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Simple protocol for the synthesis of the asymmetric PCP pincer ligand [C_6H_4-1-(CH_2PPh_2)-3-($CH(CH_3)PPh_2$)] and its Pd(II) derivative [PdCl{C_6H_3-2-(CH_2PPh_2)-6-($CH(CH_3)PPh_2$)}]

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Abstract

The asymmetric PCP pincer ligand [C_6H_4-1-(CH_2PPh_2)-3-($CH(CH_3)PPh_2$)] (**4**) has been synthesized in a facile manner in three simple steps in high yield. Metallation of PCP pincer ligand (**4**) with [Pd(COD)Cl_2] affords complex [PdCl{C_6H_3-2-(CH_2PPh_2)-6-($CH(CH_3)PPh_2$)}] (**7**) in good yield.

Keywords: PCP pincer ligands; PCP pincer complexes; Palladium complexes

1. Introduction

Pincer compounds are a group of species with very particular and interesting physical 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. Thus, till date, 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] and amines and imines [7]. Moreover, the very same system can be modified to include functional groups that enable these species to be anchored to solid supports [8] or to allow 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 (see Scheme 1).

Hence, nowadays pincer compounds of many elements are known and their chemistries are motif of continuous and numerous studies. Noteworthy is the fact that the number of examples of complexes including asymmetric pincer type ligands is limited in comparison with those of their symmetric analogs [10]. This is partly because their preparation is a considerable challenge, which is laborious

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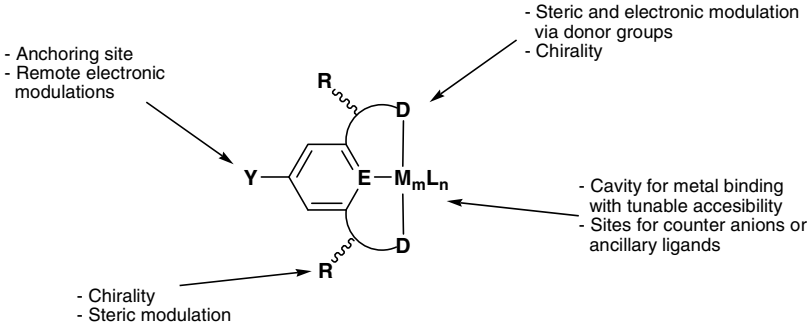


Scheme 1. Versatility of the pincer framework.

and requires a series of steps to introduce different groups or donors. Moreover, complexes bearing asymmetric pincer ligands have shown enhanced and in many cases markedly different reactivities, such as hemilability [11].

From the above discussion, it clearly results that the design of ligands is one of the most important aspects in the chemistry of this kind of compounds, this being specially important in homogeneous catalysis. The ability to simply and independently vary the steric and electronic properties of a given ligand may provide a wealth of opportunities to influence reactivity, stability, catalysis and other important properties at the metal center. Hence, following our continuous interest in the development on pincer chemistry [12], herein we would like to report a simple protocol for the high yield synthesis of the asymmetric ligand [C_6H_4-1-(CH_2PPh_2)-3-($CH(CH_3)PPh_2$)] (**4**) and its Pd(II) derivative [PdCl{C_6H_3-2-(CH_2PPh_2)-6-($CH(CH_3)PPh_2$)}] (**5**).

2. Experimental

2.1. Materials and methods

Unless otherwise stated, all reactions were carried out under an atmosphere of purified argon using conventional Schlenk glassware and glovebox techniques; solvents were dried using the established procedures and distilled under dinitrogen and freeze–pump–thaw degassed immediately prior to use. The ^1H, $^{13}C\{1H\}$, $^{31}P\{^1H\}$ NMR spectra were recorded at 300, 75.4 and 121.4 MHz, respectively at 295 K, using a Bruker Avance DRX 300 MHz NMR spectrometer. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from TMS. ^1H NMR chemical shifts are referenced to the residual hydrogen signal of the deuterated solvents and in $^{13}C\{^1H\}$ NMR the ^{13}C signal of the deuterated solvents was used as a reference. $^{31}P\{^1H\}$ NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to high frequency of 85% H_3PO_4. Elemental analyses were determined on a Heraeus CHN-O-RAPID elemental analyzer. The starting materials α,α′-dibromo-*m*-xylene, chlorodiphenylphosphine, $PdCl_2$, $CDCl_3$ were purchased from Aldrich Chemical Co. and used without further purification. The complex [$PdCl_2$-(COD)] was synthesized according to the published procedure [13].

