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Synthesis, characterization, structure and catalytic activity of (NNN) tridentate azo-imine nickel(II), palladium(II) and platinum(II) complexes

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#### Abstract

The newly designed tridentate ligand, 2,2'-(bisdiamino)azobenzene, H<sub>2</sub>L,1 derived from the oxidative coupling of *o*-phenylenediamine in presence of NaOH base, upon reaction with Ni(II), Pd(II) and Pt(II) separately in methanol yielded [(HL)Ni(PPh<sub>3</sub>)]ClO<sub>4</sub>,**2**, [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>, **3** and [(L)Pt(PPh<sub>3</sub>)], **4** which were characterized by spectral data and authenticated by single crystal x-ray diffraction of **1-4**. The diffraction analysis revealed that the ligand binds the metals (Ni(II), Pd(II))in monoanionic and Pt(II) in dianionic tridentate (N,N,N) fashion offering distorted square planar geometry where fourth position is occupied by one PPh<sub>3</sub> group. One ClO<sub>4</sub><sup>-</sup> ion satisfies the charge of the former aggregate [(HL)Ni(PPh<sub>3</sub>)]<sup>+</sup> and [(HL)Pd(PPh<sub>3</sub>)]<sup>+</sup>. Suzuki and Heck coupling reactions were carried out, in presence of air and moisture, using [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>, **3**as catalysts for a variety of substrates.

Keywords: Crystal structure, Ni(II), Pd(II) and Pt(II), Suzuki and Heck Reaction

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#### 1. Introduction

Transition metal complexes with azo chromophore have received much attention in research areas both fundamental and a variety of applications such as colouring agent [1-4]. The strong electronic absorption can be changed by ring substitution which controls the chemical fine-tuning of color [4]. Moreover the coordination chemistry incorporating ortho substituted azo benzene ligands have versatile properties such as C-H activation [5-11], C-C activation [12-16], C-C coupling [17], -N=N- bond cleavage [18-21], electron transfer reaction [13-16, 22-25], hydroxylation [26-29], isomerization [30], photoisomerization [31-35], cytotoxicity toward cancer cells and application in catalytic transformations [36-40]. Metal complexes of chelating ligands with azo-imine function have significant properties i.e. isomerization, metal assisted transformation, catalytic and biological activity [30,38,39, 41-44]. Among them, azo-imine complexes of (C,N,N) and (N,N,N) donor have specific properties for example oxidative addition, structural isomerization, metal assisted transformation and catalytic activity [30,38,39,45]. The N,N,N donors, where one "N" is pyridyl nitrogen, between another two "N" one is azo nitrogen and other is secondary amino nitrogen or one "N" is azo nitrogen another two "N" are secondary amino nitrogen is known [22-25,30,38,45,46]but2,2'-(bisdiamino)azobenzene ligand where one "N" is azo nitrogen and other two "N" are primary amino nitrogen have not been utilized to explore the chemistry of transition metal ions.

Herein we report the reactions of tridentate 2,2'-(bisdiamino)azobenzene, H<sub>2</sub>L, **1** ligand with Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O, Na<sub>2</sub>PdCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>4</sub> separately to form complexes of composition [(HL)Ni(PPh<sub>3</sub>)]ClO<sub>4</sub>, **2**, [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>, **3** and [(L)Pt(PPh<sub>3</sub>)], **4** respectively where the ligand offers (N,N,N) binding mode to the metal. The ligand and complex have been characterized by the spectroscopic data. The x-ray structure of the ligand H<sub>2</sub>L, **1** and complexes **2-4** have

beendetermined to confirm the molecular structure. The complex [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>, **3** acts as potential catalyst towards C-C bond formation for a variety of substrate.

#### 2. Experimental

#### 2.1. Materials

The solvents used in the reactions were of reagent grade (E. Marck, Kolkata, India) and were purified and dried by general procedure [47]. Orthophenylenediamine was purchased from Loba, India. Palladium chloride, sodium hydroxide, triphenyl phosphine and sodium chloride were purchased from E. mark, India. Sodium perchlorate, Potassium tetrachloroplatinate, Iodo benzene, Bromo benzene, 1-Iodo-2-nitrobenzene, 1-Iodo-3-nitrobenzene, 1-Bromo-2-nitrobenzene, Phenyl boronic acid, Nickel(II) perchlorate hexahydrate and Styrene were purchased from Aldrich. Sodium tetrachloropalladate was prepared following reported procedure [48].

#### 2.2. Physical measurements

Microanalysis (C, H, N) was performed using a Perkin-Elmer 2400 C, H, N, S / O series II elemental analyzer. Infrared spectra were recorded on a Parkin-Elmer L120-00A FT-IR spectrometer with the samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV- 1800 PC spectrophotometer. <sup>1</sup>H NMR spectra were obtained on Brucker 400 NMR spectrometers in CDCl<sub>3</sub> using TMS as the internal standard.

#### 2.3. Syntheses

#### 2.3.1. Synthesis of ligand 1

*o*-Phenylenediamine (10 g) and sodium hydroxide (5.2 g) were mixed and triturated followed by heating at  $70^{\circ}$ C with constant scratching for 2h. The dark pasty mass thus obtained was cooled to room temperature and extracted with benzene. The benzene soluble part was

subjected to column chromatography on a silica gel (60-120 mesh) column. The orange band that eluted by benzene-petroleum ether mixture (1/1; V/V) were collected and upon evaporation of solvents, the pure H<sub>2</sub>Lwas obtained. Yield:10%. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>4</sub>: C, 67.90; H, 5.70; N, 26.40%. Found: C, 67.72; H, 5.39; N, 26.85%. UV/VIS ( $\lambda_{max}/nm$  ( $\epsilon/dm^2 mol^{-1}$ ), dichloromethane): 450 (11280); 315 (11035); 260(13328). IR (KBr, cm<sup>-1</sup>): 3462, 3363 v(NH<sub>2</sub>), 1457 v(N=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 5.48 (NH<sub>2</sub>, s, 4H), 6.75-6.80 (ArH, m, 4H), 7.15-7.19 (ArH, m, 2H), 7.67 (ArH, d, 2H).

#### 2.3.2. Synthesis of complex 2

A solution of Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (205 mg, 0.62 mmol) in methanol (15 mL) a solution of ligand H<sub>2</sub>L(130 mg, 0.62mmol) in methanol (10 mL) was added under stirring. The solution immediately changed to pink-violet and the stirring was continued for 1h at room temperatureand then added PPh<sub>3</sub> (185 mg, 0.7 mmol). The resulting pink-violet solution was then filtered and allowed to stand. After slow evaporation of the solvent at room temperature, dark coloured x-ray quality crystals were obtained. Yield: 80%. Anal. Calcd. For C<sub>30</sub>H<sub>26</sub>ClN<sub>4</sub>NiO<sub>4</sub>P: C, 57.04; H, 4.15; N, 8.87%. Found: C, 57.35; H, 4.26; N, 8.65%. UV/VIS ( $\lambda_{max}/nm$  ( $\varepsilon/$  dm<sup>2</sup> mol<sup>-1</sup>), dichloromethane): 580 (10530); 540 (11030); 365 (18490); 270(44900). IR (KBr, cm<sup>-1</sup>): 3480, 3343 v(NH<sub>2</sub>, NH), 1346 v(N=N), 1100 v(Cl-O), 1434 and 697 v(PPh<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 4.64 (NH<sub>2</sub>, s, 2H), 6.32 (ArH, d, 1H), 6.84 (ArH, t, 1H), 7.14 (ArH, t, 1H), 7.27 (ArH, t, 1H), 7.38 (ArH, t, 1H), 7.48 (ArH, d, 1H), 7.65-7.77 (PPh<sub>3</sub>, m, 9H), 7.83 (ArH, d, 1H), 7.95-8.0 (PPh<sub>3</sub>, t, 6H), 8.32 (ArH, d, 1H).

#### 2.3.3. Synthesis of complex 3

A solution of  $H_2L$  (85 mg, 0.4 mmol) in 10 cm<sup>3</sup> methanol was added to a solution of Na<sub>2</sub>PdCl<sub>4</sub> (120 mg, 0.4 mmol) in 5 cm<sup>3</sup> methanol. The mixture was stirred for 1 h and then added PPh<sub>3</sub> (130 mg, 0.52mmol). The dark solid precipitate was separated by filtration and purified by column chromatography using silica gel (60-120 mesh). The eluent was toluene-acetonitrile (95:5)

mixed solvent. The volume of the solution was reduced to ~20 ml and added NaClO<sub>4</sub> (75 mg, 0.6 mmol). Upon evaporation of solvent the pink solid of pure  $[(HL)Pd(PPh_3)]ClO_4$  was obtained. Yield: (60%). Anal. Calcd. For C<sub>30</sub>H<sub>26</sub>ClN<sub>4</sub>O<sub>4</sub>PPd: C, 53.04; H, 3.86; N, 8.25%. Found: C, 53.25; H, 4.12; N, 8.15%. UV/VIS ( $\lambda_{max}$ /nm ( $\epsilon$ / dm<sup>2</sup> mol<sup>-1</sup>), dichloromethane): 520 (13100); 270 (17200). IR (KBr, cm<sup>-1</sup>): 3401, 3336 v(NH<sub>2</sub>, NH), 1344 v(N=N), 1097 v(Cl-O), 1435 and 696 v(PPh<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 5.60 (NH<sub>2</sub>, s, 2H), 6.37 (ArH, d, 1H), 6.71 (ArH, t, 1H), 7.13-7.18 (ArH, m, 1H), 7.45-7.48 (NH and ArH, m, 3H), 7.52-7.57 (ArH, m, 1H), 7.52-7.69 (PPh<sub>3</sub>, m, 9H), 7.73-7.78 (PPh<sub>3</sub>, m, 6H), 7.85 (ArH, d, 1H), 8.30 (ArH, d, 1H).

#### 2.3.4. Synthesis of complex 4

A solution of H<sub>2</sub>L (65 mg, 0.3mmol) in 10 cm<sup>3</sup> methanol was added to a solution of K<sub>2</sub>PtCl<sub>4</sub> (125 mg, 0.3mmol) in 5 cm<sup>3</sup> methanol. The mixture was stirred for 1 h and then added PPh<sub>3</sub> (105 mg, 0.4 mmol). The dark solid precipitate was separated by filtration and purified by column chromatography using silica gel (60-120 mesh). The eluent was benzene-acetonitrile (90:10) mixed solvent. Upon evaporation of solvent the pink solid of pure [(L)Pt(PPh<sub>3</sub>)] was obtained. Isolated yield: (50%). Anal. Calcd. For C<sub>30</sub>H<sub>25</sub>N<sub>4</sub>PPt: C, 53.97; H, 3.77; N, 8.39%. Found: C, 53.75; H, 3.95; N, 8.48%. UV/VIS ( $\lambda_{max}/nm$  ( $\epsilon/dm^2 mol^{-1}$ ), dichloromethane): 525 (12300); 270 (19240). IR (KBr, cm<sup>-1</sup>): 3401, 3336 v(NH<sub>2</sub>, NH), 1345 v(N=N), 1098 v(Cl-O), 1435 and 696 v(PPh<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 5.52 (NH<sub>2</sub>, s, 2H), 6.72 (ArH, d, 1H), 6.75-6.82 (ArH, m, 2H), 6.90 (NH, s, 1H), 7.14 (ArH, t, 1H), 7.17-7.22 (ArH, m, 1H), 7.30-7.37 (ArH and NH, m, 2H), 7.47-7.60 (PPh<sub>3</sub>, m, 9H), 7.81-7.86 (PPh<sub>3</sub>, m, 6H), 8.27 (ArH, d, 1H), 8.83 (ArH, d, 1H).

#### 2.3.5. General procedures for the Suzuki reaction

To the catalyst (1.0 mol%) dissolved in 10 ml THF, aryl halide (1.0 mmol), phenyl boronic acid (1.2 mmol),  $K_2CO_3$  (2.0 mmol) were all added. The mixture was heated to reflux for 3 h. Then, the mixture was evaporated to dryness, water was added and the product was extracted with diethyl ether. The organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, passed through silica column (60-120 mesh), the complex remain trapped. Upon evaporation of the ether, solid of pure products were obtained. The yields of the products obtained from all the reactions were determined after isolation and characterized by <sup>1</sup>H NMR spectra and melting points with the literature data.

#### 2.3.6. General procedures for the Heck reaction

Aryl halide (0.5 mmol), styrene (1.0mmol) were combined with  $K_2CO_3$  (1 mmol) and catalyst (1 mol%) in THF (10 ml) in a small round-bottom flask. The mixture was heated to reflux for 4 h. Then, the mixture was evaporated to dryness, water was added and the product was extracted with diethyl ether. The organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, passed through silica column (60-120 mesh), the complex remain trapped. After extraction of desired compound complex was extracted using dichloromethane. Upon evaporation of the ether, solid of pure products were obtained. The yields of the products obtained from all the reactions were determined after isolation andidentified by <sup>1</sup>H NMR spectroscopy and melting points with the literature data.

#### 2.4. Crystallography

Single crystal of H<sub>2</sub>L, **1**, [(HL)Ni(PPh<sub>3</sub>)]ClO<sub>4</sub>, **2**, [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>, **3** and [(L)Pt(PPh<sub>3</sub>)], **4** were grown by diffusion of dichloromethane into petroleum ether at 298 K. Data were collected by  $\omega$ - scan technique on a Bruker Smart CCD diffractometer with monochromated Mo-K<sub>a</sub> radiation( $\lambda = 0.71073$  Å). Structure solution was done by direct method with SHELXS–

2013program [49,50]. Full matrix least square refinements on  $F^2$  were performed using SHELXL– 2013program [49,50]. All non-hydrogen atoms were refined anisotropically using reflections I >  $2\sigma$  (I). The C-bound hydrogen atoms were included in calculated positions and refined as riding atoms. The N-H hydrogens were obtained by difference electron density synthesis. Data collection parameters and relevant crystal data are collected in Table 1.

Please insert Table 1 here

#### 3. Results and discussion

3.1. Synthesis

The new ligand 2,2'-(bisdiamino)azobenzene, H<sub>2</sub>L,1 has been prepared by oxidative coupling of *o*-phenylenediamine in the presence of strong base sodium hydroxide (Scheme 1). The

Please insert Scheme 1 here

ligand was isolated as orange solid after column chromatographic purification. The reactions of  $H_2L$ , **1** with Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O, Na<sub>2</sub>PdCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>4</sub> separately in methanol in the presence of PPh<sub>3</sub> afforded pink-violet [(HL)Ni(PPh<sub>3</sub>)]ClO<sub>4</sub>, **2**, and pink [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>, **3** and [(L)Pt(PPh<sub>3</sub>)], **4** respectively (Scheme 1). In complexes [(HL)Ni(PPh<sub>3</sub>)]ClO<sub>4</sub> and [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub> the ligand binds in tridentate (N, N, N) fashion through one deprotonated imino N, azo N and amino N whereas in the case of [(L)Pt(PPh<sub>3</sub>)] the ligand bind the metal in similar fashion through both deprotonated imino N and azo N atom forming two fused rings- one six membered and other five membered.

#### 3.2. Characterization

Ligand  $H_2L$ , 1 and complexes 2-4 are soluble in common organic solvents furnished orange and pink-violet and pink colours respectively. UV-vis spectra of the ligand and complex were

recorded in dichloromethane solutions (Fig. 1). Ligand shows three absorption bands at 450 nm, 315 nm and 260 nm attributed to the intraligand  $\pi - \pi^*$  and  $n - \pi^*$  transitions [51,52].

Please insert Fig. 1 here

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A Characteristic low energy absorption band for all the complexes in the range 520-580 nm is assigned to the MLCT transition [51,52].

The IR spectrum of the ligand in solid KBr support  $v_{NH2}$  appeared as twin band in 3462 and 3363 cm<sup>-1</sup>, whereas for the complexes **2-4**, the  $v_{NH2}$  and  $v_{NH}$  (dissociation of the amino proton on complexation) appeared as multiple bands in the range 3481-3332cm<sup>-1</sup> [21,53]. The  $v_{N=N}$  of the ligand (1457 cm<sup>-1</sup>) shifted to lower frequency upon complexation (1344-1346), consistent with coordination of the azo nitrogen [21,38-44]. A very strong broad band in the range 1097-1100 cm<sup>-1</sup> and strong band near 622 cm<sup>-1</sup> are observed in the IR spectra of the Ni(II) and Pd(II) complexes, which could be due to the antisymmetric stretching and bending of uncoordinated perchlorate ions, respectively [54]. Two new bands near 1435 cm<sup>-1</sup> and 696 cm<sup>-1</sup> assigned for the coordinated triphenylphosphine ligand for the all complexes [55].

The ligand  $H_2L$ , 1 and complexes 2-4 shows highly resolved <sup>1</sup>H-NMR spectra in CDCl<sub>3</sub>, which are in complete agreement with the X-ray structures of the ligand and complexes. A sharp singlet at 5.48 ppm is assigned for an NH<sub>2</sub> proton of the ligand which is shifted to 4.64-5.60 in the complexes. All the aromatic protons appeared in the range of 6.75-7.75 ppm, appeared as one doublet, and two set of multiplet which are matched well with the composition of the ligand in solution. In all the complexes 2-4 the aromatic protons (except PPh<sub>3</sub>) appeared in the range 6.22-8.83 ppm for different eight protons as separate doublets, triplets and multiplets. Fifteen PPh<sub>3</sub>

protons appeared as two set of multiplets in the range 7.47-7.60 ppm and 7.73-7.80 ppm for nine and six protons respectively.

#### 3.3. X-ray crystallography

The structures of **1-4** were determined by single crystal X-ray diffraction method. Thermal ellipsoid plots of ligand **1** and complexes **2-4** are shown in Figs. 2–5 respectively. The

Please insert Fig.2-5& Table 2-5 here

crystallographic and measurement data are shown in Table 1. Selected bond lengths and bond angles are listed in Tables 2-5.Ligand 1and complexes 2-3 are monoclinic, complex 4 is orthorhombic and crystallize in the space group C2/c, P2<sub>1/n</sub>, P2<sub>1/c</sub> and P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with Z = 4 respectively.

The centrosymmetric structure of  $H_2L$  reveals the planar geometry of the ligand. All the non hydrogen atoms of  $H_2L$  make a good plane (mean deviation 0.017 Å). The N(1)-C(1) 1.418(2) