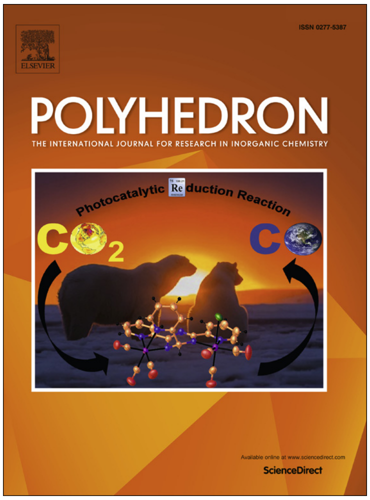

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PII: S0277-5387(16)30422-3
DOI: http://dx.doi.org/10.1016/j.poly.2016.09.002
Reference: POLY 12190

To appear in: *Polyhedron*

Received Date: 16 May 2016
Revised Date: 29 August 2016
Accepted Date: 4 September 2016

Please cite this article as: K. Gholivand, R. Salami, K. Farshadfar, R.J. Butcher, Synthesis and structural characterization of Pd(II) and Cu(I) complexes containing dithiophosphorus ligand and their catalytic activities for Heck reaction, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly.2016.09.002

Synthesis and structural characterization of Pd(II) and Cu(I) complexes containing dithiophosphorus ligand and their catalytic activities for Heck reaction

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Abstract

2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (*Lawesson's reagent*) was made to react with benzylamine to produce $[(PhCH_2NH)(p\text{-}C_6H_4OMe)PS_2]^-$ $[PhCH_2NH_3]^+$ in a very facile manner. From the abovementioned product, two new complexes $\{Pd[(PhCH_2NH)(p\text{-}C_6H_4OMe)PS_2]_2\}$ (C1) and $\{Cu_2(PPh_3)_2[(PhCH_2NH)(p\text{-}C_6H_4OMe)PS_2]_2\}$ (C2) were obtained in high yields whose molecular structures were ascertained by X-ray diffraction analysis, IR and NMR spectroscopy, and elemental analysis. The catalytic properties of both complexes were evaluated in the Heck reaction. High turnover numbers (TONs) and yields were observed for palladium catalyst and It was revealed that dicopper(I) complex by a distance of 2.84 Å between metal ions, bearing triphenylphosphine and dithiophosphorus ligands, can catalyze the Heck reaction. This is the first report of Cu(I) complex as catalyst in the Heck reaction. Natural bonding orbital (NBO) analysis for C1 indicated that natural charge on Pd atom is -0.07e and Pd atom has formed four sigma bonds with S atoms. Similarly, NBO analysis revealed no significant Cu…Cu interaction in dicopper complex C2.

Keywords: **Copper, Palladium, Dithiophosphorus Ligand, NBO analyses, Heck Reaction,**

1. Introduction

Nowadays the Mizoroki-Heck or simply the Heck reaction, catalyzed by transition-metal complexes, has become one of the most powerful and versatile tools in the formation of carbon-carbon bonds which provides a basis for synthesizing a variety of important compounds used in many areas such as pharmaceuticals, antioxidants, drug intermediates, UV absorbers and industrial applications [1-4]. The catalytic performances of transition-metal complexes are strongly dependent upon the nature of their ligands and the donor groups and thus, ligand design is substantial to improvement of catalytic science. In this regard, the ancillary ligands play a key role in the steric and electronic properties of the catalyst complexes. Moreover, the ligands are determinative in the stability of the active species and catalyst lifetime [5,6].

In recent years, dithiophosphorus (DTP) derivatives come into focus owing to the potential application as extraction agents for actinides from lanthanides via liquid/liquid extraction [7-11]. It has been shown that dithiophosphorus ligands are exceptional for this extraction as they are classified as soft-donor species [7-14]. Furthermore, dithiophosphorus ligands can be coordinated to the main group and transition metals, in particular, with soft metal centers such as palladium(II) and copper(I) [15,16]. DTPs are common bidentate ligands that can create stable complexes with soft acid type cations. Since in most homogeneous catalytic processes in C-C bond coupling based on palladium, the formation of palladium aggregates is common under the reaction conditions (which considerably reduces the catalytic activity), the use of stable palladium(II) complexes as catalyst help achieve highest turnover numbers [17-19]. Some of Pd(II) complexes with stabilizer chelating ligands showed very good catalytic activity in the Heck reaction [17-21]. But mechanistic details and, particularly, the question of how these stable complexes allow active species to be formed in catalytic cycle remain still unsolved.

Among transition-metal catalysts, palladium was mostly utilized for Heck coupling of aryl halides with olefins. Despite this fact, there are few reports on the use of copper for this reaction [22-26].However, there is a growing interest in using less expensive transition metal catalysts due to the high price of palladium.

In the present paper, we prepared two novel complexes of Pd(II) and Cu(I) with dithiophosphorus ligand (scheme 1) whose structural characterization and electronic properties were studied by X-ray crystallography and NBO analyses. The catalytic activity of both complexes in the Heck reaction was investigated.

3. Results and discussion

3.1. *Spectral characterization*

Ligand [$PhCH_2NH_3$] L was synthesized by reaction of two equivalent of benzylamine with one equivalents of *Lawesson's reagent* in toluene, giving 94% yield. The ligand was used for preparation of new complexes labeled with C1 (PdL_2) and C2 ($Cu_2(PPh_3)_2L_2$), Scheme 1.

The infrared spectra of the C1 complex showed strong and medium-strong IR bands at 655 and 543cm^{-1} which are ascribed to ν_{asym} (PS) and ν_{sym} (PS), respectively. Similarly, two strong IR bonds at 646 and 524 cm^{-1} were observed in the spectra of C2 complex for ν_{asym} (PS) and ν_{sym} (PS), respectively. A number of studies suggest that the interval between the position of symmetric and asymmetric P-S bonds ($\Delta\nu$) can be used to estimate the coordination mode of the dithiophosphinate ligands [27-31]. Based on the literature [27-31], $\Delta\nu$ values larger than 95 cm^{-1} are observed when dithiophosphinate ligands are monodentate. We found $\Delta\nu$ value of 112 and 124 cm^{-1} for C1 and C2 complexes respectively, even though the X-ray data showed bidentate chelating ligand for both complexes.

Cis and trans isomers are able to be formed regarding the nature of the chelating asymmetrical ligands in C1. The solid state structure shows that the trans isomer is the only present one in single crystals .The phosphorus atoms of cis and trans isomers are not chemically equivalent, because the cis isomer has a dipole moment and no inversion center, while the trans isomer has an inversion center and no dipole moment [32]. The $^{31}P\{^1H\}$ NMR spectrum for C1 reveals two singlet peaks at 91.38 and 92.32 ppm by separation of about 1 ppm. It seems that these two peaks are related to two isomers of cis and trans [32]. As the crystals are dissolved in the solvent, the trans isomer quickly rearranges and also forms cis isomer. The ^1H NMR spectrum of C1 for OMe protons shows distinct peaks for each isomer: two singlet peaks at 3.80 and 3.83 ppm. The protons of CH_2 moiety and phenyl groups show multiplets with overlap of the peaks of the two isomers. The $^{31}P\{^1H\}$ NMR spectra of C2 displays two doublet peak (PS_2 and PPh_3 moiety) with a coupling constant ($^3j_{PP}$) at around 7 Hz.