2.2. Synthesis of {C_6H_4-1-(CH_2Br)-3-(CH_2PPh_3Br)} (**1**)

To a stirred solution of α,α′-dibromo-*m*-xylene (3.70 g, 14 mmol) in THF (100 ml) was added a solution of triphenylphosphine (4.3 g, 16 mmol) in THF (20 ml) at room temperature and the solution allowed to reach 60 °C slowly. The resulting white suspension was stirred overnight. The reaction mixture was allowed to reach room temperature, the mixture was filtered off and the remaining solid was washed with THF (3 × 10 ml) and dried under vacuum to give a pure white powder of **1** (6.3 g, 12 mmol, 85%). ^1H NMR (300 MHz, $CDCl_3$): δ 4.17 (s, 2H, CH_2Br); 5.32 (d, $J = 14.39$ Hz, CH_2P); 6.97–7.27 (m, 4H, Ph); 7.53–7.73 (m, 15H, PPh_3). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$): δ 30.37 (d, $J_{CP} = 47.66$ Hz, CH_2P); 32.64 (CH_2Br); 116.62, 117.76, 127.64, 128.83, 129.09, 130.01 (d, $J = 12.1$ Hz), 131.29, 131.90, 134.09 (d, $J = 9.80$ Hz) 134.84, 138.08. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 24.22. *Anal.* Calc. for $C_{26}H_{23}Br_2P$ ($M_r = 526.24$): C, 59.34; H, 4.41. Found: C, 59.38; H, 4.45%.

2.3. Synthesis of {C_6H_4-1-(CH_2Br)-3-($CH{=}CH_2$)} (**2**)

To a stirred solution of **1** (2.63 g, 5 mmol) in dichloromethane (40 ml) was added *para*-formaldehyde (0.27 g, 9 mmol) and KOH solution (6 ml, 50%) at room temperature, respectively and stirred for 1 h. The organic layer was separated and the aqueous layer extracted with ether. The combined organic extracts were washed and dried over $MgSO_4$. After filtration, the solution was passed through a short plug of celite and the solvent evaporated under vacuum to afford a white solid. The remaining solid was extracted with *n*-hexane and then the solvent evaporated under vacuum to afford **2** as a pure colorless oil (0.79 g, 4 mmol, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ 4.37 (s, 2H, CH_2Br), 5.18 (d, $J_{HH} = 11.1$ Hz, 1H, CH_2), 5.67 (d, $J_{HH} = 17.4$ Hz, 1H, $CH{=}CH_2$), 6.60 (dd, $J_{HH} = 17.70$ HZ, $J_{HH} = 10.8$ Hz, $CH{=}CH_2$), 7.15–7.314 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$): δ 33.39 (CH_2Br), 114.54 ($CH{=}CH_2$), 126.17, 126.78, 128.32, 128.93, 136.13

(CH=CH_2), 137.93, 138.02. *Anal.* Calc. for C_9H_9Br ($M_r = 197.07$): C, 54.85; H, 4.60. Found: C, 54.90; H, 4.57%.

