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FULL PAPER

Palladium(II) complexes of aminothiazole-based phosphines: Synthesis, structural characterization, density functional theory calculations and catalytic application in heck reaction

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Three Pd(II) complexes of some hemilabile ligands, aminothiazole-based phosphines, were synthesized to investigate the catalytic activity of them in Heck cross-coupling reactions. The crystal structures of complexes $PdCl_2[(Ph_2P)HN(C_3H_2NS)]$ (**C_1**) and $PdCl_2[(Ph_2P)HN(C_7H_4NS)]$ (**C_3**) were determined using X-ray crystallography, which reveals that the ligand coordinates in a chelating mode through P and N (endocyclic) atoms in square planar geometry. Experimental and theoretical studies (atoms in molecules and natural bond orbital analyses) show that the Pd(II) interacts more strongly with the P atom than the N atom in the chelated ligand, N^P. This trait can promote catalytic activity of the complexes in comparison with our previous work in which chelated ligands with two phosphorus atoms, P^P, were used. The influence of non-covalent intermolecular interactions on the assembly of the solid-state structures is also discussed in terms of geometrical analysis. The prepared complexes turn out to be useful pre-catalysts in Heck cross-coupling reactions owing to the coordinative flexibility of the hemilabile ligands. The protocol affords the corresponding products in greater yield than the same reactions with bis(phosphino)amine Pd(II) complexes, as the catalysts in our previous work.

KEYWORDS

aminothiazole-based phosphines, crystal structure, heck coupling reaction, hemilabile ligands, palladium complexes

1 | INTRODUCTION

Tuning of the stereoelectronic properties of ligands, effective on structure and reactivity of the complexes of those ligands, is an important object of research concerning metal-catalysed carbon–carbon bond formation reactions.[1–5] In this regard, hemilabile phosphines are of interest due to the variety of ways for coordination[6–11] and also their potential in catalysis.[12–17] Indeed, these ligand systems, with P,N-donors, are able to coordinate reversibly to a metal centre providing or protecting temporarily a vacant coordination site, a feature that is very desirable for catalysts.[18]

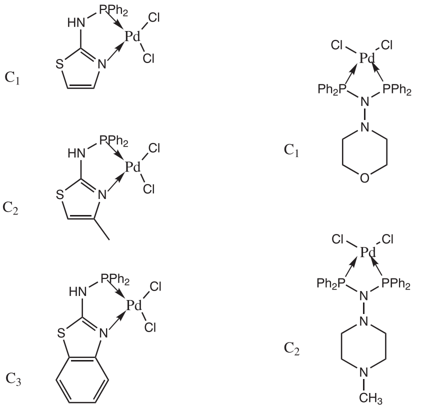
Recent studies of platinum complexes with aminothiazole-based phosphines have revealed structural diversity including monodentate P and bidentate PN or PS bound in versatile compositions, whereas we have not found any report of analogous palladium complexes in the literature.[19–23] The substituents at the aminothiazole backbone can play an important role in determining the structure of products.[24,25] Besides, the presence of large groups attached to the phosphorus centre also causes the aminophosphine to be more stable against hydrolysis.[26–31]

To improve and extend this area, we selected three new complexes of palladium with hemilabile N^P ligands, aminothiazole derivatives, to compare with our previous work in which palladium complexes with P^P donor ligand were used (Scheme 1).[32] According to the literature, catalytic activity of complexes in coupling reactions may be related to the metal–ligand interactions and lability of Pd–ligand bond and facile breaking of it during the Heck reaction.[18] New ligands were selected with P^N donor instead of P^P donor. The new products were characterized using infrared (IR) and NMR spectroscopies. The crystal structures of $PdCl_2[(Ph_2P)HN(C_3H_2NS)]$ (**C_1**) and $PdCl_2[(Ph_2P)HN(C_7H_4NS)]$ (**C_3**) were determined using X-ray crystallography which reveals a shortening of P─Pd bond distances of about 0.02 Å in **C_1** and **C_3** in comparison with our previous work on palladium complexes of P^P ligands. The Heck coupling reaction yields for the compounds used in this study are more than those for analogous complexes which were investigated in our previous work. The nature and strength of Pd─P and Pd─N interactions in the three palladium complexes were investigated using quantum theory of atoms in molecules (AIM) and natural bond orbital (NBO) analyses.

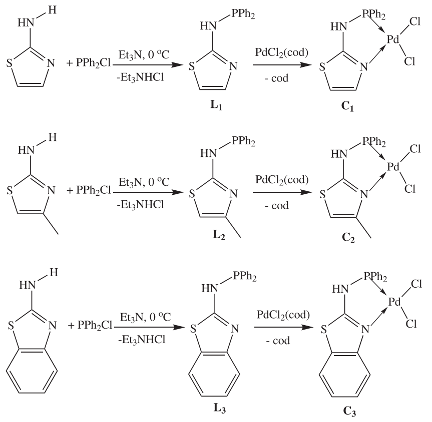
2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization

In this work, three aminophosphine ligands based on aminothiazole were prepared via phosphination of 2-aminothiazole, 2-amino-4-methylthiazole or 2-aminobenzothiazole, with one equivalent of Ph_2PCl in the presence of triethylamine in dichloromethane solution at 0 °C (Scheme 2). Compounds **L_1**, **L_2** and **L_3** were isolated as white and air-stable solids in high yields (71, 82 and 80%, respectively). Although these ligands have already been synthesized using a different method,[18,19] the present synthesis pathway is simpler because of the use of a more appropriate temperature. Reaction of the ligands with $[PdCl_2(COD)]$ afforded chelate complexes $[PdCl_2L]$.



