH_2–Ar, *n*-dodecyl), 6.47–6.89 (m, 2H, Ar). $^{31}P\{^1H\}$ NMR (121.379 MHz, $CDCl_3$): δ = 169.86, 173.27 (s, $^2J_{PaPb}$ = 414.60 Hz, P_a) and 173.87, 177.29 (s, $^2J_{PaPb}$ = 414.60 Hz, P_b); δ = 160.64, 185.89 and 161.26, 186.49 (s, $^1J_{PPt}$ = 3054 Hz). FAB$^+$-MS [M]$^+$ = 740 (20%) *m*/*z*, [M−Cl]$^+$ = 704 (53%) *m*/*z*. *Anal.* Calc. for $C_{30}H_{55}ClO_2P_2Pt$ (M_r = 740.24): C, 48.68; H, 7.49. Found: C, 48.55; H, 7.43%.

2.10. General method for the Heck reactions

A DMF solution (5 ml) of 4.0 mmol of halobenzene, 4.0 mmol of styrene, and the prescribed amount of catalyst (0.1% 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 and (Na_2CO_3-0.4 g, 4 mmol), sealed, and fully immersed in a 140 °C silicon oil bath. After the prescribed reaction time (6 h), the mixture was cooled to room temperature and the organic phase analyzed by gas chromatography (GC–MS) by duplicate.

2.11. General method for the Suzuki-Miyaura couplings

A DMF solution (5 ml) of 4.0 mmol of halobenzene, 4.0 mmol of phenyl boronic acid, and the prescribed amount of catalyst (0.1% 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 (Na_2CO_3, 4 mmol), and sealed, and fully immersed in a 110 °C silicon oil bath. After the prescribed reaction time (8 h), the mixture was cooled to room temperature and the organic phase analyzed by gas chromatography (GC–MS) by duplicate.

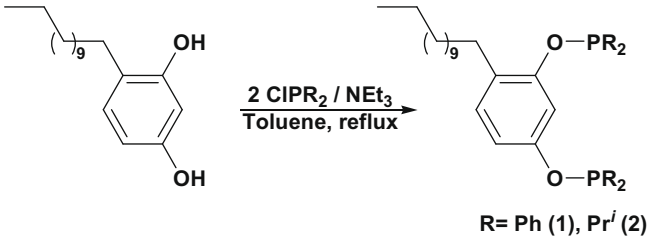
2.12. Mercury drop experiments

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 Pd(0) is not involved. These experiments were performed under the optimized condition for entries 4 in both transformations (e.g. with bromobenzene).

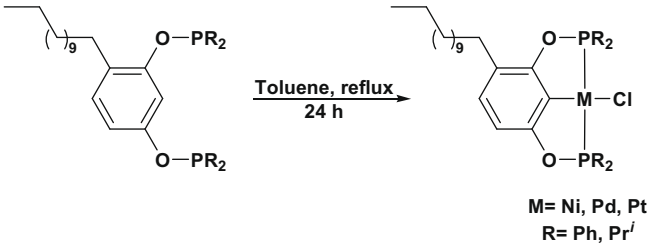
3. Results and discussion

The phosphinite POCOP pincer ligands [4-(*n*-$C_{12}H_{25}$)-C_6H_3-1,3-(OPR_2)$_2$] R=Ph (**1**), Pr^i (**2**) were synthesized in a similar manner as described by our group for [C_6H_4-1,3-($OPPr^i_2$)$_2$] [3a]. Thus, the reaction of [4-(*n*-$C_{12}H_{25}$)-C_6H_3-1,3-$(OH)_2$] with $ClPR_2$ (R=Ph, Pr^i) in a 1:2 molar ratio in the presence of slight excess of NEt_3 under reflux in toluene (Scheme 2) affords ligands (**1**) and (**2**) in good yields and pure enough to be used for the synthesis of the corresponding group 10 transition metal complexes.

