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Synthesis and characterization of new Pd(II) non-symmetrical Pincer complexes derived from thioether functionalized iminophosphoranes. Evaluation of their catalytic activity in the Suzuki–Miyaura couplings

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ABSTRACT

The iminophosphorane ligands ($Ph_3P{=}NC_6H_4SR$) [R = CH_3 (**1**) and C_6H_5 (**2**)] were easily synthesized from triphenylphosphine and 2-(methylthio)aniline or 2-(phenylthio)aniline respectively by the Horner and Oediger variation of the Kirsanov reaction. The reactivity of both ligands was explored with [Na_2PdCl_4] to afford the corresponding non-symmetric iminophosphorane pincer derivatives [PdCl{$C_6H_4(Ph_2P{=}NC_6H_4SR\text{-}\kappa^3\text{-}C,N,S)$}] [R = CH_3 (**3**) and C_6H_5 (**4**)]. A careful monitoring of the reaction by $^{31}P\{^1H\}$ NMR experiments revealed the *N,S* chelated species [$PdCl_2${$C_6H_4(Ph_2P{=}NC_6H_4SR\text{-}\kappa^2\text{-}N,S)$}] [R = CH_3 (**5**) and C_6H_5 (**6**)] to be stable intermediates through the formation of the pincer compounds. Thus, carrying out the reaction for the attaining of (**4**) at room temperature allowed the isolation and full characterization of the chelated complex [$PdCl_2${$C_6H_4(Ph_2P{=}NC_6H_4SPh\text{-}\kappa\text{-}N,S)$}] (**6**). All above mentioned species were unequivocally characterized by single crystal X-ray diffraction experiments. In addition, the newly synthesized pincer complexes [PdCl{$C_6H_4(Ph_2P{=}NC_6H_4SR\text{-}\kappa^3\text{-}C,N,S)$}] [R = CH_3 (**3**) and C_6H_5 (**4**)] were tested as catalyst, proven to be efficient in the Suzuki–Miyaura C–C cross coupling reactions of a series of *para*-substituted bromobenzenes.

1. Introduction

Pincer complexes bearing a monoanionic tridentate backbone constitute an exceptional class of organometallic compounds. Mainly due to their extraordinary reactivities and high catalytic activity in numerous chemical transformations. The vast majority of pincer complexes reported so far include symmetrical ligands (biphosphines, dithioethers, diamines etc.) and their structural features as well as physical and chemical properties have been amply reviewed [1,2]. However, in recent years there has been an increasing interest in non-symmetric pincer compounds, particularly those combining "hard" and "soft" donor atoms, in the search of increasing activities and enhanced reactivities in potentially relevant catalytic transformations [3]. Some of these compounds have demonstrated hemilabile properties and high catalytic activity when compared to their symmetric analogs [4], for instance in Suzuki–Miyaura cross-couplings.

On the other hand, the chemistry of iminophosphines has had a steady growth and been the focus of considerable interest in the last decade. In this sense, functionalized iminophosphines with additional donor groups attached either to the imine or phosphine backbones are of particular interest since they can be easily modified to fine tune the chemical properties of their metal complexes. The potential of functionalized iminophosphines in coordination chemistry is now well established, and recent studies have highlighted their utility as ligands in homogeneous catalysis [5]. In addition, iminophosphines can undergo C–H bond activation [6]. Thus, turning the neutral molecule into an anionic (or dianionic) ligand increasing the number of possibilities for potential coordination. This chemical property has enabled iminophosphines, in many cases, to easily provide cyclometallated complexes avoiding the use of more complicated metallation methods such as transmetallation with lithium derivatives [7].

Urriolabeitia et al. reported in 2008 the straightforward palladation *via* C–H activation of non-stabilized iminophosphines

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$Ph_3P{=}N{-}CH_2{-}R$ (R = CO_2Me, $CONMe_2$, CH_2SMe, NC_5H_4-2) as a consequence of their treatment with [$Pd(OAc)_2$]. They observed that the resulting anionic ligand often ended up just bonded as a C,N-chelate to the Pd center. Moreover, these ligands exhibited a preference for a tridentated coordination (C,N,O–, C,N,S– or C,N,N–) leading to palladacycles remarkably stable towards the addition of phosphine ligands. However, in comparison with the increasing number of publications devoted to the chemistry of iminophosphines functionalized with ether, amine or phosphine moieties (N ~ N, N ~ O, N ~ P) examples of iminophosphines functionalized with sulfur fragments are still scarce. To the best of our knowledge, besides one compound reported by Urriolabeitia (R = CH_2SMe), only two other examples of mixed iminophosphine-thioether or -thiolate derivatives have been described. A titanium phosphinimide with a pendant hemilabile thioether attached to the phosphine reported by Stephan [8]. This compound was tested as catalyst in the polymerization of ethylene exhibiting an increasing stability at elevated reaction temperatures. The other example reported by Auffrant [9], explored the coordination chemistry of the iminophosphorane-thiolate anion [(PhNPPh$_2$CH$_2$SLi)THF] with Pd(II) and Ru(II), these species were not further used in catalysis.

Until recently sulfur-containing ligands were neglected from their use in catalysis due to the common belief that sulfur would poison the complexes rendering the potential catalytic systems inefficient. However, in the last decade this view has changed and sulfur containing ligands and their complexes have had a renaissance and nowadays it is common to find reports including sulfur or other chalcogen containing ligands and their complexes used successfully in different potentially relevant catalytic transformations [10]. Thus, in this opportunity we would like to report our findings on the study of the coordination chemistry of iminophosphine ligands functionalized with sulfur-containing groups to Pd(II) starting materials and the screening of the catalytic activity of these complexes.

2. Experimental

2.1. Material and methods

Solvents were dried and distilled under nitrogen using standard procedures [11] before use. [Na_2PdCl_4], PPh_3, Br_2, 2-(methylthio) aniline and 2-(phenylthio)aniline were obtained commercially from Aldrich Chem. Co and were used without further purification. NEt_3 was dried with CaH_2 and distilled under nitrogen atmosphere. The ligand $Ph_3P{=}NC_6H_4SMe$ was prepared by a slight modification of a literature procedure [12]. Mass measurements (FAB^+) were 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. NMR spectra were acquired at ambient temperature with Varian Gemini 200 MHz and Varian UnityInova 400 MHz instruments in $CDCl_3$, which was used as internal reference. ^{31}P NMR spectra were recorded with complete proton decoupling and are reported in ppm using 85% H_3PO_4 as external standard. Melting points are uncorrected and they were measured in a Mel Temp II device using sealed capillaries. Infrared spectra were recorded in KBr using a Bruker Vector 22 instrument. Catalytic activity experiments were carried out in sealed Schlenk tubes and a silicon oil bath. GC analyzes were carried out in an HP 5890A flame ionization detector (FID) and HP 5890 SERIES II with a 5971A mass selective detector gas chromatographs, and an HP-1 capillary column (25.0 m) from Hewlett–Packard. 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.

2.2. Synthesis of [$Ph_3P{=}NC_6H_4SCH_3$] (**1**)

To a solution of Ph_3PBr_2 (9.75×10^{-3} mol) in 25 ml of freshly distilled benzene under N_2 atmosphere at 0 °C, a solution of $NH_2C_6H_4SCH_3$ (1.18 ml, 9.75×10^{-3} mol) with Et_3N (19.75×10^{-3} mol) in 20 ml of benzene was added dropwise. The addition was completed in 20 min. The resulting suspension was taken to room temperature and further stirred for 4 h, and additional 30 h at reflux temperature. Then the resulting suspension was filtered through celite and the solvent was evaporated to dryness, giving a yellowish powder. mp: 125 °C. Yield (3.35 g, 86%). MS-FAB$^+$: 499 (35%) [M]$^+$. Anal. Calc. for $C_{25}H_{22}N_1P_1S_1$ (399.49). C, 75.16; H, 5.55; N, 3.81. Found: C, 75.14, H, 5.58, N, 3.79. IR (ν, cm^{-1}): 1327 (ν_{PN}). ^1H NMR ($CDCl_3$): δ 2.323 (s, 3H, SCH_3), 6.675 (dd, $1H_3$ SC_6H_4N), 6.940 (t, $1H_4$ SC_6H_4N), 7.737 (m, $1H_5$ SC_6H_4N), 6.125 (dd, $1H_6$ SC_6H_4N), 7.435 (m, $6H_o$ PPh_3), 7.361 (m, $6H_m$ PPh_3), 7.706 (m, $3H_p$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.734 (C_i, SCH_3), 136.900 (d, $^3J_{PC} = 24.3$, C_i–S, SC_6H_4N), 147.280 (C_i–N, SC_6H_4N), 126.743 (C_3, SC_6H_4N), 132.010 (C_4, SC_6H_4N), 129.447 (C_5, SC_6H_4N), 129.352 (C_6, SC_6H_4N), 131.250 (d, $^1J_{PC} = 100$, C_i PPh_3) 128.857 (d, $^2J_{PC} = 10.6$, C_o PPh_3), 136.808 (d, $^3J_{PC} = 9.1$, C_m PPh_3), 132.020 (d, $^4J_{PC} = 3$, C_p PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 2.80$.