SCHEME 1 General structures of (a) currently synthesized $[PdCl_2(P\text{^}N)]$ complexes and (b) previously reported[32] $[PdCl_2(P\text{^}P)]$ complexes



SCHEME 2 Synthesis of ligands **L_1**, **L_2** and **L_3** and their complexes **C_1**, **C_2** and **C_3**

Aminothiazole-based phosphines can exist in solution in two tautomeric forms, in which the N─H proton involves the *endo*-cyclic or *exo*-cyclic nitrogen atom.[18,19,22] The ^{31}P chemical shifts of the ligands at 41.1 to 42.2 ppm are in agreement with the reported values for aminophosphines with the exocyclic N─H group.[19,22] Upon coordination of the ligand, the ^{31}P resonance shifts to 77.5–85.2 ppm. The ^1H NMR spectrum of **C_1** shows thiazolyl ring protons at 6.84 ppm, which are only slightly downfield shifted from the value observed for the free ligand. The CH_3 group signal in the spectrum of **C_2** (at 2.37 ppm) shows downfield shift relative to that of ligand **L_2**. The (NH_{amine}) signal of the complexes appears at about 10 ppm, as a broad peak, indicative of extensive hydrogen bonding. IR spectra of ligands **L_1**–**L_3** show that the ν(N─H), ν(C─N) and ν(P─N) frequencies are in the ranges 3430–3444, 1523–1592 and 870–925 cm^{-1}, respectively. Vibrations of (C─N) and (P─N) bonds in the IR spectra of the palladium complexes, in the range 1552–1642 and 932–986 cm^{-1}, show an increase in comparison to those of the corresponding ligands which can be related to chelating of ligands in the complexes.

2.2 | Structural study

Single crystals of **C_1** and **C_3**, suitable for X-ray analysis, were obtained from solutions of dichloromethane by slow evaporation at room temperature. But attempts to obtain qualified crystals of **C_2** were not successful. The crystallographic data and the most relevant geometric parameters are summarized in Tables 1 and 2, respectively.

The title compounds crystallize in the space group *P21/n* with $Z = 4$. In each complex, the ligand binds in a chelating mode through P1 and N1 (*endo*-cyclic). The other coordination sites of the square planar Pd(II) centres are occupied by chlorine atoms (Figure 1). The angles around the Pd atoms

TABLE 1 Crystal data and structure refinement for C_1 and C_3

	C_1	C_3
Empirical formula	$C_{15}H_{13}Cl_2N_2PPdS$	$C_{19}H_{15}Cl_2N_2PPdS$
Formula weight	461.60	511.66
Wavelength, cu Kα (Å)	1.54184	1.54184
T (K)	173	173
Crystal system	Monoclinic	Monoclinic
Space group	P21/n (no. 14)	P21/c (no. 14)
a (Å)	10.0789(2)	12.7157(6)
b (Å)	14.6339(2)	12.2188(5)
c (Å)	11.7561(2)	13.1840(6)
α (°)	90	90
β (°)	106.018(2)	97.696(4)
γ (°)	90	90
V (Å^3)	1666.63(5)	2029.96(16)
Z	4	4
Density (g cm^{-3})	1.840	1.674
μ (mm^{-1})	13.976 mu(cu Ka)	11.546
F(000)	912.0	1016
θ min, max (°)	4.9, 71.2	3.5, 71.2
Crystal size (mm)	0.05 × 0.05 × 0.20	0.15 × 0.15 × 0.50
Index ranges	$-12 \le h \le 11$; $-13 \le k \le 17$; $-14 \le l \le 13$	$-15 \le h \le 15$; $-14 \le k \le 14$; $-9 \le l \le 15$
Reflections collected	17 181	6214
R_{int} (%)	0.0414	0.0417
Data/restraints/parameters	3207/0/199	3781/0/235
Goodness-of-fit on F^2	1.024	1.045
R_1 [$I > 2\sigma(I)$]	0.0457	0.0201
WR_2 [$I > 2\sigma(I)$]	0.0481	0.1096
Largest diff. Peak/hole (e Å^{-3})	0.325 and −0.595	1.093 and −1.555
Observed data [$I > 2.0\sigma(I)$]	2917	3270

present a distortion from the values for a regular square planar coordination mode. P1–Pd1–N1 angles are acute (83.73(5)° and 84.07(11)° for $\mathbf{C_1}$ and $\mathbf{C_3}$, respectively), while Cl1–Pd1–Cl2, N1–Pd1–Cl1 and P1–Pd1–Cl2 ones deviate by about 1–10° from 90° (Table 2).

The Pd—P, Pd—N and Pd—Cl bond lengths are nearly equal in these compounds. Notably, the Pd—Cl distances are in the reverse correlation with the binding strength of the corresponding *trans* donors. The longer Pd1—Cl2 bond than the Pd1—Cl1 one in both complexes indicates a higher donating ability of P with respect to N_{endo} (*trans* influence). Similarly, a comparison between the structure of $\mathbf{C_1}$ and $\mathbf{C_3}$ reveals that the shortening of Pd—N or Pd—P bond (in $\mathbf{C_1}$ or $\mathbf{C_3}$, respectively) is also accompanied by an increase in the opposite Pd—Cl bond length. For instance, the shorter Pd1—P1 distance (2.184 Å in $\mathbf{C_3}$ versus 2.205 Å in $\mathbf{C_1}$) corresponds to the longer Pd1—Cl2 bond (2.400 Å in $\mathbf{C_3}$ versus 2.388 Å in $\mathbf{C_1}$).

We also noticed that on coordination of the ligand to Pd(II), the P—C and P—N_{amine} bond lengths reduce (about 0.022 and 0.015 Å, respectively), while the C—N_{endo} distances are longer than those found in the free ligands.[19,20] The electronic redistribution of the ligand upon complexation, moreover, causes some geometrical changes in the thiazole rings. The other bond distances and angles within the ligand do not vary significantly in the coordinated structures.

In the structure of $\mathbf{L_1}$ and $\mathbf{L_3}$, the P and N_{endo} atoms adopt *anti*-configuration as a result of the formation of pairwise intermolecular N_{amine}—H···N_{endo} hydrogen bonds, creating dimeric aggregates.[19,20] The P,N-coordination mode leads to the *syn*-configuration for these atoms in the complexes.

TABLE 2 Selected bond lengths (Å) and bond angles (°) for solid-state structures of C_1 and C_3

	C_1	C_3
P1–N2	1.690(2)	1.693(5)
Pd1–Cl1	2.2900(7)	2.2871(11)
Pd1–Cl2	2.3882(6)	2.3997(10)
Pd1–P1	2.2047(6)	2.1842(11)
Pd1–N1	2.0346(18)	2.082(4)
∠Cl1–Pd1–Cl2	93.49(2)	91.03(4)
∠Cl1–Pd1–P1	89.96(2)	100.99(11)
∠Cl1–Pd1–N1	173.68(5)	174.59(4)
∠Cl2–Pd1–P1	172.94(2)	167.92(11)
∠Cl2–Pd1–N1	92.83(5)	83.87(4)
∠P1–Pd1–N1	83.73(5)	84.07(11)

Herein, the NH group participates in a head-to-tail hydrogen bonding (N2─H2···Cl2), giving rise to the formation of [001] chains of the Pd complexes (Table 3).

In the structure of C_1, the Cl2 atom is also involved in other non-classic hydrogen bonding (C13─H13···Cl2) which links the neighbouring chains in the *bc*-plane (Figure 2a). From another perspective, CH···π (C8─H8···Cg, $d_{H\cdots Cg} = 2.87$ Å, $d_{C\cdots Cg} = 3.620(3)$ Å, $\theta = 136°$: Cg is the centroid of thiazolyl ring; C2H (2A)···Cg, $d_{H\cdots Cg} = 2.93$ Å, $d_{C\cdots Cg} = 3.696(3)$ Å, $\theta = 138°$ and C14─H14···Cg, $d_{H\cdots Cg} = 2.85$ Å, $d_{C\cdots Cg} = 3.523(1)$ Å, $\theta = 131°$: Cg is the centroid of Ph ring) and CH···S interactions (Table 3) between these chains arrange the molecules in (101) layers (Figure 2b). Finally, the combination of all the mentioned intermolecular interactions completes a three-dimensional network in crystal C_1. Notably, the Cl1 atom is only involved in an intramolecular interaction C9H9···Cl1 (Table 3) which forms a six-membered (Cl1–Pd1–P1–C4–C9–H9) ring.

In the structure of C_3, both of the chlorine atoms contribute in stabilizing the crystal packing. Non-classic C10H10···Cl1 hydrogen bonds link the neighbouring N2H2···Cl2 chains (mentioned already) thus generating two-dimensional arrangements (Figure 3a). Also, CH···π interactions (C17─H17···Cg, $d_{H\cdots Cg} = 2.99$ Å, $d_{C\cdots Cg} = 3.911(9)$ Å, $\theta = 162°$: Cg is the centroid of C1–C6 ring) are the driving force in extending the third dimension of the crystal network. It is worth noting that the supramolecular association of C_3 also includes two other interesting interactions: C─H···Pd and S···Cl (3.385 Å) interactions which link the neighbouring units into chains along the *b*-axis (Figure 3b).

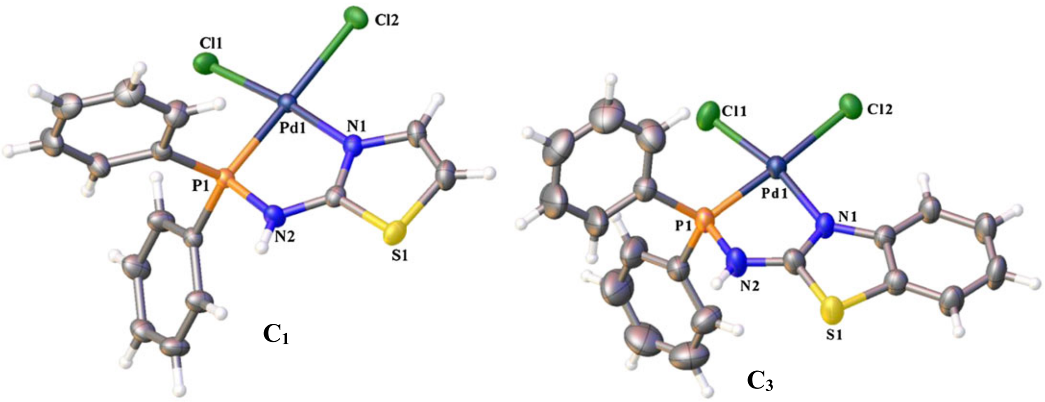


FIGURE 1 Molecular structure of **C1** (top) and **C3** (bottom) with displacement ellipsoid at the 50% level

TABLE 3 Hydrogen bond data for solid-state structures of C_1 and C_3

Compound	D–H···A (°)	D···A (Å)	D–H (Å)	H···A (Å)	∠D–H···A (°)	Symmetry codes
C_1	N2–H2···Cl2	3.092(2)	0.88	2.22	171	−½ + *x*, ½ − *y*, −½ + *z*
	C5–H5···N2	3.008(3)	0.95	2.56	109	Intra
	C9–H9···Cl1	3.485(2)	0.95	2.69	142	Intra
	C9–H9···S1	3.678(2)	0.95	2.96	133	½ + *x*, ½ − *y*, −½ + *z*
	C13–H13···Cl2	3.599(2)	0.95	2.80	142	1 − *x*, −*y*, 1 − *z*
C_3	N2–H2···Cl2	3.115(4)	0.88	2.24	174	*x*, ½ − *y*, −½ + *z*
	C2–H2A···Cl2	3.386(5)	0.95	2.55	147	Intra
	C10–H10···Cl1	3.699(1)	0.95	2.85	150	*x*, ½ + *y*, 3/2 − *z*
	C5–H5···Pd1	3.608(1)	0.95	2.78	146	1 − *x*, ½ + *y*, 3/2 − *z*

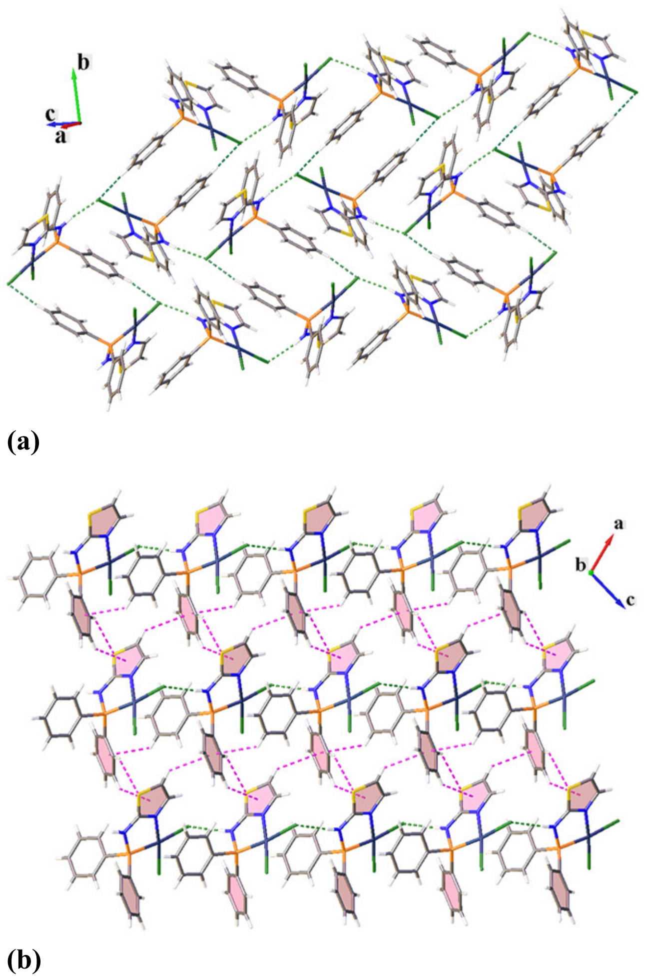


FIGURE 2 Representation of (a) NH...Cl, CH...Cl linkages in the *bc*-plane and (b) CH...π and CH...S interactions between the NH...Cl chains, creating (101) layers in **C1**

2.3 | NBO and AIM analysis of metal–ligand interactions

Application of AIM to the title complexes allowed us to find bond critical points (BCPs), and analyse their properties (electron density, ρ, its Laplacian, $\nabla^2\rho$, and total electronic energy density, $H(r)$). Generally, a large value of ρ and $\nabla^2\rho < 0$ refers to a shared interaction or covalent bond, while a small ρ value and $\nabla^2\rho > 0$ correspond to closed-shell interactions (e.g. ionic and hydrogen bonds and van der Waals interactions). However, a clear distinction between closed-shell and covalent-type interactions is impossible without determining $H(r)$. Strong interactions with ($\nabla^2\rho < 0$ and $H(r) < 0$) indicate covalent character and medium-strength interactions with ($\nabla^2\rho > 0$ and $H(r) < 0$) indicate partial covalent character, whereas weak interactions with ($\nabla^2\rho > 0$ and $H(r) > 0$) are mainly electrostatic. Thus, the magnitude of $H(r)$ at a BCP, instead of $\nabla^2\rho$, might be a more reliable index for characterizing a weak interaction.[33–35] Analysing the obtained BCPs for the Pd—N and Pd—P bonds shows more covalent property for the Pd—P interaction than the Pd—N one (Table 4) Indeed, Pd—P charge densities are larger and the related $H(r)$ values are more negative than those at Pd—N BCPs which correspond to stronger interactions in the former.

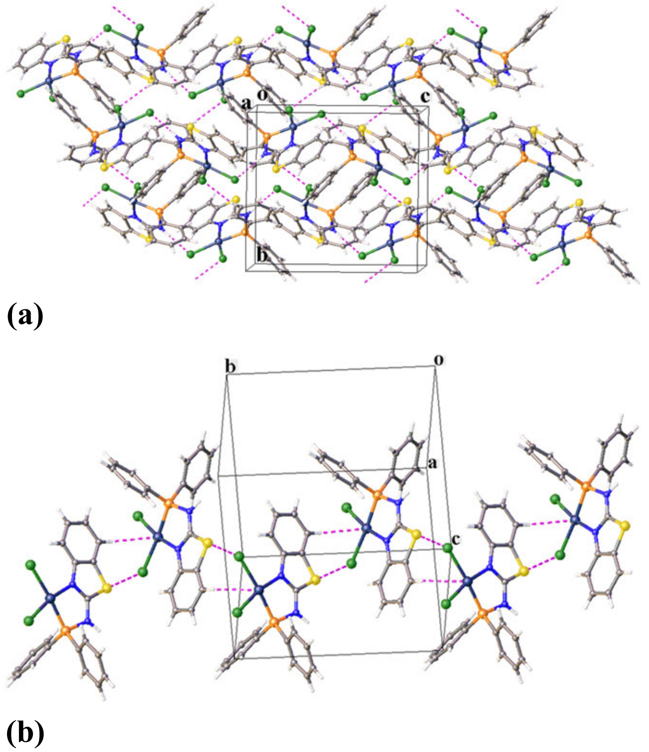


FIGURE 3 (a) a side view of the *bc*-plane in **C3**, formed by NH...Cl, CH...Cl H-bonds, (b) CH...Pd and s...Cl interactions along the *b*-axis

Also, the NBO analysis reveals an electronic delocalization from the lone pair of the nitrogen donor, Lp(N), to the acceptor orbitals LP*(Pd) and σ*(Pd—Cl$_{trans\text{-to-N}}$). Stabilization energies E_2 of 55.86, 49.52 and 49.96 kcal mol^{-1} are obtained for Lp(NP) → LP*(Pd) and 22.55, 16.78 and 16.93 kcal mol^{-1} for the Lp(N) → σ*(Pd—Cl$_{trans\text{-to-N}}$) interactions in $\mathbf{C_1}$, $\mathbf{C_2}$ and $\mathbf{C_3}$, respectively. However, for the case of Pd—P interaction, NBO analysis suggests a covalent characteristic with amounts of 1.80971, 1.80017 and 1.79881 electron density for $\mathbf{C_1}$, $\mathbf{C_2}$ and $\mathbf{C_3}$, respectively.

TABLE 4 Calculated AIM parameters (electron density, $\boldsymbol{\rho}$, its Laplacian, $\nabla^2\boldsymbol{\rho}$, and total electronic energy density, H(r)) at Pd–N and Pd–P critical points of compounds $\mathbf{C_1}$–$\mathbf{C_3}$

	Pd–N			Pd–P		
Complex	ρ	$\nabla^2\rho$	$H(r)$	ρ	$\nabla^2\rho$	$H(r)$
$\mathbf{C_1}$	0.091	0.396	−0.022	0.103	0.141	−0.043
$\mathbf{C_2}$	0.076	0.298	−0.016	0.104	0.137	−0.044
$\mathbf{C_3}$	0.077	0.304	−0.017	0.105	0.136	−0.045

This result clarifies the greater strength of Pd─P bond (with the covalent overlap) compared with the Pd─N interaction which is mainly electrostatic in nature (donor–acceptor like).

The values for Wiberg bond indices (Table 5) furthermore confirm the more covalent character for the Pd─P bond compared with the Pd─N interaction.

2.4 | Heck coupling reactions

In order to compare catalytic activity of the title complexes with the corresponding compounds, we used the same optimization condition as in our previous work.[32] These compounds were found to be efficient catalysts for the Heck coupling reaction (Table 6). The coupling of aryl iodides and bromides was superior and afforded the desired products in good to excellent conversions (entries 1–13). Using 4-substituted aryl iodides led to excellent conversions of the desired products (entries 4 and 5). Although, due to the crowding effect of aryl halides substituted at the *ortho* position, 2-methoxyiodobenzene provided only low conversions copared with the *para* derivative (entries 6 and 7). As expected, for aryl bromides, the catalytic activity depended on the halide and substituent of the electron-withdrawing groups on the aryl ring increased the reaction rate. However, the Heck coupling of bromobenzene was rather difficult under the same reaction conditions (entries 8–13). The *trans*/*cis* product ratio for Heck coupling reactions of iodobenzene/bromobenzene and styrene was about 94–98%, but for all other substrates it was higher than 99%.

The results show that all three complexes **C_1–C_3** are almost equally effective in catalysing Heck coupling reactions of olefins and aryl halides. The obtained conversions for five-membered ring Pd–P–N–C–N (entries 8, 9 and 13 with 91, 94 and 64%, respectively) were more than those of the same reactions with bis(phosphino)amine Pd(II) complexes with four-membered ring Pd–P–N–P (61, 59, 13% for the same entries) in our previous work. Moreover, Pd─P bond distances in complexes **C_1** and **C_3** were about 0.02 Å shorter than those of the mentioned complexes with the two phosphorus connected to the metal centre. These results confirm that the presence of a hemilabile site could promote both the stability and reactivity of the metal complex.[32] Indeed, high catalytic reactivity of complexes **C_1–C_3** can be related to the lability of Pd─N bond and facile breaking of it during Heck reactions.[18] The mercury poisoning test in Heck coupling between iodobenzene and styrene was carried out in the presence of complexes **C_1–C_3**. The addition of a large excess of Hg(0) (300 equiv.) to the reaction mixture did quench the catalytic activity of complexes (conversion =41, 55 and 49%, respectively, for **C_1**, **C_2** and **C_3**). Thus, the best interpretation is that bare palladium (Pd(0)) is participating in the catalytic cycle.

TABLE 5 Calculated Wiberg bond indices for selected bonds at B3LYP/LANL2DZ/6–311 + G**

Complex	Pd–P	Pd–N	Pd–Cl$_{trans\text{-to-P}}$	Pd–Cl$_{cis\text{-to-P}}$
C_1	0.6455	0.3788	0.6269	0.6661
C_2	0.6421	0.3490	0.6233	0.6637
C_3	0.6448	0.3498	0.6125	0.6630

Also, the catalytic activity of the complexes presented in this work is more favourable than that of previously reported complexes containing (O, N)[3] or (P, P)[36,37] coordinated ligands in terms of the reaction conditions; harsh reaction conditions, such as using high reaction temperatures and long reaction times, are not required.

3 | EXPERIMENTAL

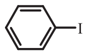
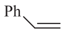
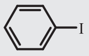
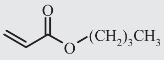
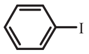
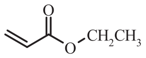
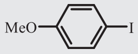
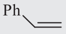
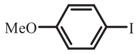
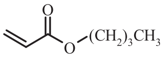
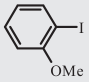
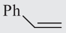
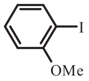
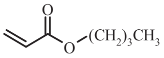
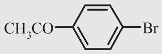
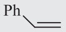
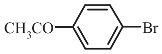
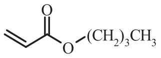
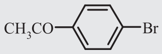
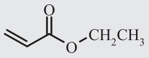
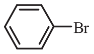
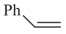
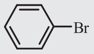
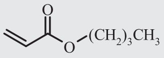
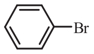
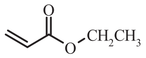
3.1 | Materials, methods and physical techniques

All starting materials were commercially available and were used without further purification. ^{1}H NMR and ^{31}P NMR spectra were recorded with a Bruker Avance DRS 250 MHz NMR spectrometer. IR spectra were recorded with a Nicolet 510P spectrophotometer using KBr discs. All reactions and manipulations were performed under argon atmosphere using standard Schlenk techniques unless otherwise stated. Ph_2PCl, 2-aminothiazole, 2-amino-4-methylthiazole and 2-aminobenzothiazole were purchased from Sigma-Aldrich and were used as received. The starting material [MCl_2(COD)] (M = Pd, COD =1,5-cyclooctadiene) was prepared according to literature procedures.[38] Solvents were dried using the appropriate reagents. The electronic properties and nature of the coordination interactions were investigated through density functional theory calculations using NBO[39] and AIM analyses at the B3LYP/LANL2DZ/6–311 + G** level on the optimized structure at the same level. The AIM analysis was performed by means of Bader's quantum theory of AIM, with the help of AIM 2000 software.[34,35] All quantum chemical calculations were carried out using the Gaussian 98 package.[40]

3.2 | General procedure for synthesis of L_1–L_3.

An amount of 1.150 g (5.056 mmol) of chlorodiphenylphosphine (Ph_2PCl) was added slowly into a solution of amine (2-aminothiazole (0.516 g, 5.050 mmol), 2-amino-4-methylthiazole (0.589 g, 5.056 mmol) or 2-aminobenzothiazole (0.775 g, 5.056 mmol)) and triethylamine(0.520 g, 5.087 mmol) in dichloromethane (20 ml) at 0 °C. The resulting suspension was stirred for 2 h and then the solvent was removed by filtration through a sintered Schlenk tube. The remaining solid was consecutively washed with distilled water and ethanol, and then dried

TABLE 6 Heck reaction between aryl halides and olefins in presence of complexes $\mathbf{C_1}$, $\mathbf{C_2}$ and $\mathbf{C_3}$ as catalysts[a]

			Conversion (%)[b] (TOF (h^{-1}))[c] (*trans*/*cis* product ratio)		
Entry	**Ar–X**	**Olefins**	C_1	C_2	C_3
1			100 (50) (94)	100 (50) (94)	100 (50) (95)
2			100 (50)	100 (50)	100 (50)
3			100 (50)	100 (50)	100 (50)
4			100 (50)	100 (50)	100 (50)
5			100 (50)	100 (50)	100 (50)
6			93 (46.5)	91 (45.5)	93 (46.5)
7			92 (46)	92 (46)	93 (46.5)
8			91 (45.5)	89 (44.5)	89 (44.5)
9			94 (47)	88 (44)	95 (47.5)
10			91 (45.5)	90 (45)	92 (46)
11			63 (31.5) (97)	60 (30) (98)	60 (30) (98)
12			61 (60.5)	58 (29)	60 (30)
13			64 (32)	66 (33)	64 (32)

[a] Reaction conditions: 1.0 mmol of aryl halides, 1.2 mmol of olefins, 2 mmol of K_2CO_3, 0.5 mol% complex, 3 ml of H_2O–DMF, 4 h.

[b] GC conversion.

[c] TOF = (mmol of product/mmol of catalyst) per hour.

in vacuum to produce a white solid. Characterization data of $\mathbf{L_1}$ and $\mathbf{L_3}$ have been reported previously.[19,20,23]

2-(Diphenylphosphino)amino-4-methylthiazole ($\mathbf{L_2}$). Yield 1.210 g, 82%; m.p. 98–100 °C. ^{31}P–{^{1}H} NMR ($CDCl_3$, δ, ppm): 41.1 (s). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.43 (m, 4H, Ph), 7.37 (m, 6H, Ph), 6.12 (s, 1H, thiazole), 2.06 (s, 3H, CH_3). Selected IR data (KBr, cm^{-1}): 3069, 1523 (C═N), 1432, 1387, 1297, 1231 (C─S), 1132, 986, 870 (P─N), 743, 695 s.

3.3 | General procedure for synthesis of C_1–C_3.