2.4. Synthesis of {C_6H_4-1-(CH_2Br)-3-($CH(CH_3)Br$)} (3)

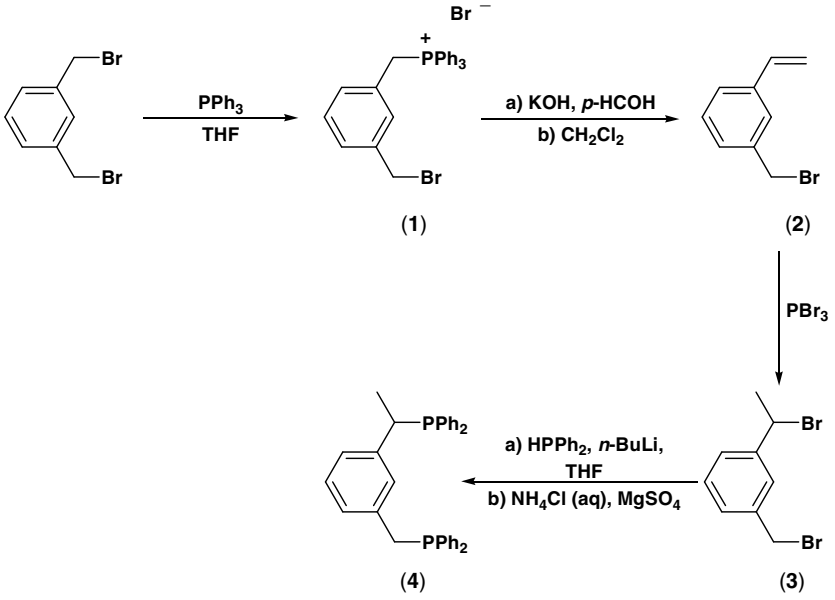
To a stirred solution of **2** (0.62 g, 3.1 mmol) in dichloromethane (15 ml), PBr_3 (0.123 ml, 1.3 mmol) was added at room temperature and stirred for 3 h. After this time, the solution is then washed with aqueous $NaHCO_3$ and then with water, the organic phase is separated and the aqueous layer extracted twice with CH_2Cl_2 (2 × 10 ml). The organic phase is dried over $MgSO_4$ and the solvent removed by rotary evaporation to afford **3** as a colorless oil (0.86 g, 3.1 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.95 (d, $J = 6.90$ Hz, 3H, CH_3); 4.39 (s, 2H, CH_2Br); 5.10 (q, $J = 6.90$ Hz, 1H, CH), 7.15–7.36 (m, 4h, Ar). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$): δ 26.65 (CH_3), 33.01 (CH_2Br), 48.76 (CHBr), 126.83, 127.35, 128.94, 129.13, 138.13, 143.74. *Anal.* Calc. for $C_9H_{10}Br_2$ ($M_r = 277.98$): C, 38.89; H, 3.63. Found: C, 38.85; H, 3.65%.

2.5. Synthesis of {C_6H_4-1-(CH_2PPh_2)-3-($CH(CH_3)PPh_2$)} (4)

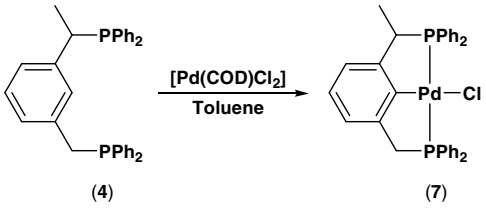
To a solution of Ph_2PH (1.17 g, 6 mmol) in THF (35 ml) was added dropwise a solution of *n*-BuLi in hexane (3.75 ml of 1.6 M/l hexane solution, 6 mmol) at −78 °C, over a period of 30 min with stirring. After this time, the reaction mixture was allowed to reach room temperature. The resulting orange suspension was cooled to −78 °C and a THF solution (20 ml) of **3** (0.834 g, 3 mmol) was added dropwise with a syringe over 30 min. The resulting mixture is allowed to reach room temperature and the stirring continued for an additional 1 h to give a clear mixture. After this time, the resulting reaction mixture is placed into a salt-ice bath (0 °C) and a solution of NH_4Cl in water (10 wt%, 45 ml) is carefully added to afford a colorless mixture. The THF layer was separated and the aqueous layer extracted twice with ether (2 × 15 ml). The combined extracts were dried over $MgSO_4$ and passed through a short column of alumina. Finally, the solvent was removed under vacuum to afford **4** as a colorless oil (1.39 g, 2.85 mmol, 95%). ^{1}H NMR (300 MHZ, $CDCl_3$): δ 1.02 (dd, $^3J_{HP} = 14.7$ Hz, $^3J_{HH} = 7.35$ Hz, 3H, CH_3), 2.94 (d, $^2J_{HP} = 18$ Hz, 2H, CH_2P), 3.10 (m, 1H, CHP), 6.52–6.91 (m, 20H, PPh_2), 7.04–7.30 (m, 4H, Ar). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$): δ 20.17 (d, $J_{CP} = 21.2$ Hz, $CHPPh_2$), 36.26 (d, $J_{CP} = 16.1$ Hz, CH_2PPh_2); 39.47 (d, $J_{CP} = 13.2$ Hz, CH_3), 126.60 (d, $J = 5.3$ Hz), 127.67, 128.00, 128.15, 128.33, 128.52, 128..60, 128.69, 129.23, 129.90, 130.76, 131.34, 133.08, 133.28, 133.33, 133.39, 133.53, 133.62, 134.36, 134.64, 137.80, 137.91, 138.02, 138.49, 139.12 (d, $J = 4.8$ Hz), 143.96 (d, $J = 8.60$ Hz), Ar. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −9.157 (CH_2PPh_2), 2.69 ($CHPPh_2$). *Anal.* Calc. for $C_{33}H_{30}P_2$ ($M_r = 488.54$): C, 81.13; H, 6.19. Found: C, 81.20; H, 6.25% (see Scheme 2).

2.6. Synthesis of [PdCl{C_6H_3-2-(CH_2PPh_2)-6-($CH(CH_3)PPh_2$)}] (7)

To a stirred suspension of [Pd(COD)Cl_2] (0.777 g, 2.72 mmol) in toluene (25 ml), a solution of ligand **4** (1.329 g, 2.72 mmol) in toluene (20 ml) was slowly added. The resulting solution was set to reflux for 5 h. After this time, the solution was filtered over cotton pad and pumped



Scheme 2. Synthesis of the asymmetric PCP pincer ligand (**4**).



Scheme 3. Synthesis of the asymmetric Pd(II)-PCP pincer complex (**7**).

off under vacuum to dryness. The crude solid was purified by recrystallization from $CHCl_3$/MeOH to afford complex **7** as a white microcrystalline powder (1.46 g, 2.31 mmol, 85%): ^{1}H NMR (300 MHZ, $CDCl_3$): δ 1.02 (dd, $^3J_{HP} = 16.04$ Hz, $^3J_{HH} = 7.1$ Hz, 3H, CH_3), 3.82 (d, $J = 6$ Hz, 2H, CH_2PPh_2), 4.00 (m, 1H, $CHPPh_2$), 6.95–7.04 (m, 3H, Ar), 7.26–7.82 (m, 20H, Ar). $^{13}C\{^1H\}$ NMR (75.40 MHz, $CDCl_3$): δ 21.46 (s, CH_3), 49.37 (d, $J =$ 31.0 Hz, CH_2PPh_2), 46.31 (d, $J = 30.4$ Hz, $CH(CH_3)PPh_2$), 122.56 (d, $J = 20.7$ Hz), 123.54 (d, $J = 22.4$ Hz), 126.21, 128.52 (d, $J = 24.1$ Hz), 128.55, 129.98, 130.42, 130.86, 132.13 (d, $J = 9.7$ Hz), 132.97 (d, $J = 17.3$ Hz), 132.99, 134.92 (d, $J = 10.86$ Hz), 147.67 (d, $J = 21.2$ Hz), 153.87(d, $J = 22.3$ Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 34.32 (d, $J_{PP} = 418$ Hz, CH_2PPh_2), 48.57 (d, $J_{PP} =$ 418 Hz, $CH(CH_3)PPh_2$). *Anal.* Calc. for $C_{33}H_{29}ClP_2Pd$ ($M_r = 629.40$): C, 62.97; H, 4.64. Found: C, 63.00; H, 4.60% (see Scheme 3).

3. Results and discussion

The initial step for the formation of PCP pincer ligand (**4**) very much resembles the initial step employed by Shaw on his seminal report in the 1970s [14]. Thus, α,α′-dibromo-*m*-xylene was treated with one equivalent of triphenylphosphine in THF to afford the single substituted triphenyphosphonium salt {C_6H_4-1-(CH_2Br)-3-(CH_2PPh_3Br)} (**1**). Analysis of the solid product (**1**) by ^{1}H reveals that the α,α′-dibromo-*m*-xylene has been substituted in only one arm. Thus, signals corresponding to two different CH_2 groups in the molecule can be observed, a singlet corresponding to the CH_2Br located at δ 4.17 ppm and a doublet due to the presence of the CH_2PPh_3Br found at δ 5.32 ppm. Similar assignation can be done from the results obtained from the analysis of the same sample by $^{13}C\{^1H\}$ NMR, where besides the signals observed for the aromatic carbons in the usual region (δ 116–138 ppm) signals corresponding to the two different CH_2 can be observed at δ 32.64 and δ 30.37 ppm for the CH_2Br and CH_2PPh_3Br moieties, respectively. Furthermore, the presence of the phosphonium group was detected by $^{31}P\{^1H\}$ NMR, this analysis showing a single signal at δ 22.24 ppm due to the PPh_3Br group. Elemental analysis is also consistent with the proposed formulation.

In contrast to the procedure employed by Shaw [14], where the phosphonium salt was treated with a mild base to afford the corresponding phosphine, compound (**1**) was treated with a strong base (KOH) in the presence of an excess of *para*-formaldehyde to afford the Witting [15] product {C_6H_4-1-(CH_2Br)-3-($CH{=}CH_2$)} (**2**). Analysis of this compound by ^{1}H NMR shows a typical pattern for a single substituted ethylene type olefin, exhibiting two sets of doublets for the terminal protons of the alkene at δ 5.18 and δ 5.67 ppm and a doublet of doublets for the methyne group at δ 6.60 ppm. A further singlet at δ 4.37 ppm and signals due to the aromatic protons between δ 7.15 and 7.31 ppm are also observed in the spectrum.

Bromination of the olefin compound (**2**) with PBr_3 gives place to the formation of the asymmetric dibromo starting material {C_6H_4-1-(CH_2Br)-3-($CH(CH_3)Br$)} (**3**). This compound afforded a ^{1}H NMR spectrum where the most notorious signal is a doublet located at δ 1.95 ppm corresponding to the newly formed CH_3 group in one of the arms. Complementary to this signal is a quartet at δ 5.10 ppm due to the methyne group of the same arm. While the signal corresponding to the un-substituted arm and those due to the aromatic protons can be observed at δ 4.39 and 7.15–7.36 ppm, respectively. Signals concurrent with the previous analysis can be observed at δ 26.65, 33.01 and 48.76 ppm in the $^{13}C\{^1H\}$ NMR spectrum, these signals being assigned to the methyl, methylene and methyne groups in (**3**), respectively. Results obtained from elemental analysis are also in agreement with the proposed formulation.

The final step leading to the synthesis of the PCP pincer ligand involved the reaction of the lithium salt of the diphenylphosphine with the dibromo compound (**3**), at a low temperature to afford compound {C_6H_4-1-(CH_2PPh_2)-3-($CH(CH_3)PPh_2$)} (**4**) as an air sensitive colorless oil in excellent yield (95%). Once again signals corresponding to the CH_3, CH_2 and CH groups can be observed in the corresponding ^{1}H NMR spectrum at δ 1.02 (dd), 2.94 (d) and 3.10 (m) ppm, respectively. The substitution of the bromides for the phosphine groups can be inferred for the multiplicity observed in these signals due to the coupling with the *P* nuclei and for the shift of these signals to higher field due to the inductive effect of the phosphine moieties. As is the case for the previous intermediates, a similar behavior is observed in the $^{13}C\{^1H\}$ NMR. More illustrative are the results of the analysis by $^{31}P\{^1H\}$ NMR, where two different signals, due to two inequivalent phosphorus nuclei are observed; one due to the substituted arm at a lower field (δ 2.69 ppm) and the other centered at δ −9.16 ppm. It is very interesting to note that these chemical shifts agree well when compared to the bis-disubstituted ligand {C_6H_4-1,3-($CH(CH_3)PPh_2$)} (**5**) reported by Venanzi [16] and Zhang [17] and the simple PCP pincer ligand {C_6H_4-1,3-(CH_2PPh_2)} (**6**) reported earlier by Venanzi [18] with only very slight variations (Fig. 1).

As for most of the cases, metallation of ligand (**4**) proceeds in a very facile manner via the C–H activation of the aromatic ring by $[Pd(COD)Cl_2]$ under reflux using toluene as solvent. The white product of [PdCl{C_6H_3-2-(CH_2PPh_2)-6-($CH(CH_3)PPh_2$)}] (**7**) thus obtained was

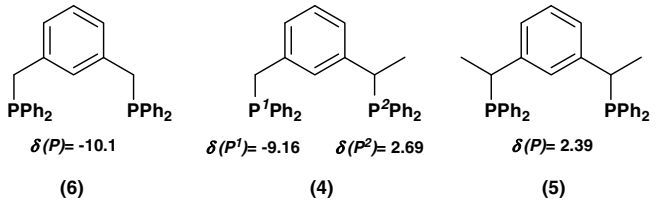


Fig. 1. Chemical shift (δ) Comparison between symmetric PCP pincer ligands and compound (**4**).

analyzed by ^{1}H NMR, showing signals similar to those of the free ligand but slightly shifted to lower field, a fact that agrees well with the metal being coordinated to the ligand. This argument is also supported for the more notorious shift to the lower field of the signals in the $^{31}P\{^{1}H\}$ NMR spectra, passing from δ −9.16 and δ 2.69 ppm in the free ligand (**4**) to δ 34.32 and δ 48.57 ppm in the metallated complex (**7**) for the CH_2PPh_2 and $CH(CH_3)PPh_2$, respectively. Moreover, the signals of the phosphorus nuclei of compound (**7**) are shown as doublets, which also accounts for the ligand to be coordinated to the metal in a κ^2-P,P form. Besides the J^2_{pp} value of 418 Hz, it is consistent with a *trans* arrangement of the two phosphorus nuclei. Once again, the chemical shifts observed for (**7**) agree well when compared to their symmetric analogous [PdCl{C_6H_3-2,6-($CH(CH_3)PPh_2$)$_2$}] (**8**) [16,17b] and [PdCl{C_6H_3-2,6-(CH_2PPh_2)$_2$}] (**9**) [18] (Fig. 2).

Results obtained from elemental analysis are also in agreement with the proposed formulation. Unfortunately, multiple attempts to obtain suitable crystals of complex (**7**) for their analysis by single crystals X-ray diffraction techniques afforded in amorphous powder or very low quality crystals all cases.

In summary, the present method represents an attractive and easy to perform methodology for the synthesis of asymmetric PCP pincer ligands and their palladium derivatives. It is important to note that the method may not be limited to the synthesis of ligand (**4**) but by careful selection of the aldehyde and reaction conditions, the methyl group in the substituted arm can be changed for various other substituents or even lead to the elongation of the arm thus affording another group of potentially interesting PCP pincer ligands having 5 and 6 membered rings. Moreover, exploitation of the different reactivities of the two different arms in compound (**3**) may offer the opportunity to attain PCP pincer ligands with different donor groups, since it is expected that the more substituted arm would react slowly when compared to the un-substituted arm. Experiments aimed to confirm these theories and the synthesis of other group 10 transition metal derivatives of ligand (**4**) and the study of the potential activity of complex (**7**) are currently underway in our laboratories.

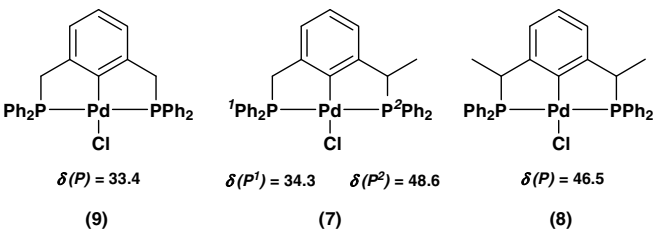


Fig. 2. Chemical shift (δ) Comparison between symmetric Pd(II)-PCP pincer complexes and compound (**7**).

Acknowledgements

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