Analysis of both ligands by ^{1}H NMR displays signals due to the presence of phenyl rings, for (**1**) between δ 6.46 and 7.72 ppm, additional signals assigned to the aliphatic chain can be observed at δ 0.85, 1.20, 1.44 and 2.50 ppm due to the terminal methyl (–CH_3, *n*-dodecyl), middle methylenes (–$CH_2(CH_2)_7CH_2$–, *n*-dodecyl), methylene (–CH_2–, *n*-dodecyl) and methylene directly bonded to the aromatic ring (–CH_2–Ar, *n*-dodecyl) respectively. Analogously, the ^{1}H NMR spectrum for ligand (**2**) exhibits signals between δ 6.56 and 7.26 ppm corresponding to the aromatic ring. Additionally, signals due to the aliphatic chain and those due to the Pr^i groups in the phosphine fragment are observed at δ 0.87 (–CH_3, *n*-dodecyl), 1.05–1.17 (CH_3, Pr^i), 1.25 (–$CH_2(CH_2)_7CH_2$–, *n*-dodecyl), 1.44 (–CH_2–, *n*-dodecyl), 1.84–1.91 (CH_2, Pr^i) and 2.50 ppm (–CH_2–Ar, *n*-dodecyl) respectively. However, more



Scheme 2. General synthesis of the phosphinite ligands (1) and (2).



Scheme 3. General method for the synthesis of the group 10 POCOP pincer complexes.

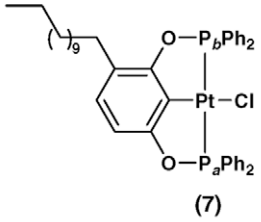
informative results were obtained from the analysis by $^{31}P\{^{1}H\}$ NMR. In this instance for both ligands, the spectra obtained shows two singlets at δ 110.35 (***P**a*) and 111.28 (***P**b*) ppm for ligand (**1**) and at δ 142.38 (***P**a*) and 149.42 (***P**b*) ppm for *iso*-propyl derivative (**2**), respectively. The later results in agreement with the two phosphorus being in different chemical and magnetic environments, as expected for a non-symmetric pincer ligand. Analysis of compounds (**1**) and (**2**) by mass spectrometry affords the molecular ion in the two cases. Elemental analysis where also in agreement with the proposed formulations.

The synthesis of all group 10 complexes with ligands (**1**) and (**2**) was carried out in a similar manner by using the corresponding starting material $NiCl_2$, $[CODPdCl_2]$ or *cis*-$[(Me_2S)PtCl_2]$ respectively, according to Scheme 3.

Thus, the reaction of both ligands with $NiCl_2{\cdot}6H_2O$ under reflux condition in toluene affords complexes [NiCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-$(OPPh_2)_2$}] (**3**) and [NiCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-$(OPPr^i_2)_2$}] (**4**) as dense greenish oily products in good yields. Analysis by proton NMR of both products yield similar spectra as those determined for the free ligands, with the signals just been slightly shifted to higher field. Further analysis of these samples by $^{31}P\{^{1}H\}$ NMR reveals the non-symmetric nature of the ligand, by displaying a spectra for an AB system, with two signals corresponding to two different ***P*** nuclei. For instance for compound [NiCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-$(OPPh_2)_2$}] (**3**) at δ 138.76 and 142.67 ppm and 143.18 and 147.08 ppm for ***P**a* and ***P**b* respectively, having a $^{2}J_{PaPb}$ coupling constant of 474.88 Hz this value being in agreement with both phosphorus nuclei to be in a mutually *trans* conformation.

A similar situation stands for complex [NiCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-$(OPPr^i_2)_2$}] (**4**) where signals in the $^{31}P\{^{1}H\}$ NMR are located at δ 180.79 and 183.46 ppm and at 184.21 and 186.88 ppm for ***P**a* and ***P**b* respectively, with a $^{2}J_{PaPb}$ coupling constant of 324.53 Hz. The values of $^{2}J_{PaPb}$ being in agreement with the general rule that the magnitude of $^{2}J_{PP}$ increases as the electronegativities of groups attached to phosphorus increase [15].

Analysis by FAB^{+}-MS showed the presence of the molecular ions in both cases at $[M]^{+}$ = 738 (50%) *m/z* and 602 (12%) *m/z* for (**3**) and (**4**) respectively. Other important peaks exhibit the losing of the Cl in the fragmentation process to afford peaks at $[M-Cl]^{+}$ = 703 (88%) *m/z* and 567 (10%) *m/z* for (**3**) and (**4**), respectively. Results



(7)