A solution of [$PdCl_2$(COD)] (0.029 g, 0.100 mmol) and 2-(diphenylphosphino)aminothiazole (0.028 g, 0.100 mmol), 2-(diphenylphosphino)amino-4-methylthiazole (0.003 g, 0.100 mmol) or 2-(diphenylphosphino)aminobenzothiazole (0.033 g, 0.100 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 1 h. The volume of the solvent was concentrated to 1–2 ml under reduced pressure and addition of Et_2O (15 ml) gave the palladium complexes (**C_1–C_3**) as yellow solids which were isolated by filtration and dried in vacuum.

3.3.1 | $PdCl_2[(Ph_2P)HN(C_3H_2NS)]$ (C_1)

Yield 0.039 g, 85%; m.p. (decomposed) 184–186 °C. ^{31}P–{^1H} NMR ($CDCl_3$, δ, ppm): 77.48 (s). ^1H NMR ($CDCl_3$, δ, ppm): 10.82 (1H, s, NH), 7.92 (m, 4H, Ph), 7.64 (m, 6H, Ph), 6.85 (br, 1H, thiazole), 6.83 (br, 1H, thiazole). Selected IR data (KBr, cm^{-1}): 3432, 2929, 1557 (C═N), 1479, 1433 (C─S), 1311, 1159, 1104 (P─C), 933 (P─N), 836, 743, 694.

3.3.2 | $PdCl_2[(Ph_2P)HN(C_3H_4NS)]$ (C_2)

Yield 0.040 g, 85%; m.p. (decomposed) 180–182 °C. ^{31}P–{^1H} NMR ($CDCl_3$, δ, ppm): 80.04 (s). ^1H NMR ($CDCl_3$, δ, ppm): 10.50 (1H, br, NH), 7.89 (m, 4H, Ph), 7.39 (m, 6H, Ph), 6.05 (s, 1H, thiazole), 2.37 (s, 3H, CH_3). Selected IR data (KBr, cm^{-1}): 3054, 1552 (C═N), 1471, 1435, 1294, 1211, 1143 (C─S), 1103, 986 (P─N), 841, 743, 692 s.

3.3.3 | $PdCl_2[(Ph_2P)HN(C7H4NS)]$ (C_3)

Yield 0.046 g, 90%; m.p. 162–164 °C. ^{31}P–{^1H} NMR ($CDCl_3$, δ, ppm): 85.21 (s). ^1H NMR ($CDCl_3$, δ, ppm): 9.27 (1H, br, NH), 7.56–8.32 (m, 14H, Ar). Selected IR data (KBr, cm^{-1}): 3430, 2995, 1642 (C═N), 1460 (C─S), 1249, 1211, 1103 (P─C), 1025, 932 (P─N), 838, 749, 688.

3.4 | Crystal structure determination

Single-crystal X-ray diffraction data were collected for both **C_1** and **C_3** using an Agilent Gemini Ultra diffractometer equipped with an Eos CCD area detector and using either Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.5418 Å). The data were collected at 173 K using an Oxford Cryosystems Cryostream 600. The data were processed with CrysAlisPro.[41] Semi-empirical absorption corrections were carried out using the Multi-Scan[42] program. The structures were solved by direct methods using SHELXT[43] and refined with full-matrix least-squares refinement by SHELXL-2013[44] within Olex2.[44] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at calculated positions and refined using a riding model based on the parent atom. The CIF files have been deposited with the CCDC and have been given the deposition numbers 1447821 and 1447820 for **C_1** and **C_3**, respectively.

3.5 | General procedure for heck reaction

A flask was charged with complex (0.5 mol%) along with an appropriate amount of aryl halide (1.0 mmol), olefin (1.2 mmol), K_2CO_3 (2.0 mmol) and H_2O–DMF (3 ml) and a magnetic stir bar. The mixture was heated to 100 °C with stirring for a specified period of time. After the reaction mixture was cooled to room temperature, hydrochloric acid (1 M, 6 ml) was added and the product was extracted with diethyl ether (3 × 15 ml). The aqueous solution was separated from the organic layer. The diethyl ether solution was washed with water (3 × 15 ml), dried over $MgSO_4$ and evaporated to dryness under reduced pressure to afford the desired product, which was then washed with hexane (3 × 5 ml). The purity of the compounds was checked by GC and yields are based on the aryl halide. Assignments of products were made by comparison with authentic samples.

4 | CONCLUSIONS

We have prepared and characterized Pd(II) complexes of some aminothiazole-based phosphine ligands. The crystal structures of the new Pd(II) complexes reveal that the ligands function in a chelating mode, coordinating through P and N_{endo} atoms in square planar complexes [$PdCl_2L$]. Structural studies indicate a higher donating ability of the P rather than N_{endo} towards Pd(II). Within the NBO framework, the Pd─N interaction was found to be stabilizing donor–acceptor delocalization, while the Pd─P bonds in **C_1–C_3** are covalent. The stronger interaction of phosphorus with Pd than N-donor is also supported by the AIM analysis. Crystal packing of **C_1** and **C_3** is firstly driven by NH···Cl hydrogen bonds, followed by weaker CH···Cl linkages and CH···π interactions. The prepared complexes present high catalytic activity in the Heck coupling reactions of aryl bromides and iodides with various olefins. Indeed, the product conversions obtained were more than those of the same reactions with bis(phosphino)amine Pd(II) complexes, as the catalysts in our previous work.[32]

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REFERENCES

[1] J. Gopalakrishnan, *Appl. Organometal. Chem.* **2009**, *23*, 291.

[2] C. Saluzzo, J. Breuzard, S. Pellet-Rostaing, M. Vallet, F. Le Guyaderm, M. Lamaire, *J. Organometal. Chem.* **2000**, *98*, 643.

[3] M. Amini, M. Bagherzadeh, Z. Moradi-Shoeili, D. M. Boghaei, *RSC Adv.* **2012**, *2*, 12091.

