Inorganica Chimica Acta 363 (2010) 1306–1310

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Note

Synthesis of a novel non-symmetric Pd(II) phosphinito–thiophosphinito PSCOP pincer compound

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A R T I C L E   I N F O

Article history:
Received 3 February 2010
Accepted 4 February 2010
Available online 10 February 2010

Dedicated to Prof. J.R. Dilworth

Keywords:
Cross coupling reactions
Suzuki–Miyaura couplings, palladium complexes
Palladacycles, pincer compounds
Crystal structures
Catalysis

A B S T R A C T

The reaction of 3-mercaptophenol with diphenylchlorophosphine in a 1:2 ratio in the presence of NEt_3 as base, affords cleanly the non-symmetric ligand $[C_6H_4\text{-}1\text{-}(SPPh_2)\text{-}3\text{-}(OPPh_2)]$ (**1**). The direct reaction of this ligand with $PdCl_2$ in refluxing toluene affords the non-symmetric phosphinito–thiophosphinito PSCOP pincer complex $[PdCl\{C_6H_3\text{-}2\text{-}(SPPh_2)\text{-}6\text{-}(OPPh_2)\}]$ (**2**).

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 heavily attracted the attention of the chemistry community for multiple applications, particularly in homogeneous catalysis [1]. The very simple backbone exhibited by these compounds did not anticipate the wide variety of possible functionalizations (Scheme 1). And today, these ligands have been modified to include a plethora of different donor groups [2–7], including chiral motifs allowing the synthesis of enantiomerically pure systems successfully employed in asymmetric synthesis and enantioselective catalysis. 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].

Additionally, the sole 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 chemistry motif of continuous and numerous studies. In this sense, phosphinite PCP 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. Additionally, 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 of pincer chemistry [12], the present report describes a very simple alternative for the synthesis of non-symmetric pincer compounds by changing the spacer between the aromatic ring and the phosphorus donor atom, this time combining hard (oxygen) and soft (sulfur) atoms.

Hence, the reaction of 3-mercaptophenol with two equivalents of diphenylchlorophosphine in the presence of triethylamine as base under toluene reflux conditions affords ligand $[C_6H_4\text{-}1\text{-}(SPPh_2)\text{-}3\text{-}(OPPh_2)]$ (**1**) as a white solid in good yields (Scheme 2).[1]

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[1] Synthesis of $[C_6H_4\text{-}1\text{-}(SPPh_2)\text{-}3\text{-}(OPPh_2)]$ (**1**). In a Schlenk flask 3-mercaptophenol (6 mmol, 0.64 mL) and triethylamine (6.6 mmol, 1.8 mL) were stirred during a few minutes until a white solid was formed. Addition of toluene (60 mL) followed by chlorodiphenylphosphine (12 mmol, 2.25 mL) resulted in a whitish solution, which was set to reflux for 18 h. During this time precipitation of $Et_3N{\cdot}HCl$ occurred as a crystalline solid. The ammonium salt was filtered off through a short plug of Celite® on a glass frit and then washed with anhydrous toluene (10 mL). The resulting solution was concentrated under vacuum affording compound (**1**) as a white solid after being washed with anhydrous hexane (2 × 10 mL). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ ppm): 112.5 (s, PO), 32.0 (s, PS).

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doi:10.1016/j.ica.2010.02.003