3.2. Crystal structure

An ORTEP view of one molecule of C1 with atom numbering scheme is given in Fig. 1, and relevant bond distances and angles are presented in Table 1. The Pd(II) is coordinated in a square–planar fashion with the four sulfur atoms from two chelating dithiophosphorus ligands, resulting in the formation of the four-membered chelate rings. The sum of bond angles around palladium is exactly 360°**,** indicating that the center atom and four sulfur atoms are located in the same plane. The S1-Pd-S1A and S2-Pd-S2A angles are 180.00°**,** which shows no deviation from linearity, while the S1-Pd-S2 (83.90(**15**)°) and S1-Pd-S2A (96.09(**15**)°) are not equal and display deviation from the ideal value of 90°. The palladium-sulfur bond lengths of 2.3426(4) and 2.3431(4) Å are within the normal Pd-S range of 2.2-2.5 Å [33, 34] and are close to those found in phosphine sulfide palladium complexes [35-37]. Approximately, equal values of phosphorus-sulfur bond lengths, 2.0336(6) and 2.0156(6) Å demonstrate that the negative charge is delocalized throughout the S-P-S moiety. The P-N distance of 1.6282(15) Å in this complex is shorter than the P-N single bond [38].

The interesting feature of this structure is a short intermolecular contact, Pd…H14-C14, between palladium(II) centers with two H atoms of two adjacent molecules [fig. 2]. These contacts are established with donor–acceptor distances of 3.324 Å. Wang et al. have shown that similar short intermolecular contacts Pt…H-C (2.94-3.02 Å) exist in platinum(II) complexes [39]. Moreover, the H14 atoms are positioned on both sides of the PdS_4 plan and, consequently they are oriented toward the dz^2 orbital of palladium(II) center, with H14…Pd…H14 angle of 180.000°. These short contacts with the Pd…H separation distance more than 2.2 Å provide a Pd…H-C interaction which can be regarded as a 3 center-4 electron (3c-4e) interaction using the electron pair in the dz^2 orbital of the central atom [39-44], whereas many complexes of transition metal showing well-known M…H-C interaction described as agostic interaction (3c-2e) with the M…H separation distance in the range of 1.8-2.2 Å [39,45-47]. For Pd…H14-C14 contact, Intermolecular binding energy, ΔE**,** was calculated at the M062X/LANL2DZ/6-311++G(d,p) level to estimate the strength of this interaction. ΔE value of - 5.21 kcal mol^{-1} was obtained for this contact, which is more than the strength of C-H…**π** interactions (2–4 kcal mol^{-1}) and is comparable with nonclassical intermolecular hydrogen bonds (5–9 kcal mol^{-1}) [48,49].

The intermolecular nonclassical hydrogen bonds O1…H11-C11 (2.550 Å) and S2…H5-C5 (2.791 Å) link the molecules together in the solid state and generate a two-dimensional (2D) framework [fig. 3]. The resulting 2D plans are further linked by S1…H1-N1 (2.56 Å), Pd…H-C and C-H…**π** [fig. 2] to generate 3D supramolecular network.

As shown in Fig. 1, Complex C2 is a dicopper compound which each Cu(I) cation is tetrahedrally coordinated by three sulfurs and one triphenylphosphine and the resultant dinuclear structure contains two $CuPS_2$ and one Cu_2S_2 rings. The L ligand acts as chelating ligand via its two sulfur atoms in way that the one sulfur atom is bridged between two copper and the other sulfur atom coordinates only to one copper. The Cu_2S_2 ring shows a particular geometry with alternative long (2.6147(6) Å) and short (2.3085(6) Å) Cu-S distances due to the nature of the orbitals and electrons of the bridging sulfur [50,51]. The Cu-P (Cu-P2, CuA-P2A) and Cu-terminal S (Cu-S1, CuA-S1A) lengths are 2.2220(5) and 2.3857(6), respectively, which fall within the range of copper(I) dithiocomplexes [52,53]. Regarding the fact that the sum of van der Waals radii for two copper is ca. 2.8 Å [54], the observed Cu–Cu distance (2.8396(5) Å) suggests the minor contribution of Cu ···Cu interaction. The bond angles around Cu(I) are in the range of 84.050(16)°-127.633(19)° for the S1-Cu-S2 and P2-Cu-S2 angles, respectively. Each of four-membered ring Cu_2S_2 and $CuPS_2$ (sum of internal angles in the range of 359-360°) are flat. The torsion angle between the two planes $CuPS_2$ is 0.0° and each of these rings generates the angle 73.359(17)° with Cu_2S_2, thus indicating that the $CuPS_2$ planes are approximately perpendicular to the Cu_2S_2 plane. The P-S distance for S in terminal position (P1-S1, P1A-S1A = 1.9914(7) Å) is slightly shorter than the P-S distance in bridging position (P1-S2, P1A-S2A = 2.0329(6) Å).

In this crystal structure, the sulfur atoms, as bifurcated acceptors, are involved in intermolecular C-H…S1 nonclassical hydrogen bonds that lead to the formation of 2D framework [fig. 4]. In these interactions, the C-H…S1 distances are 2.925 and 3.011 Å. The cooperation of nonclassical hydrogen bonds with multiple weaker C-H…**π** and C-H…H-C interactions leads to generation of 3D supramolecular network.

It is noteworthy, that no S···S intermolecular stacking, often found in dithiocomplexes, was detected in the C1 and C2 complexes (probably because of the steric bulk of the ligands).

3.3. Theoretical calculations

Full geometry optimization of dithiophosphorus ligand L, C1 and C2 complexes were performed using DFT calculation with B3LYP functional and also, NBO analyses were carried out to gain more insight about bonding and electronic aspects of the complexes. The obtained optimized geometries of the compounds are shown in fig. 5 and some selected geometric parameters are listed in Table 1. The optimized structure of C1 reproduces the square-planar coordination surrounding the palladium center and its geometric parameters show good agreement with the X-ray structure of C1. The comparison of the calculated P-S bond lengths in L and C1 reveal the lengthening of the P-S bonds from free ligand L to C1 and C2 complexes. Cu…Cu distance in the optimized C2 structure is larger by 0.896 Å than the corresponding one in solid state structure. As can be seen in fig. 5, the optimized structure of C2 comprises an eight-membered $Cu_2P_2S_4$ ring in which two Cu are bridged by two S atoms of the L ligands. The minimum calculated energy for C2 in the observed structure at the solid state is slightly higher compared to the optimized one in gas phase ($\Delta E = 8.74$ kcal mol^{-1}). However, this structure can be stabilized (as observed in the X-ray structure) by intermolecular interactions with neighboring molecules, which is a determinant factor in the solid state structure.

3.4. NBO analysis

Initially, it’s noteworthy that NBO analyses for C1 and C2 were performed on optimized structures cut out from X-ray structures by freezing non-hydrogen atoms. Table 2 shows that in C1 complex, the negative charges on sulfur atoms decrease by an average value about 0.34e upon complexation, indicating the strong donor-acceptor interactions between the metal atom and the sulfur atoms. But in C2 complex the negative charges on sulfur atoms increase by an average value about 0.06e upon complexation, owing to the electrostatic field of Cu(I) ion [55]. The positive charge on phosphorus atom increases from L ligand to complexes. Meanwhile, no significant π-bond contribution for P-S bonds was observed in any of the compounds within the NBO framework. The electron configuration of palladium in C1 is [core]$5s^{0.37}4d^{9.19}5p^{0.49}6s^{0.01}5d^{0.01}$, indicating nearly full occupation of the 4d orbital by 9.19 electrons. The sum of core electrons (36e), valance electrons (9.56e on 5s and 4d) and Rydberg electrons (0.51e on 5p, 6s and 5d) give 46.07 electrons in agreement with the calculated natural charge of -0.07e at Pd atom. According to the NBO, the Pd atom forms four sigma bonds with S atoms as a result of electron donation from the S lone pairs to the Pd orbitals in which $\sigma(\mathrm{Pd}-\mathrm{S})$ bonds are strongly polarized toward sulfur atoms (ca.79% at S). Therefore, as a consequence of electron density donation from S to Pd, the positive charge of Pd(II) was fully compensated. The hybrid of $\sigma(\mathrm{Pd}-\mathrm{S})$ bonds on Pd atom is a mixture of s (24.35- 24.50%), p (50.00%) and d (26.50-26.65 %) and also is a mixture of s (11.64-11.70%), p (88.15-88.21%) and d (0.15%) on S atoms. The bonding orbital are occupied by about 1.82e for Pd-S bonds.