[4] M. Amini, M. Bagherzadeh, S. Rostamnia, *Chin. Chem. Lett.* **2013**, *24*, 433.

[5] M. Bagherzadeh, M. Amini, A. Ellern, L. K. Woo, *Inorg. Chim. Acta* **2012**, *383*, 46.

[6] P. Braunstein, *Chem. Rev.* **2006**, *106*, 134.

[7] P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, *40*, 680.

[8] L. Crociania, G. Bandolib, A. Dolmellab, M. Basato, B. Coraind, *Eur. J. Inorg. Chem.* **1811**, *1998*.

[9] D. B. G. Williams, T. Traut, F. H. Kriel, W. E. van Zyl, *Inorg. Chem. Commun.* **2007**, *10*, 538.

[10] T. Chivers, M. Krahn, M. Parvez, G. Schatte, *Chem. Commun.* **1922**, *2001*.

[11] K. G. Gawa, M. B. Smith, J. W. Steed, *J. Organometal. Chem.* **2002**, *664*, 294.

[12] G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **2000**, *33*, 336.

[13] N. C. Zingales, A. R. Shaffer, J. A. R. Schmidt, *Organometallics* **2013**, *32*, 578.

[14] T. Morimoto, Y. Yamaguchi, M. Suzuki, A. Saitoh, *Tetrahedron Lett.* **2000**, *41*, 10025.

[15] T. Z. Nagy, A. Csampai, A. Kotschy, *Tetrahedron* **2005**, *61*, 9767.

[16] B. R. Aluri, N. Peulecke, B. H. Muller, S. Peitz, A. Spannenberg, M. Hapke, U. Rosenthal, *Organometallics* **2010**, *29*, 226.

[17] W. L. Warton, S. Tanaka, C. M. Standfest, Ö. Öztopcu, J. C. Hsieh, K. Mereiter, K. Kirchner, *Polyhedron* **2010**, *29*, 3097.

[18] a) B. Crociani, S. Antonaroli, A. Marini, U. Matteolib, A. Scrivantib, *Dalton Trans.* **2006**, 2698; b) A. R. Shaffer, J. A. R. Schmidt, *Organometallics* **2009**, *28*, 2494; c) A. R. Shaffer, J. A. R. Schmidt, *Organometallics* **2008**, *27*, 1259.

[19] O. Kuhl, B. Walfort, T. Ruffer, *Cryst. Growth Design* **2006**, *6*, 366.

[20] Z. G. Hernandez, A. F. Parra, J. M. Grevy, A. R. Organillo, R. Contreras, *Polyhedron* **2006**, *25*, 1662.

[21] H. L. Milton, M. V. Wheatley, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chim. Acta* **2005**, *358*, 1393.

[22] G. Margraf, R. Pattacini, A. Messaoudi, P. Braunstein, *Chem. Commun.* **2006**, 3098.

[23] R. Pattacini, C. Giansante, P. Ceroni, M. Maestri, P. Braunstein, *Chem. – Eur. J.* **2007**, *13*, 10117.

[24] Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* **2003**, *42*, 2125.

[25] F. Durap, N. Biricik, B. Gumgum, S. Ozkar, W. H. Ang, Z. Fei, R. Scopelliti, *Polyhedron* **2008**, *27*, 196.

[26] M. Aydemir, A. Baysal, N. Gurbuzb, I. Ozdemirb, B. Gumgum, S. Ozkar, N. Caylak, L. T. Yildirim, *Appl. Organometal. Chem.* **2010**, *24*, 17.

[27] Z. Fei, R. Scopelliti, P. J. Dyson, *Dalton Trans.* **2003**, 2772.

[28] O. Scherer, W. M. Janssen, *J. Organometal. Chem.* **1969**, *20*, 111.

[29] J. D. Dunitz, A. Gavezzotti, *Angew. Chem.* **2005**, *117*, 1796.

[30] P. Gamez, G. A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, *Inorg. Chim. Acta* **2005**, *358*, 1975.

[31] O. Kuhl, S. Goutal, *Cryst. Growth Design* **2005**, *5*, 1875.

[32] K. Gholivand, M. Kahnouji, R. Latifi, F. T. Fadaei, A. Gholami, K. J. Schenk, *Inorg. Chim. Acta* **2016**, *448*, 61.

[33] I. Rozas, A. I. Elguero, J. Elguero, *J. Am. Chem. Soc.* **2000**, *122*, 11154.

[34] a) R. F. W. Bader, *Atoms in Molecules – A Quantum Theory*, Oxford University Press, New York **1990**; b) R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893.

[35] F. Biegler-Konig, J. Schonbohm, D. Bayles, *J. Comput. Chem.* **2001**, *22*, 545.

[36] N. Biricik, C. Kayan, B. Gumgum, Z. Fei, R. Scopelliti, P. J. Dyson, N. Gurbuz, I. Ozdemir, *Inorg. Chim. Acta* **2010**, *363*, 1039.

[37] M. Aydemir, F. Durap, A. Baysal, O. Akba, B. Gumgum, S. Ozkar, L. T. Yildirim, *Polyhedron* **2009**, *28*, 2313.

[38] D. Drew, J. R. Doyle, *Inorg. Synth.* **1972**, *13*, 52.

[39] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.

[40] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.7*, Gaussian Inc., Pittsburgh, PA **1998**.

[41] CrysAlisPro, *Agilent Technologies*, Yarnton, UK **2014**.

[42] R. H. Blessing, *Acta Crystallogr. A* **1995**, *51*, 33.

[43] G. M. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3.

[44] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

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