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

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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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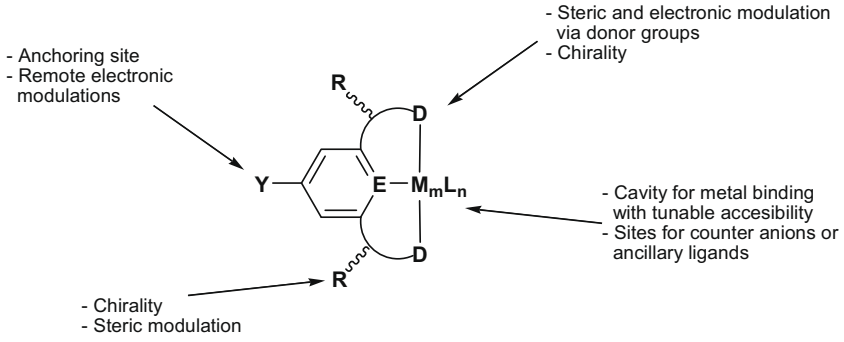

Scheme 1. Versatility of the pincer backbone and potential sites for modification.

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