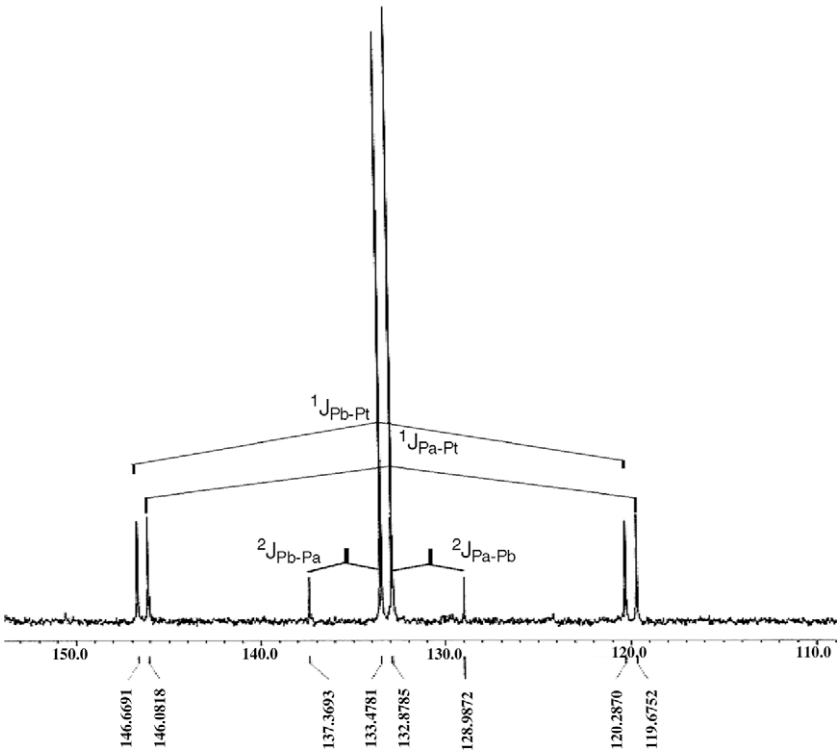
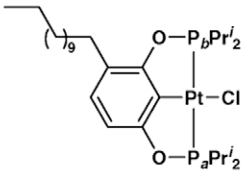


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectrum of complex [PtCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-$(OPPh_2)_2$}] (**7**).

obtained from elemental analysis of both species are also in agreement with the proposed formulations.

Palladium (II) complexes [PdCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-(OPR_2)$_2$}] R=Ph (**5**), Pr^i (**6**), were obtained in a similar manner as that of their nickel analogous as viscous amber oily products, from the stoichiometric reaction of [CODPdCl_2] with the corresponding ligand under reflux conditions in toluene. In this instance also, analysis by ^{1}H NMR allows the identification of the aromatic and aliphatic fragments in both complexes (see Section 2). Analysis by ^{31}P{^{1}H} NMR of these compounds exhibit similar patterns (AB systems) as those observed for the nickel counterparts, with four different signals caused by the presence of two different phosphorus nuclei. The chemical shifts in the case of the phenyl derivative (**5**) are located at δ 138.75 and 142.65 ppm for $\boldsymbol{P_a}$ and at δ 143.17 and 147.09 ppm for $\boldsymbol{P_b}$ with a $^2J_{PaPb}$ coupling constant of 473.06 Hz. Similarly, in the ^{31}P{^{1}H} RMN spectrum for complex (**6**) four signals can be observed at δ 182.71 and 186.11 ppm and δ 186.65 and 190.03 ppm assignable to the $\boldsymbol{P_a}$ and $\boldsymbol{P_b}$ phosphorus nuclei respectively with a $^2J_{PaPb}$ coupling constant of 412.36 Hz. The FAB$^+$-MS spectra were obtained for both complexes showing a similar fragmentation behavior as that observed for the Ni(II) species, with the molecular ions $[M]^+$ = 787 (8%) m/z and 651 (11%) m/z for (**5**) and (**6**), respectively, being in agreement with the expected molecular weights. In both cases, the parent peak corresponds to the fragment $[M-Cl]^+$ (751 (100%) m/z (**5**) and 615 (100%) m/z (**6**)). Elemental analysis results are in agreement with the proposed formulations.