2.3. Synthesis of [$Ph_3P{=}NC_6H_4SPh$] (**2**)

To a solution of Ph_3PBr_2 (9.75×10^{-3} mol) in 25 ml of freshly distilled benzene under N_2 atmosphere at 0 °C, was added dropwise a solution of $NH_2C_6H_4SPh$ (1.96 g, 9.75×10^{-3} mol) with Et_3N (19.75×10^{-3} mol) in 20 ml of benzene. The addition was completed in 20 min. The resulting suspension was taken to room temperature and stirred for 4 h and additional 30 h at reflux temperature. Then the resulting suspension was filtered through celite and the solvent evaporated to dryness, giving a yellowish powder. mp: 116 °C. Yield (3.9 g, 85%). MS-FAB$^+$: 462(25%) [M]$^+$. Anal. Calc. for $C_{30}H_{24}N_1P_1S_1$ (461.56 IR): C, 79.07; H, 5.42; N, 3.40. Found: C, 79.08; H, 5.43; N, 3.38. (ν, cm^{-1}): 1330(ν_{PN}). NMR ($CDCl_3$): $\delta = 7.19$ (dd, $1H_3$ SC_6H_4N), 6.973 (t, $1H_4$ SC_6H_4N), 7.235 (m, $1H_5$ SC_6H_4N), 6.780 (dd, $1H_6$ SC_6H_4N), 7.496 (m, $6H_o$ PPh_3), 7.418 (m, $6H_m$ PPh_3), 7.736 (m, $3H_p$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.563 (C_i, SPh), 136.726 (C_i–S, SC_6H_4N), 149.517 (C_i–N, SC_6H_4N), 126.466 (C_3, SC_6H_4N), 130.110 (C_4, SC_6H_4N), 130.988 (C_5, SC_6H_4N), 126.861 (C_6, SC_6H_4N), 131.200 (d, $^1J_{PC} = 98.1$, C_i PPh_3) 131.881 (d, $^2J_{PC} = 14.6$, C_o PPh_3), 128.703 (d, $^3J_{PC} = 11.8$, C_m PPh_3), 132.876 (d, $^4J_{PC} = 8.8$, C_p PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 0.29$.

2.4. Synthesis of [$PdCl\{C_6H_4(Ph_2P{=}NC_6H_4SMe$-$\kappa$-C,N,S)$\}$] (**3**)

[Na_2PdCl_4] (0.015 g, 5×10^5 mol) was slowly added under N_2 atmosphere to a mixture of **1** (0.02 g, 5×10^{-5} mol) and excess Na_3PO_4 (0.0123 g, 7.5×10^{-5} mol) in 1,2-dichloroethane (20 ml). The resulting reaction was refluxed for 1.5 h. After this time, the solvent was removed under vacuum leading to the isolation of a bright yellow powder. Mp (°C): 152. Yield (0.022 g, 82%). IR (ν, cm^{-1}): 1269 (ν_{PN}). MS-FAB$^+$: 541 (5%) [M]$^+$. Anal. Calc. for $C_{25}H_{21}Cl_1N_1P_1Pd_1S_1$ (540.35): C, 55.67; H, 3.92; N, 2.59. Found: C, 55.68; H, 3.57; N, 2.55. ^1H NMR ($CDCl_3$): $\delta = 2.830$ (–SCH_3), 6.873 (dd, $1H_3$ SC_6H_4N), 7.024 (t, $1H_4$ SC_6H_4N), 8.173 (d, $1H_5$ SC_6H_4N), 7.251 (dd, $1H_6$ SC_6H_4N), 7.865 (m, $4H_o$ PPh_2), 7.567 (m, $4H_m$ PPh_2), 7.658 (m, $2H_p$ PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.303 (–SCH_3), 125.447 (d, $^4J_{PC} = 26.8$, C_i–S, SC_6H_4N), 152.855 (C_i–N, SC_6H_4N), 129.133 (C_3, SC_6H_4N), 128.817 (C_4, SC_6H_4N), 126.736 (C_5, SC_6H_4N),

Table 1
Crystal data and structure refinement for compound (**1**), (**2**), (**3**), (**4**) and (**6**).

	(**1**)	(**2**)	(**3**)	(**4**)	(**6**)
Emp. formula	$C_{31}H_{28}NPS$	$C_{36}H_{30}NPS$	$C_{29}H_{31}ClNOPPdS$	$C_{30.25}H_{23.50}Cl_{1.50}NPPdS$	$C_{30}H_{24}Cl_2PdS$
Formula mass	477.57	539.64	614.43	623.61	638.83
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a [Å]	10.005(2)	9.5436(13)	11.1834(9)	9.3538(8)	10.3189(10)
b [Å]	26.972(6)	19.416(3)	15.8514(13)	22.0993(19)	16.6942(16)
c [Å]	9.496(2)	15.812(2)	15.8230(13)	14.0577(12)	16.6933(15)
β [°]	94.538(3)	98.817(2)	92.6880(10)	103.7770(10)	107.618(2)
V [Å^3]	2554.4(9)	2895.4(7)	2801.9(4)	2822.3(4)	2740.8(4)
Z	4	4	4	4	4
D_c [Mg m^{-3}]	1.242	1.238	1.457	1.468	1.548
μ [mm^{-1}]	0.209	0.193	0.912	0.950	1.027
Refl. collected	18,373	18,823	22,890	23,026	29,863
Unique reflections	4636 [R_{int} = 0.0959]	5306 [R_{int} = 0.0638]	5132 [R_{int} = 0.0495]	5145 [R_{int} = 0.1033]	5023 [R_{int} = 0.0425]
Data/restr./param.	4636/0/309	5306/300/407	5132/141/363	5145/48/353	5023/0/325
$R_1/wR_2[I > 2\sigma(I)]$	0.0643/0.1059	0.0469/0.0962	0.0343/0.0671	0.0388/0.0929	0.0392/0.0956
Goodness of fit	1.020	0.918	0.898	0.967	1.066
T [K]	173(2)	173(2)	298(2)	298(2)	173(2)
λ (Mo-K_α)	0.71073	0.71073	0.71073	0.71073	0.71073

136.113 (C_6, SC_6H_4N), 125.822 (d, $^1J_{PC}$ = 113.02, C_i PPh_2), 132.996 (d, $^2J_{PC}$ = 10, C_o PPh_2), 129.484 (d, $^3J_{PC}$ = 11.8, C_m PPh_2), 133.566 (d, $^4J_{PC}$ = 2.8, C_p PPh_2), 141.937 (d, $^1J_{PC}$ = 141.937, C_i—P, PC_6H_4Pd), 156.927 (d,$^2J_{PC}$ = 31.9, C_i—Pd, PC_6H_4Pd).$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 47.41.

2.5. Synthesis of [PdCl{C_6H_4(Ph_2P═NC_6H_4SPh-κ-C,N,S)}] (**4**)

[Na_2PdCl_4] (0.015 g, 5 × 10^5 mol) was slowly added under N_2 atmosphere to a mixture of **2** (0.02 g, 5 × 10^{-5}) and excess of Na_3PO_4 (0.0123 g, 7.5 × 10^{-5} mol) in 1,2-dichloroethane (20 ml). The resulting medium was refluxed for 1.5 h. After this reaction time, the solvent was removed and a deep yellow powder was obtained, mp: 150 °C. Yield (0.021 g, 81%). MS-FAB$^+$: 603 (15%) $[M]^+$. Anal. Calc. for $C_{30}H_{23}Cl_1N_1P_1Pd_1S_1$ (602.42): C, 59.98; H, 3.95; N, 2.33. Found: C, 60.01; H, 3.99; N, 2.30. IR (ν, cm^{-1}): 1270 (ν_{PN}). NMR ($CDCl_3$): δ = 7.190 (dd, $1H_3$ SC_6H_4N), 7.269 (t, $1H_4$ SC_6H_4N), 8.270 (d, $1H_5$ SC_6H_4N), 7.370 (dd, $1H_6$ SC_6H_4N), 7.800 (m, $4H_o$ PPh_2), 7.474 (m, $4H_m$ PPh_2), 7.622 (m, $2H_p$ PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 125.365 (d, $^4J_{PC}$ = 16.0, C_i—S, SC_6H_4N), 153.903 (C_i—N, SC_6H_4N), 134.775 (C_3, SC_6H_4N), 128.817 (C_4, SC_6H_4N), 136.606 (C_5, SC_6H_4N), 131.070 (C_6, SC_6H_4N), 128.457 (d, $^1J_{PC}$ = 102.4, C_i PPh_2), 132.892 (d, $^2J_{PC}$ = 10.3, C_o PPh_2), 129.420 (d, $^3J_{PC}$ = 11.7, C_m PPh_2), 133.442 (d, $^4J_{PC}$ = 2.6, C_p PPh_2), 141.456 (d, $^1J_{PC}$ = 143.2, C_i—P, PC_6H_4Pd), 167.935 (s, C_i—Pd, PC_6H_4Pd).$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 47.27.