As follows from Table 2, the calculated charge distribution of +0.829 for Cu atoms in C2 complex is also consistent with the electron configuration of Cu, [core]$4s^{0.40}3d^{9.74}4p^{0.02}5S^{0.01}$. In bonding the L ligand and triphenylphosphine to Cu atoms, no σ-bond is found in the NBO analysis, and the bonds of Cu with S or P can be described as predominant Coulomb-type interactions [56]. According to the NBO, the amount of delocalization of electron density between occupied Lewis-type orbitals, LP (S or P), and unoccupied non-Lewis orbitals, LP*(Cu), corresponds to a stabilizing donor-acceptor interaction. The calculated second order interaction energy (E^2) between donor-acceptor orbitals can be used as a measure of interaction strength. A strong donor–acceptor interaction by E^2= 99.69 kcal mol^{-1} was found between P atom of PPh_3 and Cu atom. The other strong interaction was observed between terminal S atom of L ligand and Cu atom by E^2= 56.25 kcal mol^{-1}. Two actually different energies of 28.27 and 67.02 kcal mol^{-1} were found for the interaction of bridge S atom with the two Cu atoms. Similarly, within the NBO framework, no significant Cu…Cu interaction was observed at E^2 higher than 3.1 kcalmol^{-1}.

3.5. Catalytic Performance of the C1 and C2 complexes in the Heck Reaction

Initially, we evaluated the thermal stability of C1 after prolonged heating at 180 ℃ in N-methylpyrrolidone (NMP) by $^{31}P\{^1H\}$ NMR spectrum. After three days, no decomposition and no palladium black were observed for the compound. Catalytic studies of the complexes in Heck reaction between bromobenzene and styrene have been performed to survey reaction parameters. The screening results presented in Table 3 show that the polar aprotic solvent N-methylpyrrolidinone (NMP) and N,N-dimethylformamide (DMF) obtain better results than other solvents. The non-polar solvents such as toluene and dioxane gave comparatively similar yield (entries 4,5) but below that of DMF and NMP. The polar protic solvent such as isopropanol gave the lowest yields (entry 3). We then used DMF as the optimal solvent to find the best base. We screened several inorganic and organic bases such as K_2CO_3, K_3PO_4, NaOH, Et_3N and pyridine. Accordingly, inorganic bases obtained higher yields than organic bases [table 3]. Of the three inorganic bases, K_2CO_3 and K_3PO_4 gave the highest yields of the desired product for Catalyst C1 (entry 1) and Catalyst C2 (entry 6), respectively. A comparatively similar result was observed using K_2CO_3 and K_3PO_4 as a base for C1 catalyst, but for C2 catalyst the reaction would be much slower if K_2CO_3 was replaced with a stronger base K_3PO_4 (entries 1,6).

Furthermore, the optimizations of catalyst loading were performed in DMF as a reaction solvent in the presence of K_2CO_3 for C1 catalyst and K_3PO_4 for C2 catalyst to determine the most efficient of catalyst amount [table 4]. Increasing the amount of C1 from 0.00002 equivalent (equiv.) in coupling of bromobenzene (PhBr) with styrene had no considerable impact on the yield but caused to a decrease in turnover number (TON) certainly. When iodobenzene (PhI) was used instead of PhBr, even C1 loading of 0.00001 equiv. (entry 9) gave 100% yield. Various amounts of C2 were also examined and the best results were obtained in 0.03 and 0.10 equiv. [table 4, entries 17, 14] for coupling of PhI and PhBr, respectively. As shown in table 4, C1 complex is a more robust catalyst compared to C2, but considering economy and toxicity, the use of the C2 complex as the catalyst can be more attractive.

The time-yield plot of the coupling of the bromobenzene with styrene under copper catalyst displays a sigmoidal-shaped curve with an induction period of 30 min and then reveals an exponential increase in the yield of the reaction [fig. 6]. These observations suggest that the copper complex acts as precursor to form catalytically active species. There have been few reports of a similar activation step for palladium (II) complexes [57-60]. Furthermore, no induction period is observed in the time-yield plot of palladium catalyst in the examined time intervals and the catalyst should be immediately active at the beginning of the reaction. After 8 h, none of the catalysts showed considerable increment in the yield.

Since NBO analysis revealed that four strong sigma bonds Pd-S for stable palladium complex (C1) and that no induction period was observed in the time-yield plot of C1, it can be concluded that C1 acts as a catalytically active species in catalytic cycle, probably, without being dissociated Pd-S bonds. Moreover, it is worth noting that a number of Cu(I) complexes built in our group were investigated for coupling aryl bromides with styrene, out of which only C2 complex was able to perform this coupling.

4. Conclusion

The new air and thermally stable complex of palladium(II) {$Pd[(PhCH_2NH)(p\text{-}C_6H_4OMe)PS_2]_2$} (C1) and the dicopper(I) complex {$Cu_2(PPh_3)_2[(PhCH_2NH)(p\text{-}C_6H_4OMe)PS_2]_2$} (C2) were prepared in satisfactory yields and characterized using X-ray diffraction analysis, IR and NMR spectroscopy, and elemental analysis. Based on NBO analysis and time-yield plot, we suggest that the C1 complex probably acts as a catalytically active species, not as a precatalyst, in catalytic cycle of the Heck reaction. Although copper complexes are often not active in the Heck reaction, the present study suggests that the dicopper complex with the metal ions separated by 2.84 Å is an effective catalyst for the Heck reaction.

2. Experimental section

2.1. Materials and methods

All chemicals and solvents are commercially available, and used without further purification. Drying of the solvents was done using standard methods. Melting points were obtained by an electrothermal instrument. Elemental analyses were performed using a Heraeus CHN-O-RAPID apparatus. Infrared spectra were recorded (400–4000 cm^{-1} region) on a Nicolet 510P spectrophotometer using KBr disk. $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker Avance DRX-500 spectrometer operating at 202 MHz with chemical shifts reported relative to a 85% H_3PO_4 in D_2O external standard solution. ^1H NMR spectra were also obtained on a Bruker Avance DRX-500 spectrometer with chemical shifts relative to the internal standard TMS. The Heck coupling reactions were analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column and flame-ionization detector.

2.2. Preparation of $[(OCH_3C_6H_4)(phCH_2NH)PS_2]^-$ $[phCH_2NH_3]^+$ ([L] $[phCH_2NH_3]^+$)

Titled compound was prepared using reported method [61]. To a suspension of Lawesson's reagent (0.404 g, 1 mmol) in 10 mL dry toluene at room temperature, benzylamine (0.536 g, 5 mmol) was added and the mixture was stirred for 6h. The colorless precipitated solid was filtered off and washed several times with dry toluene. The structure of ligand L is given in scheme 1. Yield 94%, M.p. 164 °C**.** Anal. Calc. for $C_{21}H_{25}N_2OPS_2$ (416.45): C, 60.56; H, 6.00; N, 6.73. Found: C, 60.60; H, 5.98; N, 6.76%. IR (KBr, cm^{-1}): ν = 3321(m), 2925(br), 2853(br), 1587(s), 1491(s), 1451(m), 1395(w), 1290(w), 1249(s), 1180(w), 1103(m), 1056(m), 964(w), 817(br,), 742(m), 696(m), 661(s, ν_{asym} (PS)), 587(m), 545(s, ν_{sym} (PS)). ^{1}H NMR (500.13 MHz, DMSO-d6): δ(ppm) = 3.21(br, 1H, NH(anion moiety)), 3.73(s, 3H, OCH_3), 3.78(t, $^3J_{PH}$ = 8.9 Hz, 2H, CH_2(anion moiety)), 4.02(s, 2H, CH_2(cation moiety)), 6.78(d, $^3J_{HH}$ = 4.3 Hz, 1H), 6.80(d, $^3J_{HH}$ = 4.65 Hz, 1H), 7.12(t, $^3J_{HH}$ = 6.95 Hz, 1H), 7.19-7.24(m, 4H), 7.35-7.45(m, 5H), 7.90(dd, $^3J_{HH}$ = 4.70 Hz, $^3J_{HH}$ = 6.74 Hz, 1H), 7.94(dd, $^3J_{HH}$ = 5.36 Hz, $^3J_{HH}$ = 6.18 Hz, 1H). $^{31}P\{^1H\}$ NMR (202.46 MHz, DMSO-d6): δ(ppm) = 80.25 (s)