Similarly, as described for the Ni(II) and Pd(II) derivatives (**3**)–(**6**), the platinum complexes were synthesized from the reaction of ligands (**1**) and (**2**) and the starting material *cis*-[$(Me_2S)_2PtCl_2$] under reflux conditions in toluene via C–H activation of the C–H aromatic bond, affording compounds [PtCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**7**) and [PtCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPr^i_2$)$_2$}] (**8**) as a colorless or amber color oily products respectively. As is the case for the Ni(II) and Pd(II) complexes, results obtained from the analyses by ^{1}H NMR for both complexes are coherent with



(8)

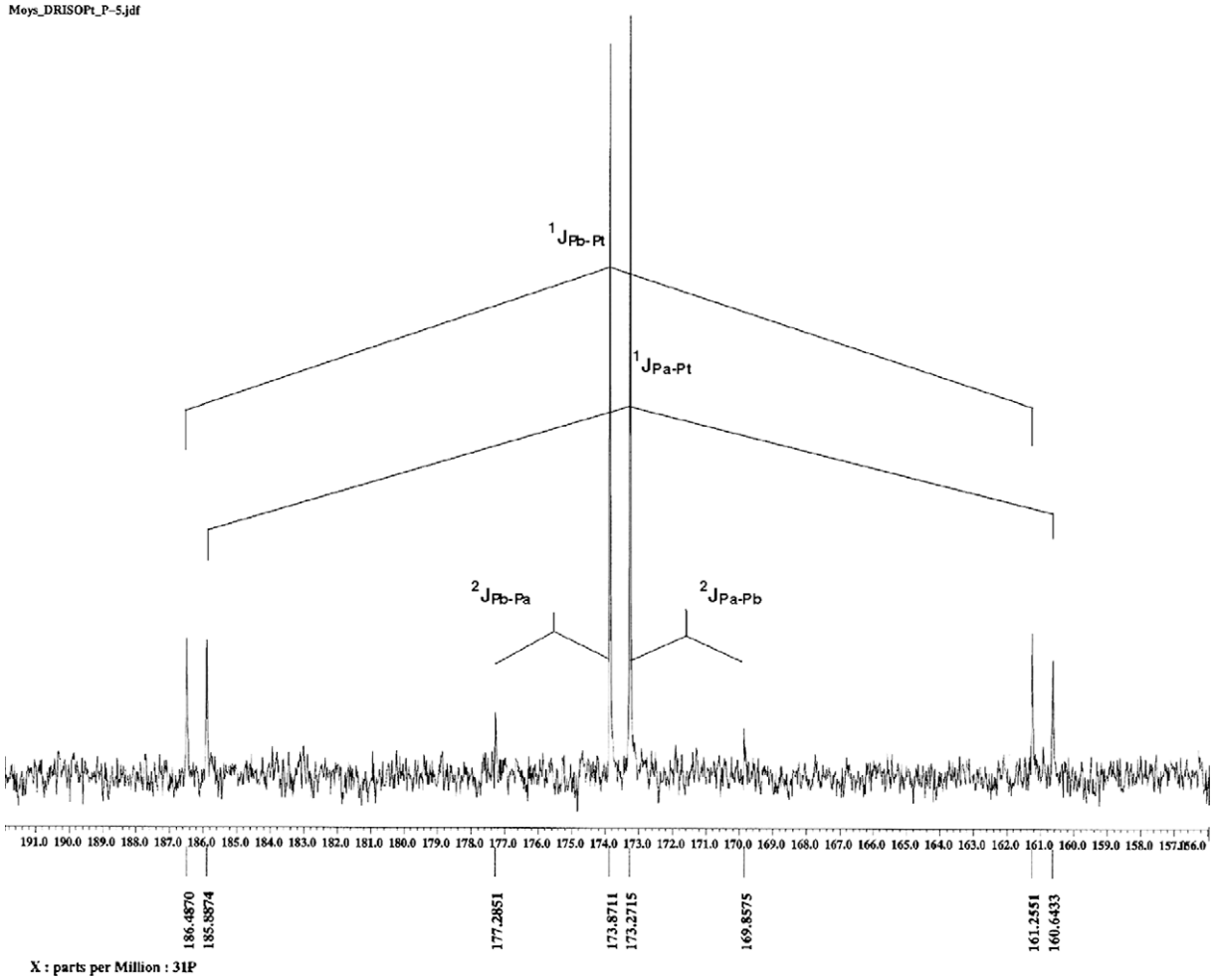


Fig. 2. ^{31}P{^{1}H} NMR spectrum of complex [PtCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPr^i_2$)$_2$}] (**8**).