2.6. Synthesis of [$PdCl_2${C_6H_4(Ph_2P═NC_6H_4SPh-κ-N,S)}] (**6**)

[Na_2PdCl_4] (0.013 g, 4.38 × 10^{-5} mol) was slowly added at 0 °C under N_2 atmosphere to a solution of (**2**) (0.02 g, 4.38 × 10^{-5} mol) in CH_2Cl_2 (20 ml). After 1 h of stirring the formation of a deep orange turbidity was evident in the reaction media. The suspension was filtered and a very insoluble orange powder was obtained. mp: 165 °C. Yield (0.021 g, 84%). MS-FAB$^+$: 638 (13%) $[M]^+$. Anal. Calc. for $C_{30}H_{23}Cl_2N_1P_1Pd_1S_1$ (637.88): C, 56.49; H, 3.63; N, 2.20. Found: C, 56.50; H, 3.65; N, 2.24. IR (ν, cm^{-1}): 1267 (ν_{PN}). ^1H NMR ($CDCl_3$): δ = 7.195 (dd, $1H_3$ SC_6H_4N), 7.207 (t, $1H_4$ SC_6H_4N), 7.754 (m, $1H_5$ SC_6H_4N), 7.372 (dd, $1H_6$ SC_6H_4N), 7.604 (m, $6H_o$ PPh_3), 7.483 (m, $6H_m$ PPh_3), 7.388 (m, $3H_p$ PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 123.426 (d, $^4J_{PC}$ = 5.3, C_i—S, SC_6H_4N), 157.253 (C_i—N, SC_6H_4N), 133.117 (C_3, SC_6H_4N), 129.853 (C_4, SC_6H_4N), 133.849 (C_5, SC_6H_4N),128.960 (C_6, SC_6H_4N), 127.014 (d, $^1J_{PC}$ = 96.6, C_i PPh_3), 129.180 (d, $^2J_{PC}$ = 8.8, C_o PPh_3), 128.690 (d, $^3J_{PC}$ = 13.2, C_m PPh_3), 133.309 (d, $^4J_{PC}$ = 2.6, C_p PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 33.09.

2.7. Suzuki–Miyaura couplings using complex (**3**) as catalyst

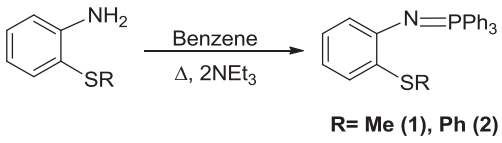
A DMF solution (5 ml) of 4.32 mmol of halobenzene, 4.75 mmol of phenylboronic acid, and the prescribed amount of catalyst (1% mol) was introduced into a Schlenk tube in the open air. The tube was charged with a magnetic stir bar, an excess of base (Na_3PO_4, 9.5 mmol), sealed and then fully immersed in a 110 °C silicon oil bath. After the prescribed reaction time (5 h), the mixture was cooled to room temperature and the organic phase analyzed by gas chromatography (GC–MS) by duplicate.

2.8. Data collection and refinement for compounds (**1**), (**2**), (**3**), (**4**) and (**6**)

Crystals of the ligands (**1**) and (**2**) were grown by slow evaporation of saturated benzene solutions in a closed Schlenk flask. Crystals of the pincer complexes (**3**) and (**4**), were obtained by slow diffusion of Pr^iOH over saturated solutions of the corresponding compound in CH_2Cl_2 in closed vials and finally compound (**6**) was crystallized by slow evaporation of a saturated solution in CH_2Cl_2 in a closed vial. The X-ray intensity data were measured at 173(2) K for compounds (**1**) and (**2**) and at 298 K for the complexes (**3**), (**4**) and (**6**) on a Bruker SMART APEX CCD-based three-circle X-ray diffractometer system using graphite mono-chromated Mo-Kα (λ = 0.71073 Å) radiation. The detector was placed at a distance of 4.837 cm from the crystals in all cases. The frames were integrated with the Bruker SAINT software package [13] using a narrow-frame integration algorithm. The structures were solved by Patterson method using SHELXS-97 [14] program. The details of the structure determinations are given in Table 1. Geometric calculations were done using PLATON [15].

3. Results and discussion

Iminophosphines (**1**) and (**2**) were easily synthesized in high yield by the classical Horner–Oediger method [16] from commercially available amines in refluxing benzene (Scheme 1).



R= Me (1), Ph (2)

Scheme 1. Synthesis of the ligands.

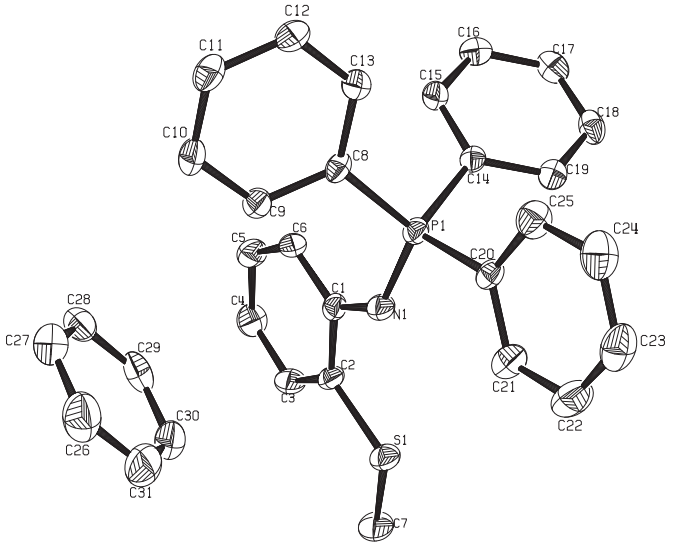


Fig. 1. Molecular structure of (**1**) (H atoms are omitted for clarity; thermal ellipsoid set at 50% probability). Selected bond lengths (Å): P1–N1 1.571(2), S1–C2 1.770(3), S1–C7 1.798(3). Selected bond angles (°): C2–S1–C7 102.30(2), N1–P1–C8 115.66(1), N1–P1–C14 116.60(1), N1–P1–C20 105.25(1), P1–N1–C1 128.98(2). Torsion angles (°): C1–N1–P1–C20 172.28, C1–N1–P1–C8 70.32, C1–N1–P1–C14 54.51, C6–C1–N1–P1 16.43.

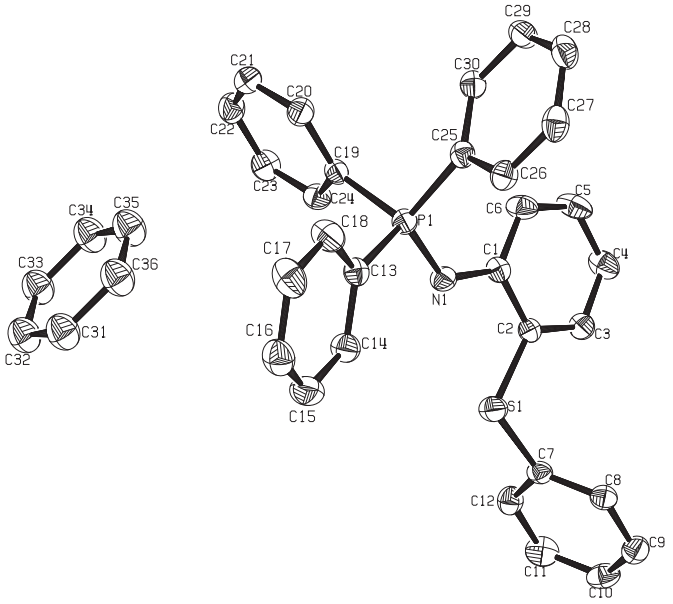


Fig. 2. Molecular structure of ligand (**2**) (H atoms are omitted for clarity; thermal ellipsoid set at 50% probability). Selected bond lengths (Å): P1–N1 1.569(19), S1–C2 1.773(2), S1–C7 1.775(2). Selected bond angles (°): C2–S1–C7 103.56(10), N1–P1–C13 103.57(10), N1–P1–C19 106.77(10), N1–P1–C25 105.83(10), P1–N1–C1 129.47(10). Torsion angles (°): C1–N1–P1–C13 160.46, C1–N1–P1–C19 83.01, C1–N1–P1–C25 42.81, C6–C1–N1–P1 14.26.