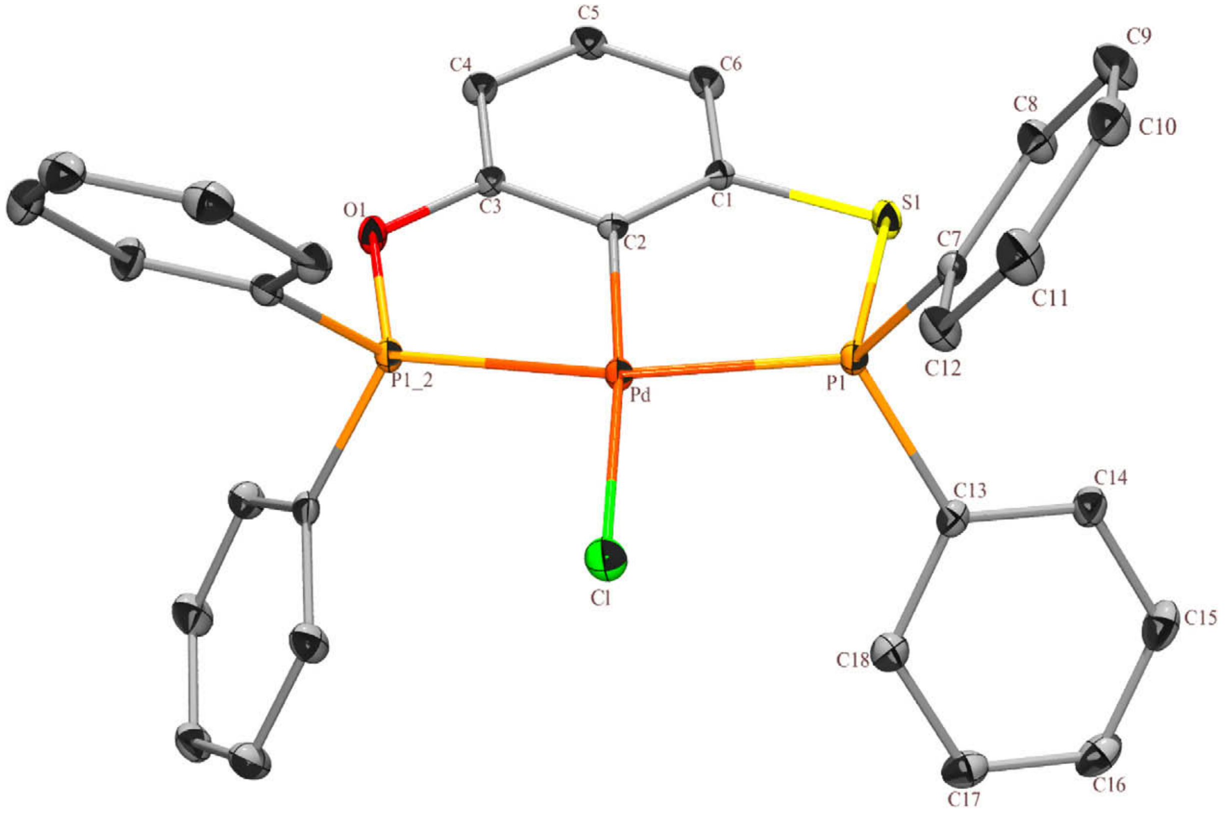
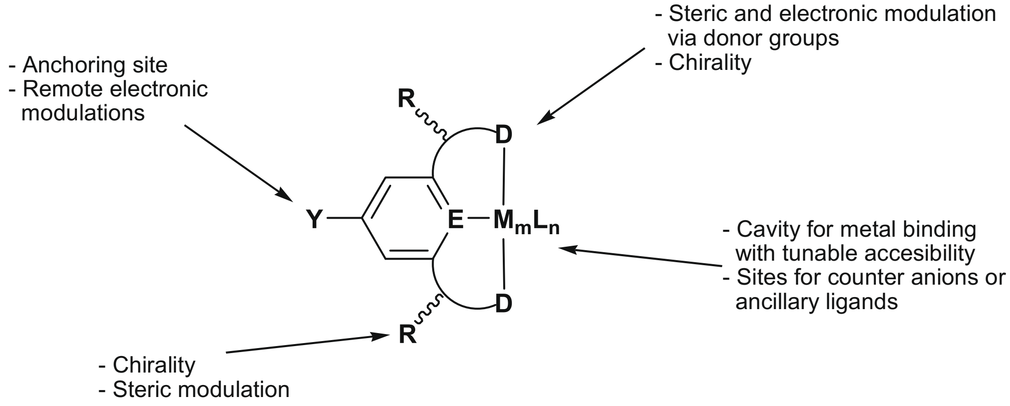
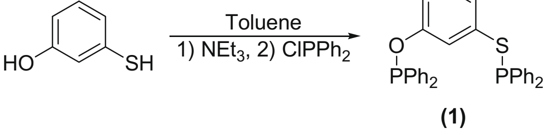


Fig. 1. An ORTEP representation of the structure of [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**) at 50% of probability showing the atom labeling scheme. Selected bond lengths (Å): Cl–Pd 2.3734(11), Pd–C(2) 2.022(5), Pd–C(2)#1 2.022(5), Pd–P(1)#1 2.2711(8), Pd–P(1) 2.2711(8), S(1)–C(1) 1.777(7), S(1)–P(1) 2.162(2), C(3)–O(1) 1.394(9), O(1)–P(1)#1 1.558(5), P(1)–O(1)#1 1.558(5). Selected Bond Angles (°):C(2)–Pd–C(2)#1 9.8(7), C(2)–Pd–P(1)#1 79.2(3), C(2)#1–Pd–P(1)#1 88.6(3), C(2)–Pd–P(1) 88.6(3), C(2)#1–Pd–P(1) 79.2(3), P(1)#1–Pd–P(1) 167.84(4), C(2)–Pd–Cl 175.1(3), C(2)#1–Pd–Cl 175.1(4), P(1)#1–Pd–Cl 96.08(2), P(1)–Pd–Cl 96.08(2), C(1)–S(1)–P(1) 97.9(3), C(3)–O(1)–P(1)#1 115.7(5), O(1)#1–P(1)–Pd 107.2(3), S(1)–P(1)–Pd 104.68(9).

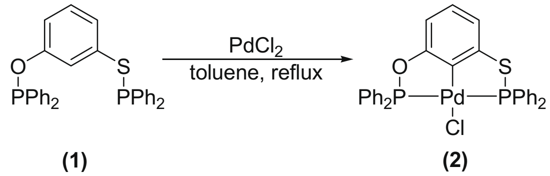


Scheme 1. Versatility of the pincer backbone and potential sites for modification.



Scheme 2. Synthesis of the ligand [C_6H_4-1-($SPPh_2$)-3-($OPPh_2$)] (**1**).

Analysis of this ligand by ^1H NMR is not very informative and only signals due to the aromatic fragments are observed in the typical region for aromatic protons. However, analysis of ligand (**1**) by $^{31}P\{^1H\}$ NMR results very illustrative, revealing the presence of two sharp singlets, one located at δ 112.5 ppm due to the phosphinito moiety, and the other, placed at higher field at δ 32.0 ppm due to the presence of the thiophosphinito fragment [13]. This analysis



Scheme 3. Synthesis of compound [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**).

Table 1
Crystal data and structure parameters for [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**).

Identification code	(**2**)
Formula	$C_{30}H_{23}Cl_1O_1P_2Pd_1S_1$
Formula weight	635.33
T (K)	298(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	17.195(2)
b (Å)	10.839(1)
c (Å)	16.528(2)
α (°)	90
β (°)	119.801(2)
γ (°)	90
V (Å^3)	2673.1(5)
Z	4
D_{Calc} (Mg/m^3)	1.579
Absorption coefficient (mm^{-1})	1.015
F(0 0 0)	1280
Crystal size	0.33 × 0.22 × 0.14 mm
θ (°)	2.32–25.35
Index ranges	$-20 \leqslant h \leqslant 20$, $-13 \leqslant k \leqslant 13$, $-19 \leqslant l \leqslant 19$
Reflections collected	10 821
Independent reflections (R_{int})	2451 (0.0485)
Absorption correction	analytical
Maximum and minimum transmission	0.8893 and 0.7191
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2451/60/200
Goodness-of-fit (GOF) on F^2	0.894
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0311$, $wR_2 = 0.0614$
R indices (all data)	$R_1 = 0.0430$, $wR_2 = 0.0642$
Largest difference peak and hole (e Å^{-3})	0.576 and −0.457

also reveals the ligand to be pure enough to be used in the following process, the metallation step. For most of the pincer ligands, the metallation process involves an aromatic C–H activation reaction. Although this process for aromatic protons is easier than that for aliphatic C–H bonds, very often this step still requires activated starting materials in low oxidation states or activation of the C–H bond (e.g. lithiation) or harsh conditions that often render in the partial or total decomposition of the starting materials leading to low or null yields. Thus, we have explored the direct synthesis of pincer complexes from readily available un-activated starting materials e.g. $PdCl_2$, these reactions resulting to be very easy to perform, facilitating and speeding up the synthesis of PCP pincer compounds. Moreover, this direct reaction results very interesting since $PdCl_2$ is not soluble in the used solvent toluene and one can easily follow the advance of the reaction by the disappearance of the metal salt and the increasing in the color tonality of the reaction mixture, for the present case colorless-yellowish, thus turning these reactions into an auto-indicative process.

Hence, the equimolar reaction of ligand [C_6H_4-1-($SPPh_2$)-3-($OPPh_2$)] (**1**) with $PdCl_2$ under reflux condition in toluene affords complex [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**) in an almost quantitative yield (Scheme 3).[2]

Complex [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**) was obtained as microcrystalline whitish powder. Analysis of this compound by ^{1}H NMR exhibits signals due to the aromatic fragments between δ 6.99 and δ 8.02 ppm. However, is the ^{31}P{^{1}H} analysis that provides fundamental information about the structure of the complex. Thus, the spectrum of (**2**) shows two doublets at δ 141.4 (doublet, PO, $J^2_{P-P} = 473$ Hz) and 60.4 (doublet, PS, $J^2_{P-P} = 472$ Hz). Characterization by ^{13}C{^{1}H} NMR afforded a set of signals (δ 164.1, 152.8, 148.7, 133.3, 132.6, 132.2, 132.1, 132.0, 131.6, 131.4, 129.0, 128.0, 117.7, 110.1 ppm) which are consistent with the proposed structure. Analysis by EI-MS of (**2**) reveals a similar fragmentation to other POCOP pincer compounds [14], showing the molecular ion [M$^+$] at 636 (35%) *m/z* and the loss of the anion chloride being accounted by the peak at [M$^+$–Cl] = 599 (55%) m/z. Elemental analysis results are also coherent with the proposed formulation.

Crystals suitable for single crystal X-ray diffraction analysis were obtained and thus complex (**2**) was unequivocally characterized.[3] For compound [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**), the Pd center is located into a slightly distorted square planar environment, flanked by the two different phosphorus donor atoms in a *trans* arrangement, and completing the coordination sphere the characteristic Pd–C σ bond and the chloride ligand. In one of this case, the strain of one of the 5 member metallocycles is partially alleviated by the larger size of the sulfur atom. In all other respects this structure resembles other PCP and POCOP Pd(II) pincer structures.

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[2] Synthesis of [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**). $PdCl_2$ (6 mmol, 1064 mg) was placed in the collecting Schlenk flask of the filtered solution containing ligand (**1**) (*vide supra*). The reaction mixture was then set to reflux for 16 h. After the prescribed reaction time precipitation of the product was observed as a white powder. The solid was filtered off, washed with toluene (10 mL) and hexane (3 × 20 mL) affording compound **3** as a microcrystalline white powder stable to moisture and air in almost quantitative yield (99%, based on $PdCl_2$). Compound (**2**) was further purified by flash chromatography to eliminate any possible impurities employing a dichloromethane/pentane solvent mixture (2:1) as eluent, affording compound 2 in its pure form as a white microcrystalline powder. ^{1}H NMR ($CDCl_3$, δ ppm): 8.02–7.95 (m, 8H, PhH_{ortho}), 7.51–7.44 (m, 12H, Ph–H_{meta}, Ph–H_{para}), 7.00 (d, 1H, $J_{HH} = 4$ Hz, Ar–H_{meta}), 6.99 (apparent q, 1H, $J_{HH} = 4.4$ Hz, Ar–H_{para}). ^{13}C{^{1}H} NMR ($CDCl_3$, δ ppm): 164.1 (dd, COP, $J = 12.2$, 3 Hz), 152.8 (dd, CSP, $J = 18.6$, 2.5 Hz), 148.7 (t, $J = 1.6$), 133.3, 133.3 (dd, $J = 13.6$, 1.8), 132.6 (d, $J = 6.5$), 132.2 (d, $J = 2.5$), 132.1 (d, $J = 3.6$), 132.0, (dd, $J = 14.3$, 1.5 Hz), 131.6 (d, $J = 3.8$), 131.4 (d, $J = 2.4$), 129.0 (d, $J = 10.9$), 128.0, 117.7 (d, $J = 17.5$ Hz), 110.1 (d, $J = 17.5$ Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, δ ppm): 141.4 (d, $J = 473$ Hz, PO) 60.4 (d, $J = 472$ Hz, PS). MS-FAB$^+$ (*m/z*): 601 [M$^+$–Cl]. IR (KBr, cm^{-1}): 1430, 1103, 907, 693. Elemental *Anal.* Calc. for $C_{30}H_{23}ClOP_2PdS$ (635.39): C, 56.71; H, 3.65; S, 5.05. Found: C, 56.69; H, 3.71; S, 4.53%.

[3] Data Collection and refinement for [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**). Crystalline colorless prisms of [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**) were grown by slow evaporation of a CH_2Cl_2/*n*-heptane solvent system, and mounted in random orientation on a glass fiber. 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 Kα ($\lambda = 0.71073$ 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 [15] using a narrow-frame integration algorithm. The integration of the data was done using a monoclinic unit cell to yield a total of 10 821 reflections for 2 to a maximum 2θ angle of 50.00° (0.93 Å resolution), of which 2451(2) were independent. Analysis of the data showed negligible decays during data collection. The structure was solved by Patterson method using SHELXS-97 [16] program. The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps, using *C2/c* 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. The final cycle of refinement was carried out on all non-zero data using SHELXL-97 [17] and anisotropic thermal parameters for all non-hydrogen atoms. The details of the structure determination are given in Table 1. The numbering of the atoms is shown in Fig. 1 (ORTEP) [18].

Having complex [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**) on hand, we decided to explore its catalytic activity[4] on the Suzuki–Miyaura (C–C) cross coupling reaction of bromobenzene and phenylboronic acid as a bench mark experiment to compare its reactivity against that of [PdCl{C_6H_3-2,6-($OPPh_2$)$_2$}] (**3**) [3a,3c].

From the results attained compound [PdCl{C_6H_3-2-($SPPh_2$)-6-($OPPh_2$)}] (**2**) resulted to be a better, faster catalyst than [PdCl{C_6H_3-2,6-($OPPh_2$)$_2$}] (**3**) (compare 100% versus 76% yield even by doubling the reaction time) for the Suzuki–Miyaura cross coupling reactions under the very same conditions.

There has been a considerable debate in the literature about the oxidation states of the species involved in the catalytic cycle using pincer compounds, with Pd(IV)/Pd(II) and Pd(II)/Pd(0) both being proposed at various times [19]. Although we generally favor the participation of Pd(II)/Pd(IV) species, in this case the presence of the thiophosphinito bond may led the behavior of ligand (**1**) to a hemilabile pincer compound (**2**) in solution [20] (a possibility that can not be ruled out). However, the presence of the sulfur on the pincer structure may just lead to a stronger electronic factors affecting the reactivity of complex (**2**) and thus perhaps assisting the oxidative addition process. Experiments, aimed to shed further light to support or decline these theories and the further application of this an other transition metal derivatives e.g. Ni, Pt, Ru, Ir, etc. of ligand (**1**) in other relevant organic transformations are currently under study in our laboratories.

Acknowledgments

The generous financial support of this research by CONACYT (F58692) and DGAPA-UNAM (IN227008) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 664411 (**2**) contains the free supplementary crystallographic data for this paper. These can be obtained free of the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.02.003.

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[4] General procedure for the Suzuki cross-coupling of bromobenzene with phenyl boronic acid. Bromobenzene (4 mmol), phenylboronic acid (6 mmol, 731 mg), K_2CO_3 (8 mmol, 1105 mg, 0.1 mol% of the palladium catalyst and toluene (12 mL) were charged in the open air into a Schlenk tube equipped with a magnetic stirrer. The tube was sealed and fully immersed in a 100 °C silicon oil bath under stirring. After the prescribed reaction time, the tube was taken out of the oil bath and allowed to reach room temperature. Samples taken from the organic phase, which was previously filtered trough a short plug of Celite®, were diluted with dichloromethane (1 mL) and analyzed by gas chromatography–mass spectrometry (GC–MS) techniques.

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