2.3. Preparation of C1 complex {$Pd[(PhCH_2NH)(p\text{-}C_6H_4OMe)PS_2]_2$} ($PdL_2$)

A solution of $PdCl_2$ (0.086 g, 0.50 mmol) in acetonitrile (5 ml) was added drop-wise to a solution of L (0.416 g, 1.00 mmol) in methanol (5 ml) and the mixture was stirred for 8h to obtain yellow clear solution. Suitable crystals for X-ray analysis were obtained by slow evaporation of solvent after 2 days. Yield 88%, M.p. 181 °C**.** Anal. Calc. for $C_{28}H_{30}N_2O_2P_2PdS_4$ (723.17): C, 46.50; H, 4.15; N, 3.87. Found: C, 46.51; H, 4.12; N, 3.88%. IR (KBr, cm^{-1}): ν = 3235(vs), 3015(br), 2928(s), 1589(s), 1495(s), 1457(m), 1403(m), 1296(m), 1252(vs), 1178(m), 1107(vs), 1060(vs), 1022(m), 967(w), 870(m), 825(m), 746(m), 695(m), 655(s, ν_{asym} (PS)), 543(s, ν_{sym} (PS)). ^{1}H NMR (500.13 MHz, DMSO-d6): δ(ppm) = 3.33(br, overlapping with the solvent signal, NH), 3.80(s, 3H, OCH_3), 3.83(s, 3H, OCH_3) 4.15(m, 4H), 6.94(m, 2H), 7.13(m, 2H), 7.23(m, 2H), 7.31-7.42(m, 8H), 7.83.7.92(4H). $^{31}P\{^1H\}$NMR (202.46 MHz, DMSO-d6): δ(ppm) = 91.37(s), 92.32(s).

2.4. Preparation of C2 complex {$Cu_2(PPh_3)_2[(PhCH_2NH)(p\text{-}C_6H_4OMe)PS_2]_2$} ($Cu_2(PPh_3)_2L_2$)

A solution of L (0.416 g, 1.00 mmol) in chloroform (12 mL) was added drop wise to stirred solution of mixture copper(I) chloride (0.134 g, 1.00 mmol) and triphenylphosphine (PPh_3) (0.263 g, 1.00 mmol) in acetonitrile (6 ml). The mixture of reaction was filtered off to obtain **a** colorless clear solution. Suitable single crystals of C2 were obtained by slow diffusion of diethyl ether in the clear solution. Yield 76%, M.p. 233 °C (decompose)**.** Anal. Calc. for $C_{64}H_{60}Cu_2N_2O_2P_4S_4$ (1268.45): C, 60.60; H, 4.77; N, 2.21. Found: C, 60.59; H, 4.78; N, 2.19%. IR (KBr, cm^{-1}): ν = 3321(m), 3050(br), 2905(br), 1588(m), 1487(m), 1433(m), 1383(m), 1287(w), 1251(m), 1174(m), 1097(s), 1055(m), 1024(m), 856(w), 802(m), 741(s), 692(s), 646(s, ν_{asym} (PS)), 614(m), 575(m), 524(s, ν_{sym} (PS)). ^{1}H NMR (500.13 MHz, DMSO-d6): δ(ppm) = 3.18(dd, $^2J_{PH}$ = 21.4 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, NH), 3.68(s, 3H, OCH_3), 4.09(d, $^3J_{HH}$ = 7.2 Hz, 2H,

CH_2), 6.73(m, 2H), 7.03(t, $^3J_{HH}$ = 6.23 Hz, 1H), 7.16-7.43(m, overlapping with the solvent signal), 7.73(m, 2H). $^{31}P\{^1H\}$NMR (202.46 MHz, DMSO-d6): δ(ppm) = -1.69(d, $^3J_{PP}$ = 6.9 Hz, PPh_3), 75.65(d, $^3J_{PP}$ = 7 Hz, PS_2).

2.5. Crystal structure determination

Crystals were selected under a microscope and mounted on a MiTeGen cryoloop using mineral oil and transferred to a Bruker Quest diffractometer in a cold stream of nitrogen gas at -173.15°C. Preliminary cell constants were obtained from a small set of frames and then a complete hemisphere of data was collected. The Bruker diffractometer control program Apex 2 was used for the preliminary setup and data collection [62]. The collected data was processed with the Bruker program Saint. A multi-scan type absorption correction was applied using SADABS [63]. The structure was solved using the program Superflip [64] and refined using Shelxl-2014. Files for publication and diagrams were prepared using Shelxtl [65]. Details of the X-ray data collection parameters are given in Table 5.

2.6. Theoretical methods

All the DFT calculations reported here were carried out using Gaussian 03 package [66] in the gas phase. The structure of the free ligand and the two complexes was fully optimized at the B3LYP level [67]. The palladium atom was described by the LANL2DZ effective core potential and basis set [68], but the standard basis set 6-311+G* was used for remaining atoms. All the vibrational frequencies were real, indicating that the optimized structures to be minimal. Natural bond orbital (NBO) analyses [69] were performed at the B3LYP/6-311+G** level for L and C2 and at the B3LYP/6-311+G**/LANL2DZ level for C1.

In order to calculate binding energy Pd…H in solid state, two selected fragment were cut out from C1 X-ray structure and optimized by freezing of non-hydrogen atoms at the B3LYP/6-311+G*/LANL2DZ level. The intermolecular Pd…H energy was evaluated at M062X/6-311++G**/LANL2DZ level, according to the energy difference between the total energy of the system and its fragments. Basis set superposition error (BSSE) in the interaction energy has been removed by the counterpoise correction method of Boys and Bernardi [69].

2.7. General procedure for preparative Heck reactions

A reaction flask was charged with an appropriate amount of aryl halide (1.0 equiv.), styrene (1.2 equiv.), base (1.5 equiv.), dodecane as internal standard (40 mg), solvent (2 mL) and stirring bar. The resulting mixture was heated to 100 °C for several minutes before the prescribed amount of catalyst was added. After a specified period of time, the suspension was cooled to room temperature, water was added, and the product was extracted with CH_2Cl_2 (three times). The combined organic portions were dried over $MgSO_4$, filtered, and evaporated under vacuum to achieve the desired product which was then washed with hexane. The coupled products were analyzed by a combination of GC analysis and NMR spectroscopy (comparison of NMR data with those in the literature).

Acknowledgements

Financial support of this work by Tarbiat Modares University is gratefully acknowledged. We thank also the assistance of Dr. Matthias Zeller for help in data collection and NSF Grant 1337296 for funds to obtain the diffractometer.

Appendix A. Supplementary material

CCDC 1447974 and 1447975 contain the supplementary crystallographic information for C1 and C2 complexes, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Figure Captions

Fig. 1: ORTEP view of C1 (left) and C2 (right) (50% probability level) with atom-labeling scheme (part of atom-labeling are omitted for clarity).

Fig. 2: Side view representation of C1, showing intermolecular S1…H1-N1 (2.56 Å), Pd…H-C (3.324 Å) and C-H…π interactions (C8A-H8A…Cg: $d_{H\ldots C}$ = 2.983 Å, $d_{C\ldots Cg}$ = 3.921 Å, θ = 137.867°).

Fig. 3: 2D nonclassical hydrogen-bonded frameworks of C1, showing O1…H11-C11 (2.550 Å) and S2…H5-C5 (2.791 Å).

Fig. 4: 2D nonclassical hydrogen-bonded frameworks of C2, showing S1…H25A-C25A (2.925 Å) and S1…H6A-C6A (3.011 Å).

Fig. 5: Optimized structures at B3LYP/6-311+G*/LANL2DZ level (Hydrogen atoms are omitted for clarity).

Fig. 6: The time-yield curves for the coupling of PhBr with styrene at 100 ℃ in optimized reaction conditions, catalyzed by C1 and C2 catalysts.

Scheme 1: Synthesis of C1 and C2 complexes.

Table 1: Selected geometrical parameters for C1 and C2 in solid state and in gas phase calculated at B3LYP/6-311+G* (L and C2) and at B3LYP/LANL2DZ/6-311+G* (C1).

copmounds	C1		C2		L
	X-ray	Calc.	X-ray	Calc.	Calc.
Bond lengths (Å)					
P-S	2.0156(6)	2.048	1.9913(6)	2.041	2.019
	2.0336(6)	2.053	2.0330(6)	2.060	2.025
P-N	1.6282(15)	1.681	1.6738(16)	1.689	1.688
M-S_t[a]	2.3427(4)	2.423	2.3857(6)	2.338	
	2.3431(4)	2.424		2.429	
M-S_b[b]			2.3084(7)		
			2.6147(6)		
M-P			2.2219(6)	2.222	
M…M			2.8396(6)	3.736	
Bond angles (°)					
S-P-S	101.36(2)	103.05	112.79(3)	113.26	100.63
S_t-M-S_t	83.905(14)	82.97	105.153(19)	105.14	
	96.095(15)	97.02			
S_b-M-S_b			84.052(17)		

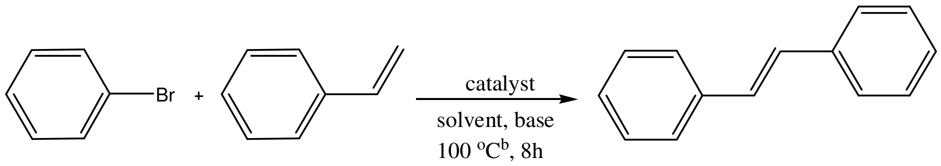
[a] S_t: terminal S atom. [b] S_b: bridge S atom

Table 2: Atomic Charge Distributions (e) and Natural Electron Configurations calculated for selected atoms in L, C1 and C2.

atoms	L	C1	C2
M= Pd, Cu		-0.07 $\text{[core]}5s^{0.37}4d^{9.19}5p^{0.49}6s^{0.01}5d^{0.01}$	+0.829 $\text{[core]}4s^{0.40}3d^{9.74}4p^{0.02}5s^{0.01}$
S	-0.71 $\text{[core]}3s^{1.84}3p^{4.84}3d^{0.01}5p^{0.01}$	-0.39 $\text{[core]}3s^{1.79}3p^{4.58}3d^{0.01}$	-0.69[a] $\text{[core]}3s^{1.81}3p^{4.85}3d^{0.01}4p^{0.01}$
	-0.72 $\text{[core]}3s^{1.84}3p^{4.86}3d^{0.01}5p^{0.01}$	-0.37 $\text{[core]}3s^{1.78}3p^{4.56}3d^{0.01}$	-0.77[b] $\text{[core]}3s^{1.81}3p^{4.93}3d^{0.02}4p^{0.02}$
P	+1.26 $\text{[core]}3s^{1.13}3p^{2.50}3d^{0.08}5p^{0.03}$	+1.36 $\text{[core]}3s^{1.11}3p^{2.42}3d^{0.08}4p^{0.02}$	+1.36 $\text{[core]}3s^{1.04}3p^{2.44}3d^{0.09}4p^{0.06}$ +0.75[c] $\text{[core]}3s^{1.26}3p^{2.87}4s^{0.01}3d^{0.03}4p^{0.07}$
N	-1.00 $\text{[core]}2s^{1.44}2p^{4.53}3p^{0.01}4p^{0.01}$	-0.98 $\text{[core]}2s^{1.40}2p^{4.56}3p^{0.01}4p^{0.01}$	-0.97 $\text{[core]}2s^{1.38}2p^{4.57}3p0.01$

[a] Related to terminal S atom. [b] Related to bridge S atom. [c] Related to PPh_3 moiety.

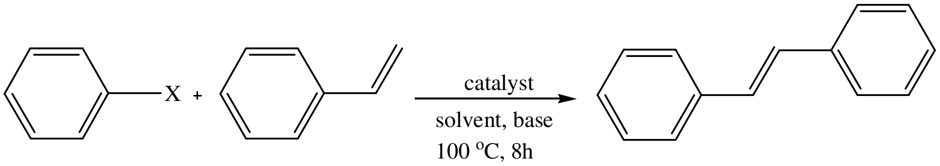
Table 3: Solvent and base effects on the Heck coupling of PhBr with styrene.[a]



Entry	solvent	base	Yield (%)[c] (isolayed yield (%))[d]	
			C1	C2
1	DMF	K_2CO_3	68 (61)	24
2	NMP	K_2CO_3	63	24
3	isopropanol	K_2CO_3	8	8
4	toluene	K_2CO_3	33	13
5	dioxane	K_2CO_3	39	11
6	DMF	K_3PO_4	61	44 (38)
7	DMF	NaOH	21	16
8	DMF	Et_3N	13	trace
9	DMF	pyridine	6	trace
10	NMP	K_3PO_4	55	41

[a]Reaction conditions: 1.0 equiv. of PhBr, 1.2 equiv. of styrene, 1.5 equiv. of base, 10^{-5} equiv. of catalyst C1 or 0.02 equiv. of catalyst C2, 2 mL of solvent. [b]Bath temperature. [c]Determined by GC, based on PhBr (dodecane as an internal standard); average of two runs. [d]Isolated yield ; average of two runs.

Table 4: Effect of catalyst loading [a]

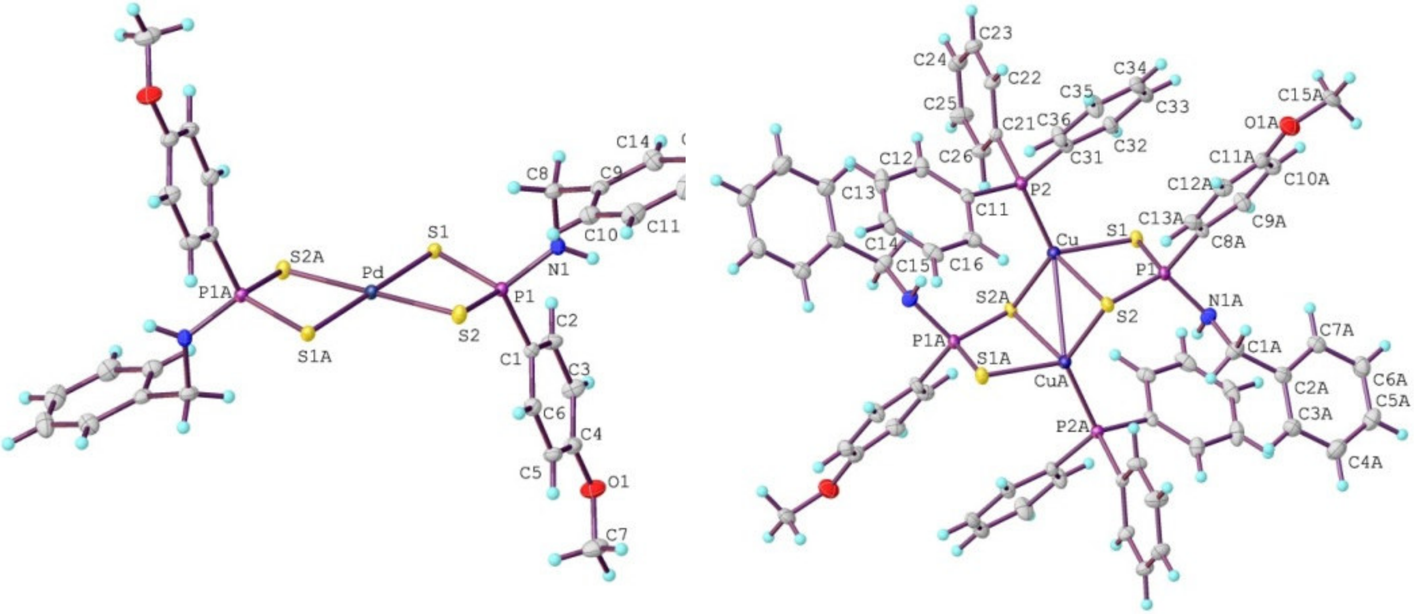


Entry	X	Catalyst (equiv)	Yield (%)[b]	TON
1	Br	C1 (0.000010)	68	68000
2	Br	C1 (0.000015)	86	57330
3	Br	C1 (0.000018)	91	50550
4	Br	C1 (0.000020)	94	47000
5	Br	C1 (0.000022)	93	42270
6	Br	C1 (0.000030)	96	32000
7	I	C1 (0.000005)	73	146000
8	I	C1 (0.000008)	95	118750
9	I	C1 (0.000010)	100	100000
11	Br	C2 (0.02)	44	22
12	Br	C2 (0.04)	61	15
13	Br	C2 (0.08)	72	9
14	Br	C2 (0.10)	83	8
15	Br	C2 (0.12)	84	7
16	I	C2 (0.020)	71	36
17	I	C2 (0.030)	96	32
18	I	C2 (0.040)	98	25

[a]Reaction conditions: 1.0 equiv. of PhX, 1.2 equiv. of styrene, 1.5 equiv. of K_2CO_3 for C1 or K_3PO_4 for C2, 2 ml of DMF. [b]Determined by GC, based on PhX (dodecane as an internal standard); average of two runs.

Table 5. Crystallographic data for compounds C1 and C2.

Compound	**C1**	**C2**
Empirical formula	$C_{28}H_{30}N_2O_2P_2PdS_4$	$C_{32}H_{60}Cu_2N_2O_2P_4S_4$
Formula weight	723.12	1268.34
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a (Å)	11.0212(5)	13.631(2)
b (Å)	16.2526(7)	10.5473(15)
c (Å)	8.5432(4)	20.374(3)
α/°	90	90
β/°	101.168(2)	95.531(2)
γ/°	90	90
V ($Å^3$)	1501.31(12)	2915.6(7)
Z, Calculated density ($g.cm^{-3}$)	2, 1.600	2, 1.445
Absorption coefficient (mm^{-1})	1.033	1.029
F(000)	736.0	1312.0
Crystal size (mm^3)	0.260 × 0.120 × 0.100	0.350 × 0.240 × 0.200
θ range for data collection (°)	4.524 to 66.438	4.016 to 61.088
Index ranges	$-13 \leq h \leq 16$ $-25 \leq k \leq 23$ $-12 \leq l \leq 13$	$-19 \leq h \leq 19$ $-15 \leq k \leq 14$ $-28 \leq l \leq 29$
Reflections collected	14026	34056
Independent reflections	5396 [R_{int} = 0.0249, R_{sigma} = 0.0362]	8871 [R_{int} = 0.0326, R_{sigma} = 0.0306]
Data/restraints/parameters	5396/12/187	8871/0/357
Goodness-of-fit on F^2	1.040	1.047
Final *R* indices	R_1 = 0.0321, wR_2 = 0.0635	R_1 = 0.0374, wR_2 = 0.0969
R indices (all data)	R_1 = 0.0488, wR_2 = 0.0691	R_1 = 0.0479, wR_2 = 0.1018
Largest diff. peak and hole ($e.Å^{-3}$)	0.93/-0.44	1.08/-0.38


S2A
Pd
S1
P1A
S1A
S2
P1
N1
C8
C9
C14
C10
C11
C2
C1
C3
C6
C4
C5
O1
C7
C23
C24
C22
C35
C34
C33
C25
C21
C36
C32
C26
C31
O1A
C15A
C12
C11A
C10A
C12A
C13
C11
P2
C13A
C9A
Cu
S1
C14
C8A
C15
C16
P1
S2A
N1A
S2
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C5A
C3A
P2A
C4A