Multinuclear NMR ($^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR) and IR spectroscopy data confirmed the proposed structures for the ligands (**1**) and (**2**). For both compounds the corresponding $^{31}P\{^1H\}$ NMR spectra, show unique signals at δ 2.80 and 0.30 ppm for (**1**) and (**2**) respectively [17]. In the IR spectra the characteristic signals due to the ν (P═N) vibration [18] were observed at 1327 and 1346 cm^{-1} for (**1**) and (**2**) respectively. The results obtained from the ^1H and $^{13}C\{^1H\}$ NMR spectra were also in agreement with the proposed formulations exhibiting the expected signals for the sulfur containing functional groups, at δ 2.30 and 14.73 ppm for the ^1H and $^{13}C\{^1H\}$ respectively in the case of ligand (**1**)–SCH_3. While the signal corresponding to the carbon S–C_i in ligand (**2**)–SC_6H_5 can be observed at δ 164.6 ppm in the ^{13}C NMR spectra. Both ligands in the solid state are stable in the open atmosphere for months. However, in solution they become unstable undergoing decomposition in time on contact with ambient moisture.

Crystals of (**1**) and (**2**) suitable for their analysis by single crystal X-ray diffraction techniques were grown by slow diffusion of Et_2O over saturated solutions of the compounds in benzene in closed Schlenk flasks under N_2 atmosphere. Compound (**1**) crystallizes in the monoclinic space group ($P\,2_1/c$) (Fig. 1) while compound (**2**) does it in the monoclinic space group ($P\,2_1/n$) (Fig. 2). There is one molecule of benzene in the asymmetric unit and four molecules in the unit cell. The data collection and refinement parameters are collected in Table 1.

Compounds (**1**) and (**2**) are monomeric and show the P atom into a slightly distorted tetrahedral environment, surrounded by three C atoms and the iminic N atom. As expected the N atom is sp^2 hybridized and the N–P distances, 1.571(2) Å for (**1**) and 1.569(19) Å for (**2**), fall in the usual range for aminophosphine compounds (1.54 Å to 1.64 Å) [19]. The molecular geometries are similar for both ligands. As can be seen from the values of the C6–C1–N1–P1 torsion angles [−16.4(5)° for (**1**) and −14.3(3)° for (**2**)], the aniline ring is almost coplanar with the P–N bond. The values of torsion angles C1–N1–P1–C14 [−54.4(3)°] in (**1**) and C1–N1–P1–C25 [42.81(2)°] in (**2**), indicate that one of the phenyl rings of the PPh_3 group is only slightly twisted compared to the plane formed by the P–N bond and the aniline ring.

The coplanarity of this phenyl ring bonded to P, the aniline ring and the carbon on the sulfur atom originates from two different intramolecular interactions (Fig. 3). The first interaction being a contact between the proton at the *ortho* position of the phenyl ring and the iminic nitrogen [C21–H21···N1 in (**1**) and C14–H14···N1 in (**2**) (2.57 Å)]. This interaction is evident from the short H···N distances of 2.50 and 2.57 Å for (**1**) and (**2**) respectively. But also from the smaller N1P1C_{ipso} angle of 105.26(1)° in (**1**) and 106.49(1)° in (**2**), when compared with the two other angles between the P–N bond and the aromatic rings of the triphenylphosphine group. These features are comparable with other triphenyl(phenylimino) phosphoranes found in the literature [2.51(2) Å–2.67 Å; 105°–110°] [19,20]. The second intramolecular interaction is a 1,4-type interaction found between the sulfur atom and the iminic nitrogen. The S1···N1 distances in (**1**) (2.78 Å) and (**2**) (2.76 Å) are rather short compared to similar compounds reported in the Cambridge Structural Database [21]. Those interactions are observed in a large number of organosulfur compounds and are believed to control the conformation of small and large molecules [22].

The reaction of the iminophosphine ligands (**1**) or (**2**) with $[Na_2PdCl_4]$ (1:1 M ratio) in refluxing 1,2-dichoroethane (1.5 h) in presence of excess of Na_3PO_4 afforded the corresponding

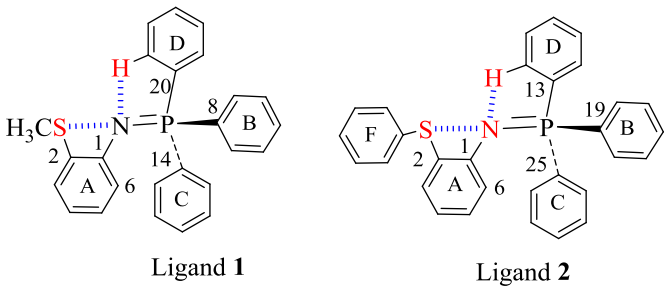
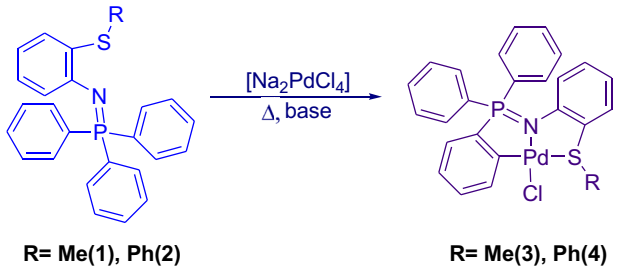


Fig. 3. Schematic drawing of non-bonded interactions present in (**1**) and (**2**).



Scheme 2.

orthometallated complexes (**3**) and (**4**) in high yields (Scheme 2). Both complexes were obtained as air- and moisture-stable yellow solids that are soluble in chlorinated solvents and spectroscopic, as well as analytical data, are consistent with the proposed structures.

The IR spectra of (**3**) and (**4**) show that the ligands are N-bonded, since the position of the ν(P═N) vibration has been shifted to lower energy in comparison with the free ligand, *e.g.* 1269 cm^{-1} for (**3**) and 1252 cm^{-1} for (**4**).

On the other hand, multinuclear NMR analysis of complexes (**3**) and (**4**) confirms that orthopalladation reaction has occurred. For both complexes, the ^{1}H NMR shows signals due to the presence of the PdC_6H_4 moiety in the aromatic region. In addition, for complex (**3**) a sharp signal due to the presence of the SCH_3 group can be observed at δ 2.83 ppm. While in the case of (**4**) the signals due to the SPh fragment overlap with those of the other aromatic protons present in the molecule. The $^{13}C\{^{1}H\}$ NMR exhibits signals for the expected functional groups and further confirms the proposed structures for (**3**) and (**4**) by showing the orthopalladated carbon atoms at δ 156.9 ($^{2}J_{PC}$ = 31.9) for (**3**) and at 167.9 ppm for (**4**) [23].

Crystals of complexes (**3**) and (**4**) were obtained by slow diffusion of $Pr^{i}OH$ in saturated solutions of both compounds in CH_2Cl_2. Both structures evidence orthometallation and show the Pd atoms into a slightly distorted square planar environments (Figs. 4 and 5 respectively). These results confirm unequivocally the previously proposed structures based in the spectroscopic evidence and the C–N–S tridentate ligand can be seen as a non-symmetric pincer ligand.

The bite angles of the chelating moieties for complex (**3**) are 87.70(1)° (N1–Pd1–C14) and 85.25(7)° (N1–Pd1–S1) and the sum of the bond angles around the Pd1 atom is 360.03(12)°. The molecule deviates only slightly from planarity: for instance the maximum deviations found in the best least-square planes defined by (C20–C19–P1–N1–Pd1) and (Pd1–N1–C2–C1–S1) are only 0.05 Å and 0.01 Å respectively. The dihedral angle between these two planes in (**3**) is only 5.05°. In the case of (**4**), the bite angles for the tridentate ligand [N1–Pd1–C14 = 87.40(1)° and N1–Pd1–S1 = 84.34(8)°] and the sum of the angles around the Pd1 [360.05(13)°], are very similar to those found in (**3**). This molecule also deviates only slightly from planarity, and the maximum deviations found in the planes defined by (Pd1–C14–C13–P1–N1) and (Pd1–S1–C2–C1–N1) are of 0.004 Å and 0.017 Å. The dihedral angle between the two planes is 5.09°.

The Pd1–$C_{metallated}$ bond distance in both complexes [1.99(3) Å (**3**) and 1.99(4) Å (**4**)] fall in the usual range for this type of bond [24,7]. The Pd1–N1 bond distances in (**3**) and (**4**) are identical and similar to other reported in the literature [2.03(2) Å for (**3**) and 2.03(2) Å for (**4**)]. The P1–N1 bond distances [1.62(3) Å (**3**) and 1.62(3) Å (**4**)] are equal even within the experimental error, and fall in the expected range. Finally, the Pd1–S1 [2.349(1) (**3**) and 2.377(1) Å (**4**)] bond distances also lay within the reported values [25].

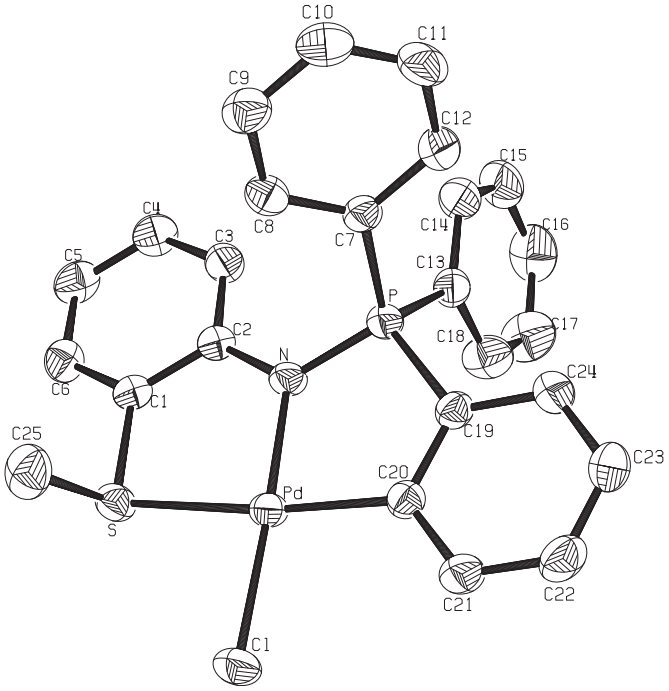


Fig. 4. Molecular structure of (**3**) (H atoms are omitted for clarity; thermal ellipsoid set at 50% probability). Selected bond lengths [Å]: Pd1–Cl1 2.310(1), Pd1–S1 2.349(1), Pd1–N1 2.036(2), Pd1–C20 1.988(3), P1–N1 1.620(3). Selected bond angles [°]: Cl1–Pd1–S1 92.38(3), Cl1–Pd1–N1 177.50(8), Cl1–Pd1–C20 94.69(1), S1–Pd1–N1 85.25(8), S1–Pd1–C20 172.89(1), N1–Pd1–C20 87.67(1). Selected torsion angles [°]: C1–N1–P1–C19–176.94, C1–N1–P1–C7 64.76, C1–N1–P1–C13–59.55, C3–C2–N1–P1 11.06.

The molecular geometries are similar for both complexes and due to their planarity they can be related to non-symmetrical pincer complexes. As seen by the torsion angle values for C1–C2–N1–P1 (**3**) and of C2–C1–N1–P1 (**4**), the aniline ring in the

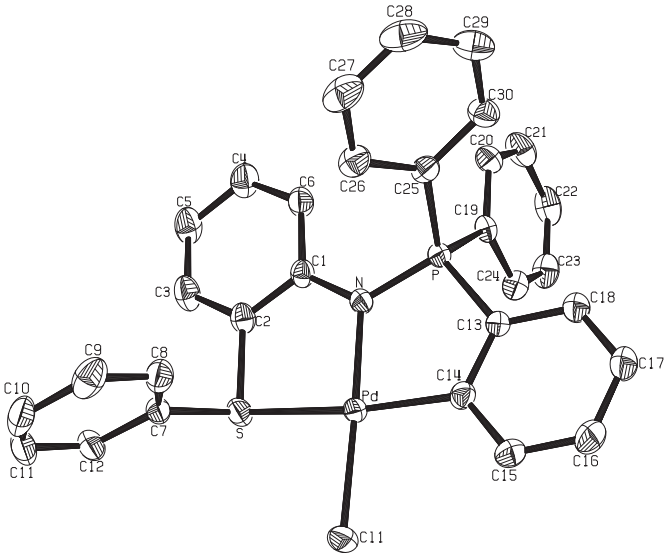
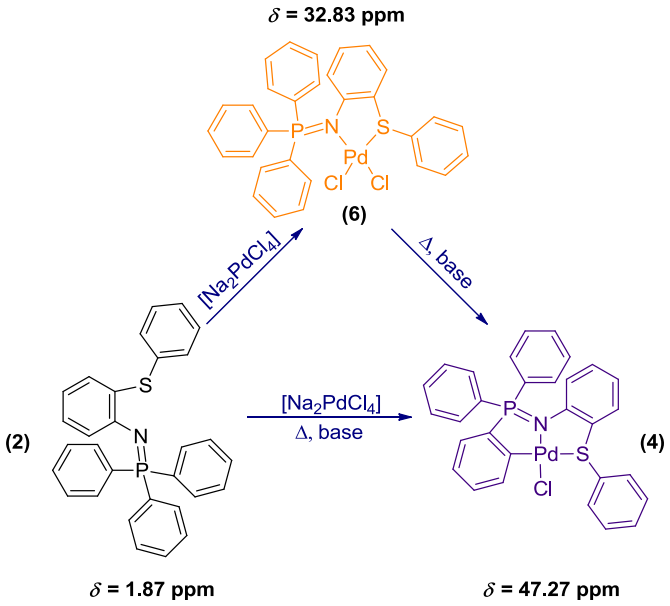


Fig. 5. Molecular structure of (**4**) (H atoms are omitted for clarity; thermal ellipsoid set at 50% probability). Selected bond lengths [Å]: Pd1–Cl1 2.316(1), Pd1–S1 2.377(1), Pd1–N1 2.031(1), Pd1–C20 1.998(3), P1–N1 1.622(3). Selected bond angles [°]: Cl1–Pd1–S1 93.71(4), Cl1–Pd1–N1 177.88(8), Cl1–Pd1–C14 94.65(11), S1–Pd1–N1 84.34(8), S1–Pd1–C14 170.33(10), N1–Pd1–C14 87.37. Selected torsion angles [°]: C1–N1–P1–C13–175.21, C1–N1–P1–C25 66.49, C1–N1–P1–C19 57.83, C6–C1–N1–P1 5.21.

complexes remains more coplanar with the N=P bond than in the free ligands, certainly because of the strained conformation. Likewise, the values of torsion angles C2–N1–P1–C19 (**3**) and C1–N1–P1–C13 (**4**), indicate that phenyl ring D bonded to P is coplanar with the P=N bond and the aniline ring A. This situation is somewhat different when compared with the free ligands, where ring D is slightly twisted from the plane of ring A and the P=N bond (Figs. 1 and 2). For both complexes, the data collection and refinement parameters are collected in Table 1.

The reactions for the attaining of the palladacycles, showed some interesting changes in color as the reaction proceeded, indicative of different species to be forming through the reaction. Thus, in order to study these changes we performed the metallation reactions at room temperature. Hence, the stoichiometric reaction of [Na_2PdCl_4] with either ligand (**1**) or (**2**) in DCE in presence of a base, first produced a deep orange solution with the formation of a small amount of precipitate. As the reaction evolved and upon further warming, the precipitate slowly dissolved and the reaction mixture changed from the initial orangey color to yellow. Analysis of the reaction mixture by ^{31}P NMR at the initial stages of the reaction afforded spectra that in both cases exhibited a signal at about δ 32 ppm [δ 31.87 ppm for (**1**) and δ 32.83 for (**2**)]. Signals that completely disappeared upon warming the reaction mixtures up (few hours of reflux). Analysis by ^{31}P NMR at this point provided NMR spectra that only showed single signals at about δ 47 ppm. Signals that are consistent with the sole presence of the pincer complexes (**3**) and (**4**) already described (*vide supra*). In view of these observations we decided to carry out VT-NMR experiments in order to follow the formation of complex (**4**) (Fig. 6). Thus, [Na_2PdCl_4], ligand (**2**), Na_3PO_4 and DCE where combined in an NMR tube at room temperature. The ^{31}P NMR spectrum collected a $T = 0$ only shows, as expected, a signal due to the presence of the free ligand at δ 1.87 ppm, with a minor signal at δ 32.83 ppm corresponding to the intermediate N,S chelated complex (**6**). After this time the reaction was gradually warmed and a new spectrum was collected after 40 min ($T = 60$ °C). At this stage, the free ligand is no longer detectable and the only signal observed is that due to the presence of the *N*,*S* chelated complex (**6**) at δ 32.83 ppm. By the time the reaction surpasses 60 °C, a new signal is starting to show at δ 47.27 ppm indicating the clear formation of the pincer product and this transformation is completed only after 15 min ($T = 75$ °C). These results are coherent with the formation of an intermediate coordination *N*,*S*-chelated complex to finally produce the more stable palladacyle product upon warming *via* electrophilic substitution on a phenyl ring of the PPh_3 ligand (Scheme 3) [6].