the proposed structures. However, far more interesting results the analysis by $^{31}P\{^{1}H\}$ NMR experiments, were a similar pattern is observed for both platinum compounds **7** (Fig. 1) and **8** (Fig. 2), both being in agreement with the presence of two magnetically different phosphorus nuclei with signals at δ 128.98 and 132.88 ppm ($\boldsymbol{P_a}$) and δ 133.48 and 137.37 ppm ($\boldsymbol{P_b}$) with a coupling constant of $^{2}J_{Pa-Pb}$ = 473.39 Hz for compound [PtCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**7**). While for the *iso*-propyl derivative [PtCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPr^i_2$)$_2$}] (**8**), the phosphorus signals are located at δ 169.86 and 173.27 ppm ($\boldsymbol{P_a}$) and δ 173.87 and 177.29 ppm ($\boldsymbol{P_b}$) with a coupling constant of $^{2}J_{Pa-Pb}$ = 414.60 Hz respectively. The platinum satellites are located at δ 119.68 and 146.08 ppm ($\boldsymbol{P_a}$) and δ 120.29 and 146.67 ppm ($\boldsymbol{P_b}$) with a coupling constant of $^{1}J_{P-Pt}$ = 3193 Hz for the phenyl derivative [PtCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**7**) and at δ 160.64 and 185.89 ppm ($\boldsymbol{P_a}$) and δ 161.26 and 186.49 ppm ($\boldsymbol{P_b}$) with a coupling constant of $^{1}J_{P-Pt}$ = 3054 Hz for the *iso*-propyl complex [PtCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPr^i_2$)$_2$}] (**8**). Analysis of both complexes by FAB$^+$-MS, exhibit the molecular ions at $[M]^+$ = 876 (45%) *m/z* and 740 (20%) *m/z* for (**7**) and (**8**), respectively. Both values being in accordance with the expected molecular weights for the proposed formulations. Elemental analysis results were also in agreement with the proposed formulations.

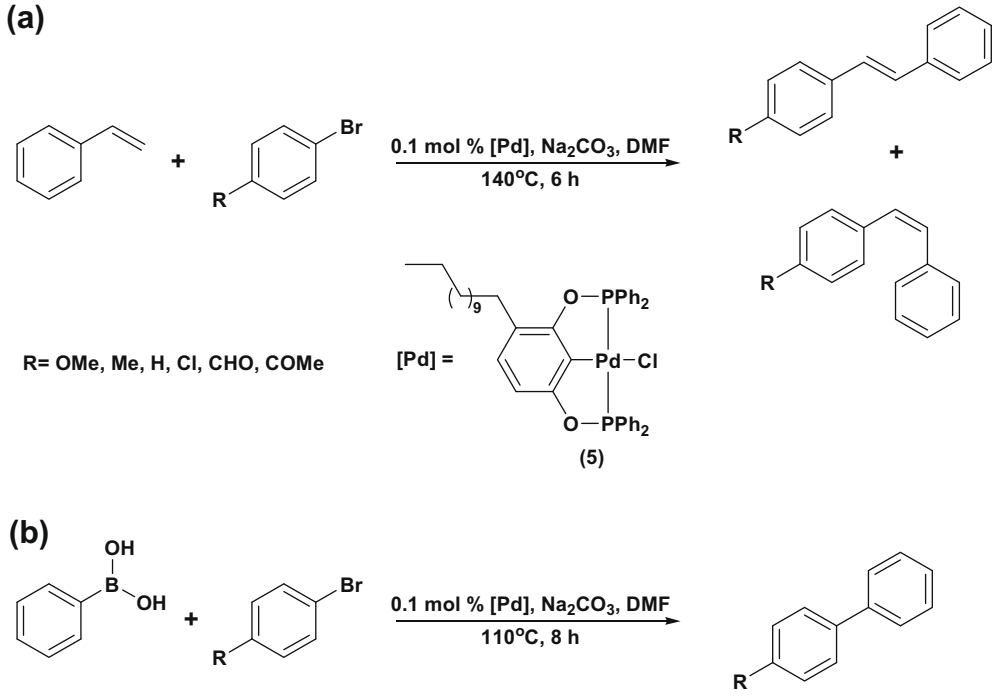
All the POCOP pincer complexes synthesized are air and moisture stable. And having on hand the Pd(II) derivatives we decided to explore their reactivity on C–C cross coupling reactions, namely Heck reaction and Suzuki–Miyaura couplings. Experiments were done finding the best catalyst to be the phenyl derivative [PdCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**5**). Hence, complex (**5**) was employed as catalyst precursor for the Heck (Scheme 4a) and Suzuki-Miyaura (Scheme 4b) couplings of different *p*-substituted bromobenzenes with styrene and phenylboronic acid, respectively.