Fig. 1

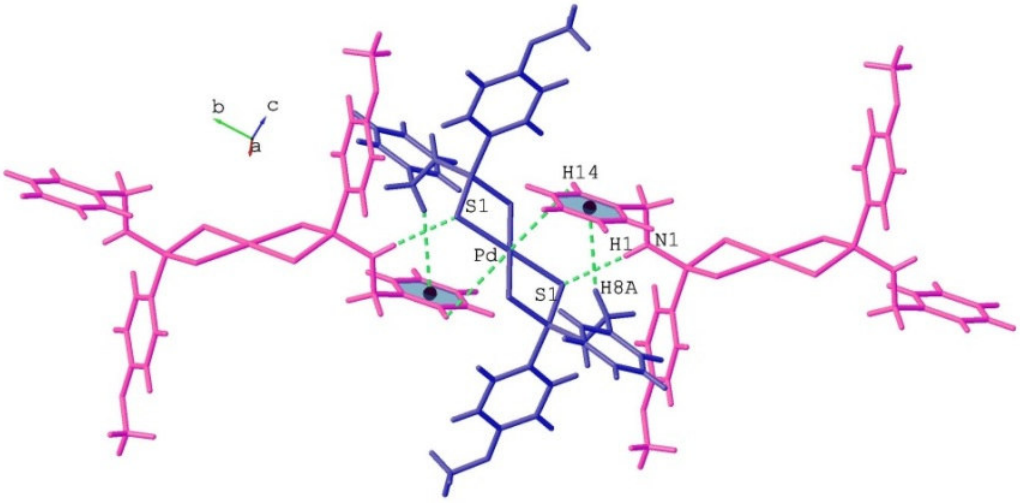


Fig. 2

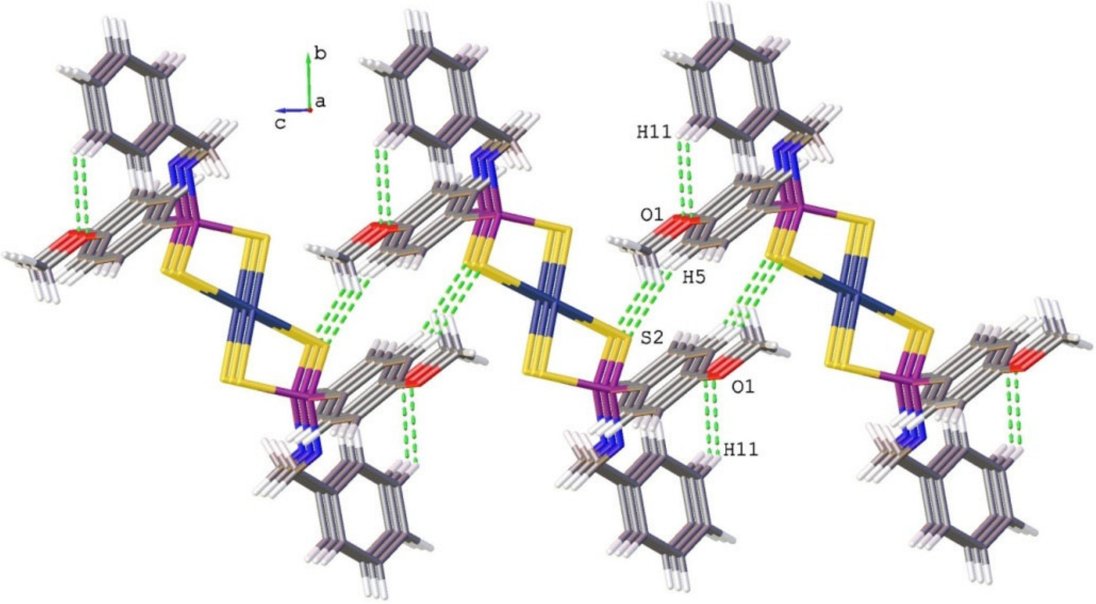


Fig. 3

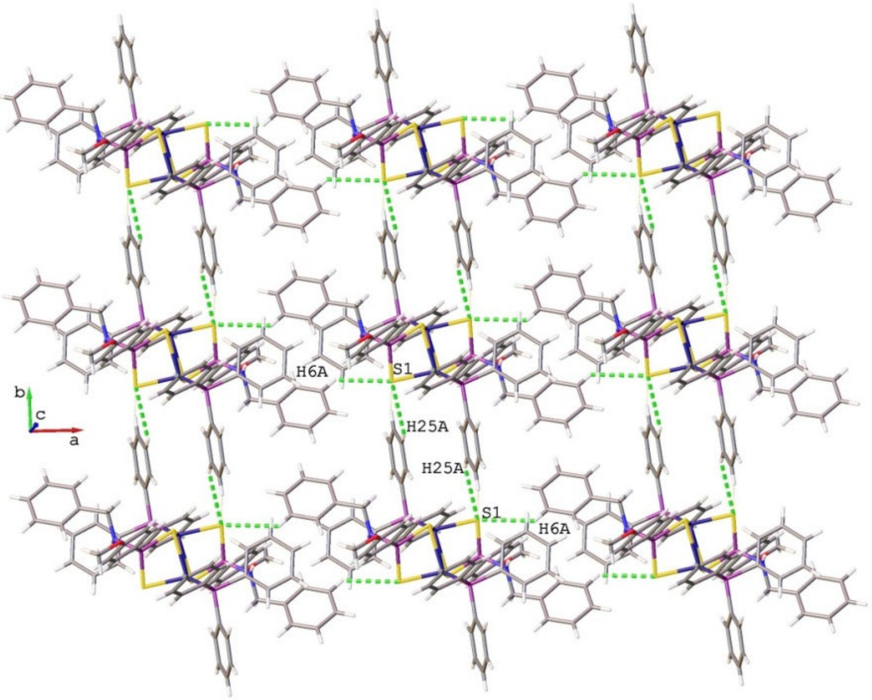
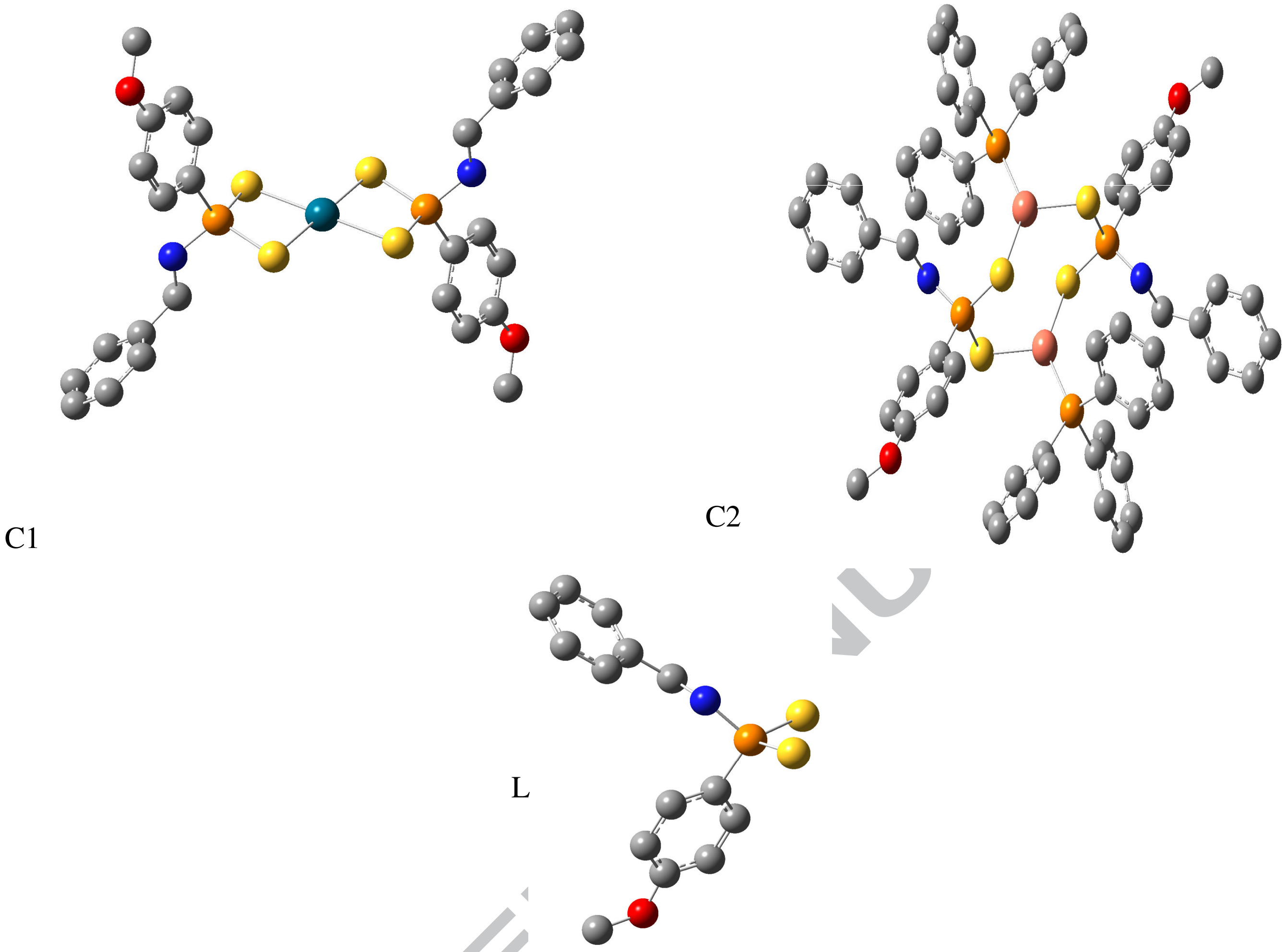


Fig. 4



C1

C2

L

Fig. 5

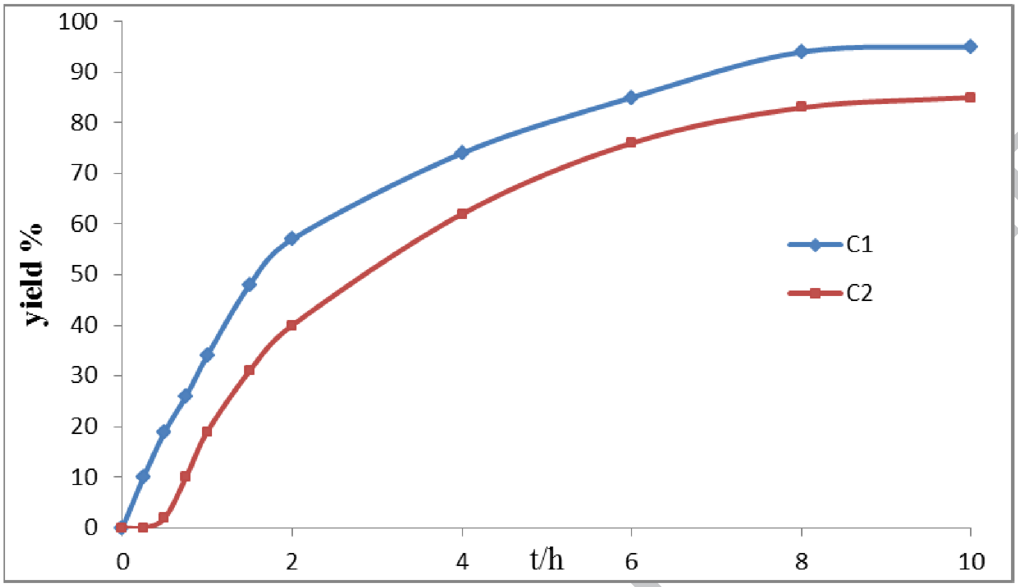
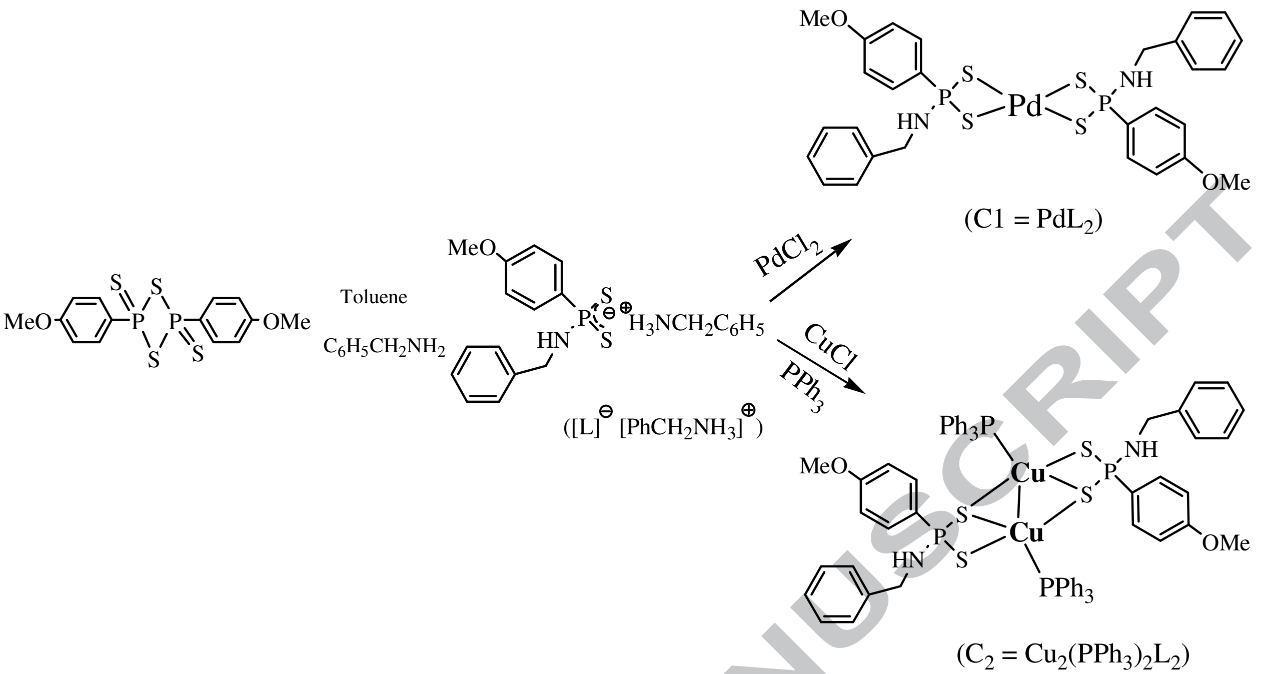


Fig. 6

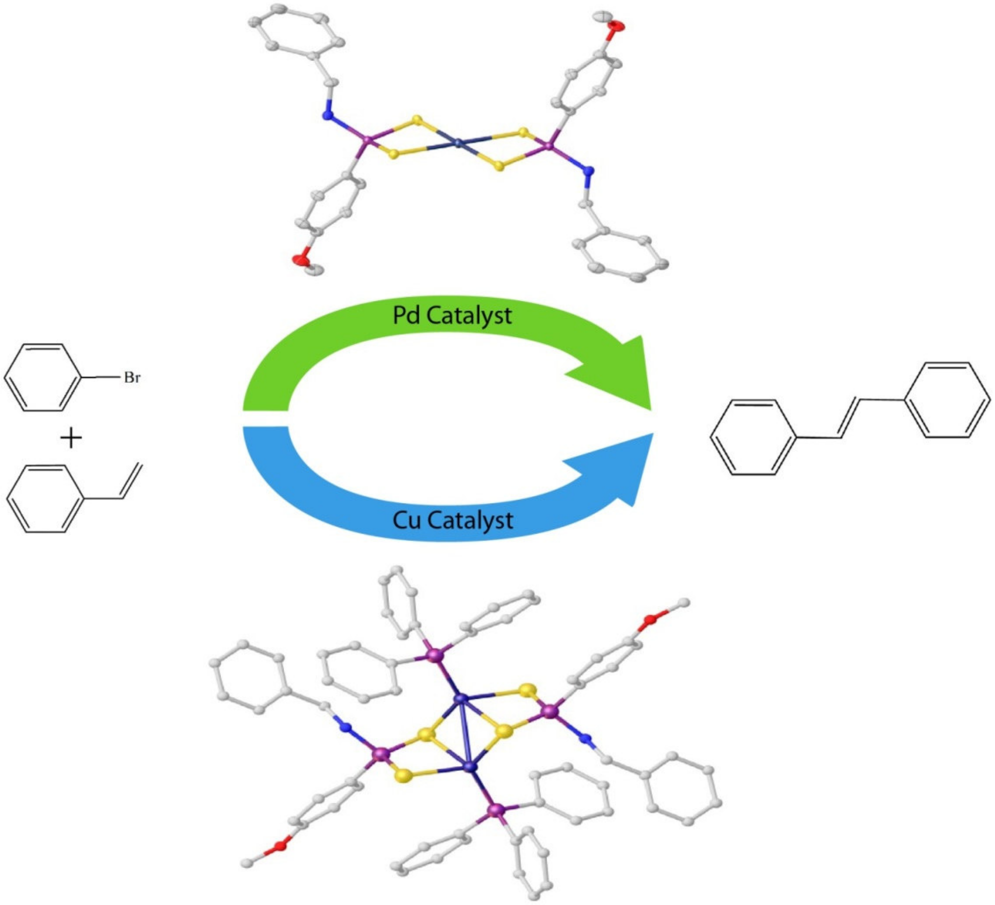

MeO
OMe
S
P
Toluene
C6H5CH2NH2
H3NCH2C6H5
HN
([L]⊖ [PhCH2NH3]⊕)
PdCl2
CuCl
PPh3
Pd
NH
(C1 = PdL2)
Ph3P
Cu
PPh3
(C2 = Cu2(PPh3)2L2)

Scheme 1

Graphical abstract

Synthesis and structural characterization of Pd(II) and Cu(I) complexes containing dithiophosphorus ligand and their catalytic activities for Heck reaction

Khodayar Gholivand[a*], Rasoul Salami[a], Kaveh Farshadfar[a], Raymond J. Butcher[b]



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Air- and thermal-stable palladium(II) complex, and dicopper(I) complex were synthesized using dithiophosphorus ligand. The Pd(II) and Cu(I) complexes were introduced as efficient catalyst for the Heck reaction.