Scheme 3.

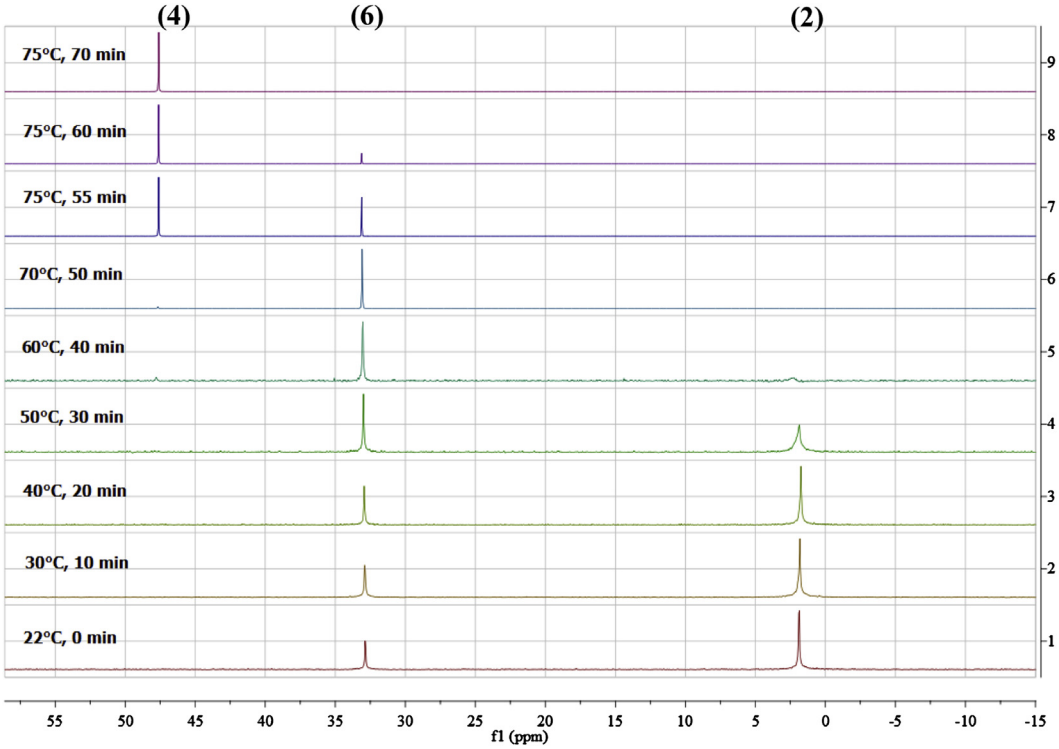


Fig. 6. $^{31}P\{^1H\}$ VT-NMR experiments for the synthesis of complex (**4**).

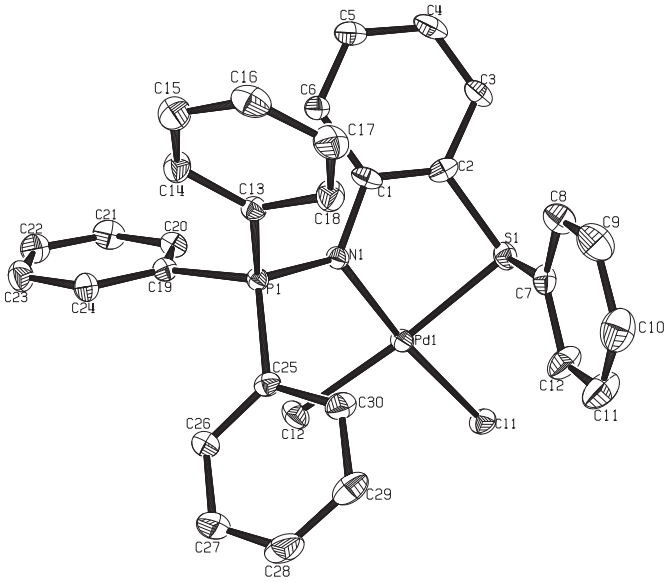


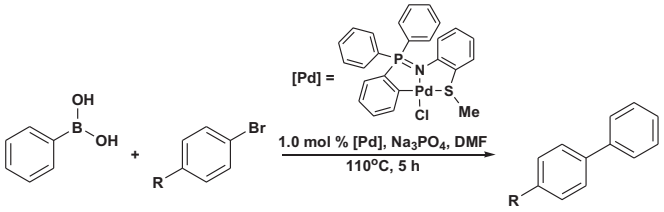
Fig. 7. Molecular structure of (**6**) (H atoms are omitted for clarity; thermal ellipsoid set at 30% probability). Selected bond lengths (Å): Pd1–Cl1 2.300(11), Pd1–Cl2 2.296(12), Pd1–S1 2.271(12), Pd1–N1 2.051(3), P1–N1 1.623(3). Selected bond angles (°): Cl1–Pd1–Cl1 91.73(4), Cl1–Pd1–S1 90.41(4), Cl1–Pd1–N1 173.61(9), S1–Pd1–N1 83.32(9), Cl2–Pd1–S1 174.45(4), Cl2–Pd1–N1 94.63(9). Selected torsion angles (°): C1–N1–P1–C13 36.10, C1–N1–P1–C25 150.33, C1–N1–P1–C19 85.75, C6–C1–N1–P1 28.05.

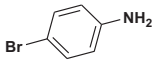
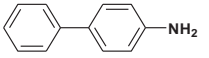
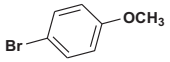
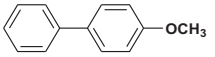
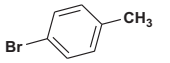
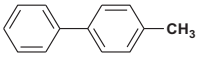
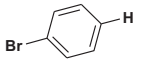
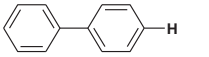
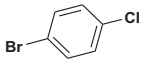
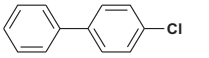
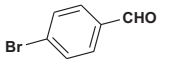
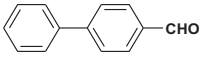
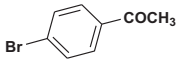
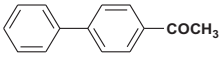
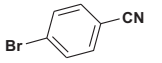
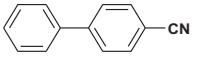
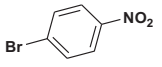
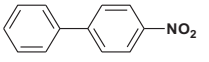
Performing the above mentioned reaction at room temperature in the absence of base allowed us to isolate the intermediate compound (**6**). Crystals of (**6**) suitable for their analysis by single crystal X-ray diffraction techniques were obtained by slow evaporation of a saturated CH_2Cl_2 solution of the crude product at room temperature, thus confirming unequivocally the *N*,*S*-chelated nature of the product (Fig. 7).

From these results it can be observed that the Pd atom is located into a slightly distorted square planar environment and completing the coordination sphere two chloride atoms (Cl1 and Cl2) and the iminophosphorane ligand coordinated in a bidentated manner through the S1 and N1 atoms. The angles, 79.74° (S1–Pd–N1) and 91.73° (Cl1–Pd–Cl2), clearly evidence the distortion around the metal. Both Pd–Cl bond distances, 2.300(11) Å and 2.296(12) Å, lay in the usual range for similar distances reported for this type of compounds [24]. The Pd1–N1 bond distance of 2.051(3) Å is also comparable with other reported values in the literature [25], and is only slightly longer than the distances found in the pincer complexes (**3**) and (**4**) [2.036(2) and 2.031(1) Å]. The P1–N1 bond distance of 1.623(3) Å is comparable with the distances found in complexes (**3**) and (**4**) [1.620(3) and 1.622(3) Å] and is slightly longer than the distances found in the free ligands (**1**) and (**2**) [1.571(2) and 1.569(19) Å]. Finally, as a result of the palladation process the Pd1–S1 bond distance 2.271(12) Å is smaller than those observed in complexes (**3**) and (**4**) of 2.349(1) and 2.377(1) Å respectively. The data collection and refinement parameters for this compound are collected in Table 1.