The conditions employed for the catalytic experiments are depicted on Scheme 4. These conditions were chosen so the results could be comparable to those obtained previously by our group with [PdCl(C_6H_3{2,6-($OPPr^i_2$)$_2$})] on the Heck experiments [3a]. The results are summarized on Table 1.

From the results obtained some general features are clear. In most of the cases the conversion proceeds quantitatively, except for the cases were electron donating groups (EDG) are present in the aromatic ring, this results can be anticipated based on the regular behavior observed for this sort of substrates based on their Hammet parameter values. The preference for the production of *E* over the *Z* product, being in most of the cases >90% it is also noticed. When compared with compound [PdCl(C_6H_3{2,6-($OPPr^i_2$)$_2$})], complex (**5**) results to be a faster catalyst, attaining similar yields for the same substrates in shorter times (compare 18 to 6 hours reaction time). Under the very same conditions employed no decomposition of the catalyst was observed and the performance of the catalysts in a control experiment in the presence of Hg^0 does not change significantly.

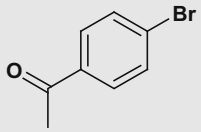
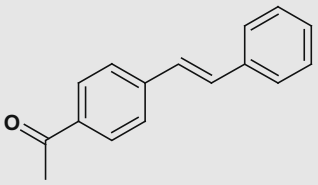
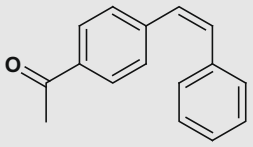
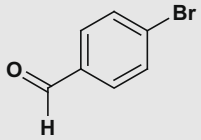
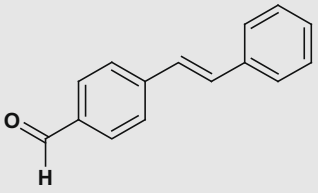
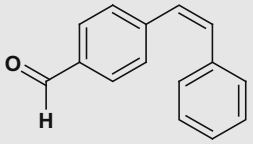
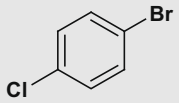
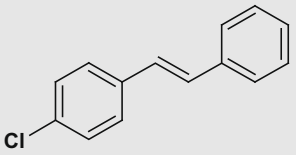
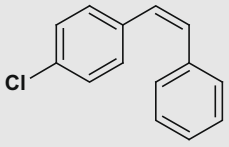
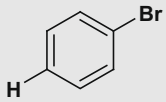
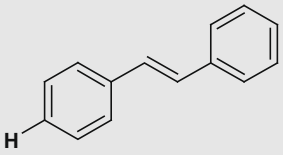
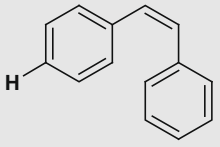
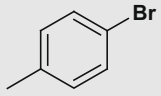
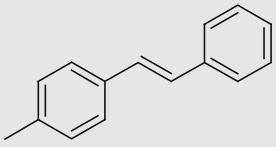
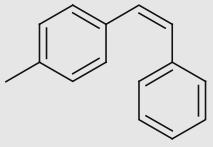
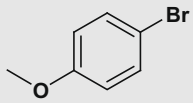
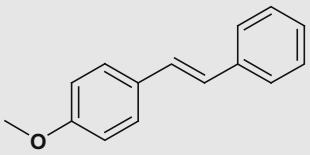
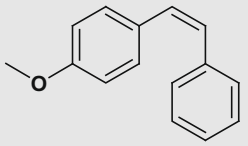
A similar behavior is observed when complex (**5**) is used as catalyst for the Suzuki-Miyaura couplings of different bromobenzenes *para* substituted (Table 2). In this case, complex (**5**) once more results to be faster that compound [Pd(TFA)(C_6H_3{2,6-($OPPr^i_2$)$_2$})] reported by Bedford [16], something that is important to mention is that in the present case the Cl substituent does not has to be substituted by a more labile group in order to make this catalysts faster. As was the case for the Heck couplings, no apparent decomposition is observed on this set of experiments, and a similar control experiment in the presence of Hg^0 does not lead to deactivation of the catalyst. It is possible that the enhanced reactivity observed in both transformations may be related to the higher solubility exhibited by palladium complex (**5**). Additionally, given the structure of complex (**5**) and the length of the hydrocarbon tail on the aromatic ring, the potential formation of aggregates (e.g. micelles) could also be conceived as a stabilization process for this species in solution, thus also enhancing the reactivity of these species during the catalytic process.

There has been a considerable debate in the literature about the oxidation states of the species involved in the catalytic cycle with Pd(IV)/Pd(II) and Pd(II)/Pd(0) both being proposed at various times [17,3c]. Another feasible proposal for the present case is that it might be possible that one or both arms may deligate at some stage enabling the compound to catalyze the reaction, thus



Scheme 4. Evaluation of the catalytic activity of complex [PdCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**5**).

Table 1
Heck-Mizoroki couplings using [PdCl{3-(n-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**5**).

Entry	*p*-Bromobenzene	*E* (%)	*Z* (%)	% Conversion[a]
1		 90.5	 9.4	>99
2		 91.9	 8.2	>99
3		 86.2	 13.7	>99
4		 68.8	 18.7	87.6
5		 70.8	 9.2	80.0
6		 40.5	 4.3	44.8

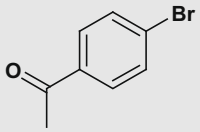
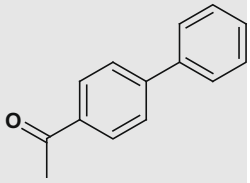
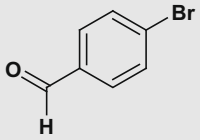
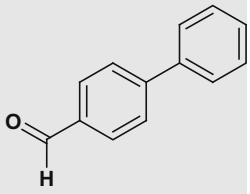
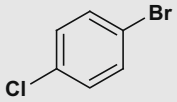
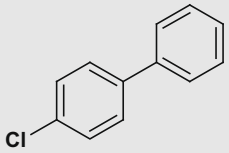
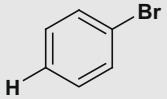
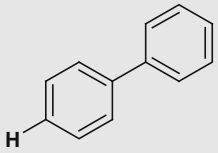
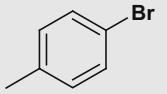
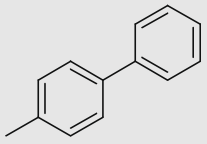
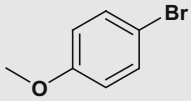
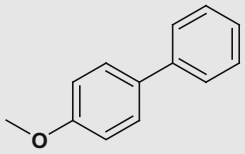
[a] Yields obtained by GC are based on bromobenzene.

behaving as a hemilabile ligand [18]. Thus, although the precise mechanism of the catalytic reaction using complex (**5**) remains to be elucidated, efforts aimed to shed some further light regarding this are currently under progress in our laboratories.

In summary, we have successfully synthesized in high yields a series of non-symmetric POCOP pincer ligands and their complexes with group 10 transition metal complexes. The non-symmetric nature of ligands (**1**) and (**2**) and their complexes (**3**) trough (**8**) is clearly demonstrated by the $^{31}P\{^1H\}$ NMR experiments. Preliminary catalytic evaluation of the Pd(II) derivatives (**5**) and (**6**), show complex (**5**) to be a faster catalyst than their symmetric counterparts compounds [PdCl(C_6H_3{2,6-($OPPr^i_2$)$_2$})] and [Pd(TFA)(C_6H_3{2,6-($OPPr^i_2$)$_2$})] in Heck-Mizoroki and Suzuki-Miyaura cross coupling reactions, respectively.

Moreover, given the physical properties and structure of the group 10 transition metal complexes obtained, these species may present interesting optical properties, particularly in the field of liquid crystals. This possibility will be explored in the near future as

Table 2
Suzuki-Miyaura couplings using [PdCl{3-(*n*-$C_{12}H_{25}$)-C_6H_2-2,6-($OPPh_2$)$_2$}] (**5**).

Entry	*p*-Bromobenzene	% Conversion[a]
1		 80.1
2		 76.3
3		 71.1
4		 68.3
5		 72.2
6		 64.4

[a] Yields obtained by GC are based on bromobenzene.

well as the potential applications of these species in other organic transformations.

Acknowledgements

We would like to thank Chem. Eng. Luis Velasco Ibarra, Dr. Francisco Javier Pérez Flores, Q. Eréndira García Ríos and M.Sc. Ma. de las Nieves Zavala for their invaluable help in the running of the FAB$^+$-Mass, IR and some NMR spectra, respectively. The financial support of this research by CONACYT (F58692) and DGAPA-UNAM (IN227008) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.07.038.

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