To the best of our knowledge Pd(II) pincer complexes including the ligands reported in this work have not yet been employed in catalysis. These compounds can be relevant and may exhibit enhanced reactivity due to the presence of the thioether moieties that in turn may confer hemilabile properties to these complexes. Thus, the catalytic activity of the C–N–S pincer palladacycles was explored in Suzuki–Miyaura reactions. Hence, complexes (**3**) and (**4**) were tested as catalysts in the Suzuki–Miyaura C–C cross couplings of different *para*-substituted bromobenzenes and phenylboronic acid [26,27].

Table 2
Suzuki–Miyaura couplings using complex (**3**) as catalyst precursor.



p-Bromobenzene	% Conversion[a]	% Values of conversion
		55
		60.5
		65
		70
		77
		>99
		93
		95
		>99

[a] Yields obtained by GC are based on remaining bromobenzene and are the average of two runs.

The well known thermal stability of palladacylces and in particular of pincer complexes both in solid state and in solution, allowed us to start the catalytic experiments in the absence of an inert atmosphere. And given the fact that these C–C couplings depend of a series of parameters, initial experiments were focused to determine the optimal conditions for these catalytic systems. Thus, experiments were performed to evaluate the effect of the reaction temperature, solvent, base and catalyst loading. Hence, we first studied the reaction of bromobenzene and phenylboronic acid using complexes (**3**) and (**4**) as catalysts. Based on previously reported results [28] we set the reaction temperature at 110 °C and used DMF as preferred solvent, employing a 1% loading of catalyst for 5 h. From these experiments it was observed that it is indeed complex (**3**) the one that afforded the best conversions and using complex (**4**) under analogous reaction conditions only provided lower conversions when compared with those attained with (**3**). From here all the following experiments were performed with complex (**3**). Further, given the fundamental importance that the proper selection of base plays in the Suzuki–Miyaura couplings we decided to explore the effect of different bases under the above mentioned reaction conditions using (**3**) as catalyst. Thus, by using Na_2CO_3 as base a 35% conversion was observed after 5 h. Replacement of this base with Na_3PO_4 improved the conversion to 50%

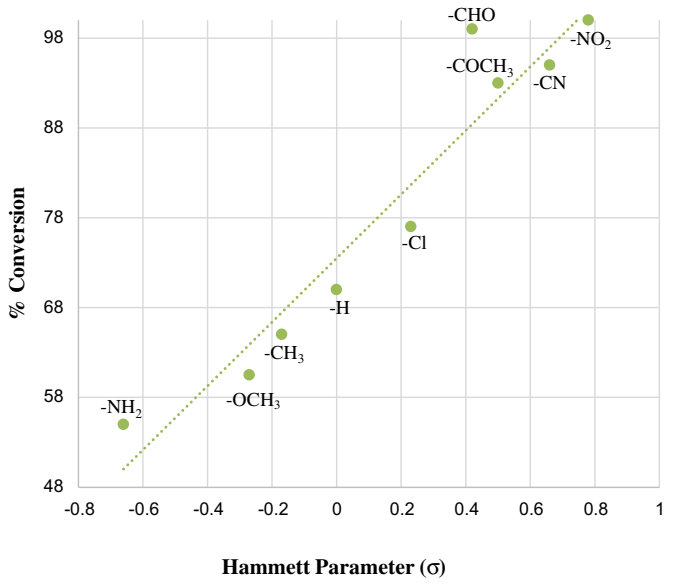


Fig. 8. % of conversion for the Suzuki–Miyaura couplings catalyzed by (**3**) of different *p*-substituted bromobenzenes *versus* Hammett parameter.

while other bases employed (K_2CO_3 29%; Cs_2CO_3 36%; Rb_2CO_3 29%; NaOH 11%) afforded reduced conversions. Under these optimized conditions (Na_3PO_4, DMF, 110 °C, 5 h), complex (**3**) was tested with different *para* substituted aryl bromides. Moderate conversions were observed when aryl bromides including strong electron donating groups were used and conversely when substrates contained electron-withdrawing substituents excellent yields were obtained (Table 2).

This behavior was expected [29] and corroborated with the percentage of conversion as a function of Hammett parameter of the aryl bromides substrates [30] (Fig. 8).

Under these reaction conditions no decomposition of the catalyst was observed and the performance of the catalyst in a control experiment in the presence of Hg^0 does not change. As it is for many similar species, it is likely that deligation of the thioether moiety by invoking hemilability may lead to the generation of a potential coordination site. This in turn may enable this species to start the catalytic cycle that giving the nature of the catalyst make us favor the potential participation of Pd(II)/Pd(IV) species. However, at this point a typical Pd(0)/Pd(II) catalytic cycle cannot be ruled out and experiments are under way to shed light into the potential hemilabile properties of these ligands and the full repercussion of its presence in the mechanism for this transformation. These results will be disclosed in due time.

In summary, iminophosphorane ligands including a thioether moiety have been easily prepared in high yields from the corresponding commercially available thioanilines and triphenylphosphine by the Horner–Oediger reaction. Reactions of both ligands with [Na_2PdCl_4] afforded *C,N,S* non-symmetric Pd(II) pincer complexes in good yields. These compounds being the product of a C–H activation process. Careful monitoring of the reactions revealed *N,S* Pd(II) chelated complexes to be important and stable intermediates previous to the orthometallation process. Reducing the reaction temperatures and avoiding the addition of base allowed the isolation and full characterization of these intermediates. Singles crystal X-ray diffraction analysis of the phenyl derivative (**6**) showed unequivocally the chelate nature of this compound. In addition, the molecular structures of both ligands and their corresponding pincer complexes were unequivocally determined by single X-ray diffraction experiments.

Preliminary catalytic experiments of the new non-symmetric pincer complexes were undertaken in Suzuki–Miyaura C–C cross coupling reactions. Showing the methyl substituted complex (**3**) to be an efficient catalyst in this process. The fact that these catalytic experiments were performed open to the air and no apparent decomposition was observed provides and optimistic view to further try this compound in other cross coupling reactions. Efforts aimed to prove this are currently under progress in our laboratories.

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Appendix A. Supplementary material

CCDC 937679–937683 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) D. Morales-Morales, C. Jensen (Eds.), The Chemistry of Pincer Compounds, Elsevier, New York, 2007;
(b) G. van Koten, D. Milstein (Eds.), Organometallic Pincer Chemistry, Topics in Organometallic Chemistry, vol. 40, Springer-Verlag, Berlin, Heidelberg, 2013.
[2] (a) M. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750;
(b) J.T. Singleton, Tetrahedron 59 (2003) 1837;
(c) M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759;
(d) D. Morales-Morales, Rev. Soc. Quim. Mex. 48 (2004) 338;
(e) J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev. 105 (2005) 2527;
(f) I. Moreno, R. San Martin, B.R. Ines, F. Churruca, E. Dominguez, Inorg. Chim. Acta 363 (2009) 1903;
(g) J.M. Serrano-Becera, D. Morales Morales, Curr. Org. Synth. 6 (2009) 169;
(h) J. Choi, A.H.R. MacArthur, M. Brookhart, A.S. Goldman, Chem. Rev. 111 (2011) 1761;
(i) N. Selander, K. Szabo, Chem. Rev. 111 (2011) 2048;
(j) C. Gunanathan, D. Milstein, Science 341 (2013) 249.
[3] I. Moreno, R. San Martin, B. Inés, M.T. Herrero, E. Domínguez, Curr. Org. Chem. 13 (2009) 878.
[4] (a) Z. Wang, M.R. Eberhard, C.M. Jensen, S. Matsukawa, Y. Yamamoto, J. Organomet. Chem. 681 (2003) 189;
(b) O.A. Wallner, K.J. Szabo, Org. Lett. 6 (2004) 1829;
(c) J.-F. Gong, Y.-H. Zhang, M.-P. Song, C. Xu, Organometallics 26 (2007) 6487;
(d) M. Gagliardo, N. Selander, N.C. Mehendale, G. van Koten, R.J.M. Klein Gebbink, K.J. Szabo, Chem. Eur. J. 14 (2008) 4800;
(e) B.-Sh. Zhang, Ch. Wang, J.-F. Gong, M.-P. Song, J. Organomet. Chem. 694 (2009) 2555;
(f) J.M. Serrano-Becerra, S. Hernández-Ortega, D. Morales-Morales, Inorg. Chim. Acta 363 (2010) 1306;
(g) M.A. Solano-Prado, F. Estudiante-Negrete, D. Morales-Morales, Polyhedron 29 (2010) 592;
(h) J.-L. Niu, X.-Q. Hao, J.-F. Gong, M.-P. Song, Dalton Trans. 40 (2011) 5135.
[5] (a) H. Dyer, A. Picot, L. Vendier, A. Auffrant, P. Le Floch, S. Sabo-Etienne, Organometallics 30 (2011) 1478;
(b) A. Picot, H. Dyer, A. Buchard, A. Auffrant, L. Vendier, P. Le Floch, S. Sabo-Etienne, Inorg. Chem. 49 (2010) 1310;
(c) L. Boubekeur, S. Ulmer, L. Ricard, N. Mézailles, P. Le Floch, Organometallics 25 (2006) 315;
(d) A. Buchard, A. Auffrant, C. Klemps, L. Vu-Do, L. Boubekeur, X.F. Le Goff, P. Le Floch, Chem. Commun. (2007) 1502;
(e) L. Boubekeur, L. Ricard, N. Mézailles, M. Demange, A. Auffrant, P. Le Floch, Organometallics 25 (2006) 3091;
(f) T.K. Panda, A. Zulys, M.T. Gamer, P.W. Roesky, J. Organomet. Chem. 690 (2005) 5078.
[6] (a) R. Bielsa, A. Larrea, R. Navarro, T. Soler, E.P. Urriolabeitia, Eur. J. Inorg. Chem. (2005) 1724;
(b) D. Aguilar, M.A. Aragüés, R. Bielsa, E. Serrano, R. Navarro, E.P. Urriolabeitia, Organometallics 26 (2007) 3541;
(c) R. Bielsa, R. Navarro, E.P. Urriolabeitia, A. Lledós, Inorg. Chem. 46 (2007) 10133.
[7] (a) K.T.K. Chan, L.P. Spencer, J.S.J. McCahill, P. Wei, D.W. Stephan, Organometallics 23 (2004) 381;
(b) J.D. Wingerter, M. Pfeiffer, T. Stey, M. Bolboaca, W. Kiefer,

V. Chandrasekhar, D. Stalke, Organometallics 20 (2001) 2730;
(c) S. Wingerter, H. Gornitzka, G. Bertrand, D. Stalke, Eur. J. Inorg. Chem. (1999) 173;
(d) P.R. Wei, K.T.K. Chan, D.W. Stephan, Dalton Trans. (2003) 3804.
[8] K. Yadav, J.S.J. McCahill, G. Bai, D.W. Stephan, Dalton Trans. (2009) 1636–1643.
[9] T.P.A. Cao, E. Payet, A. Auffrant, X.F. Le Goff, P. Le Floch, Organometallics 29 (2010) 3991–3996.
[10] (a) D. Morales-Morales, R. Redon, Y. Zheng, J.R. Dilworth, Inorg. Chim. Acta 328 (2002) 39;
(b) C. Herrera-Álvarez, V. Gómez-Benítez, R. Redón, J. García-Alejandre, S. Hernández-Ortega, R.A. Toscano, D. Morales-Morales, J. Organomet. Chem. 689 (2004) 2464;
(c) G. Ríos-Moreno, R. Toscano, R. Redón, H. Nakano, Y. Okuyama, D. Morales-Morales, Inorg. Chim. Acta 358 (2005) 303;
(d) V. Gómez-Benítez, S. Hernández-Ortega, R. Toscano, D. Morales-Morales, Inorg. Chim. Acta 360 (2007) 2128;
(e) J.R. Dilworth, P. Arnold, D. Morales, Y.L. Wong, Y. Zheng, in: Modern Coordination Chemistry. The Legacy of Joseph Chatt, Royal Society of Chemistry, Cambridge, UK, 2002, p. 217;
(f) J.G. Fierro-Arias, R. Redon, J.J. Garcia, S. Hernández-Ortega, R.A. Toscano, D. Morales-Morales, J. Mol. Catal. A Chem. 233 (2005) 17;
(g) R. Redón, H. Torrens, Z. Wang, D. Morales-Morales, J. Organomet. Chem. 654 (2002) 16;
(h) M. Corona-Rodríguez, S. Hernández-Ortega, J. Valdés-Martínez, D. Morales-Morales, Supramol. Chem. 19 (2007) 579;
(i) F. Estudiante-Negrete, R. Redon, S. Hernández-Ortega, R.A. Toscano, D. Morales-Morales, Inorg. Chim. Acta 360 (2007) 1651.
[11] W.L.F. Armarego, C. Chai, Purification of Laboratory Chemicals, seventh ed., Butterworth Heinemann, Oxford, 2012.
[12] M. Takahashi, M. Ohba, Heterocyles 3 (1995) 455.
[13] Bruker AXS, SAINT Software Reference Manual, Madison, WI, 1998.
[14] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[15] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.
[16] L. Horner, H. Oediger, Anal. Chem. 627 (1959) 142.
[17] H.B. Stegmann, G. Wax, S. Peinelt, K. Scheffler, Phosphorous Sulfur Relat. Elem. (1983) 277.
[18] W. Wiegräbe, H. Bock, Chem. Ber. 101 (1968) 1414.
[19] R. Borger, A. Collas, R. Dommisseb, F. Blockhuysa, Acta Crystallogr. C66 (2010) o50.
[20] A. Llamas-saiz, C. Foces-Foces, Acta Crystallogr. C50 (1994) 255.
[21] F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 31.
[22] K. Hayashi, S. Ogawa, S. Sano, M. Shiro, K. Yamaguchi, Y. Sei, Y. Nagao, Chem. Pharm. Bull. 6 (2008) 802.
[23] R. Bielsa, R. Navarro, T. Soler, E. Urriolabeitia, Dalton Trans. (2008) 1203.
[24] J. Vicente, J. Abad, R. Clemente, J. López-Serrano, Organometallics 22 (2003) 4248.
[25] L.R. Favello, M.M. García, I. Lázaro, R. Navarro, E.P. Urriolabeitia, New J. Chem. 23 (1999) 227.
[26] I.P. Beletskaya, A.V. ChepraKov, Chem. Rev. 100 (2000) 3009.
[27] J. Bravo, C. Cativela, R. Navarro, E.P. Urriolabeitia, J. Organomet. Chem. 650 (2002) 157.
[28] (a) D. Morales-Morales, R. Redón, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619;
(b) D. Morales-Morales, R. Redón, Z. Wang, D.W. Lee, C. Magnuson, C.M. Jensen, Can. J. Chem. 79 (2001) 823;
(c) D. Morales-Morales, R.E. Cramer, C.M. Jensen, J. Organomet. Chem. 654 (2002) 44;
(d) X. Gu, W. Chen, D. Morales-Morales, C.M. Jensen, J. Mol. Catal. A 189 (2002) 119;
(e) D. Morales-Morales, R. Redón, C. Yung, C.M. Jensen, Inorg. Chim. Acta 357 (2004) 2953;
(f) D. Morales-Morales, in: L. Kollár (Ed.), Modern Carbonylation Methods, Wiley-VCH, Federal Republic of Germany, 2008, pp. 20–64;
(g) D. Morales-Morales, in: L.A. Oro, C. Claver (Eds.), Iridium Complexes in Organic Synthesis, Wiley-VCH, Federal Republic of Germany, 2009, pp. 325–344;
(h) M. Albrecht, D. Morales-Morales, in: L.A. Oro, C. Claver (Eds.), Iridium Complexes in Organic Synthesis, Wiley-VCH, Federal Republic of Germany, 2009, pp. 299–323;
(i) D. Morales-Morales, Mini-rev. Org. Chem. 5 (2008) 141 and references therein;
(k) F.E. Hahn, M.C. Jahnke, V. Gómez-Benítez, D. Morales-Morales, T. Pape, Organometallics 24 (2005) 6458;
(l) V. Gómez-Benítez, O. Baldovino-Pantaleón, C. Herrera-Álvarez, R.A. Toscano, D. Morales-Morales, Tetrahedron Lett. 47 (2006) 5059;
(m) O. Baldovino-Pantaleón, S. Hernández-Ortega, D. Morales-Morales, Adv. Synth. Catal. 348 (2006) 236.
[29] J.K. Stille, K.S.Y. Lau, Acc. Chem. Res. 10 (1977) 434.
[30] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165.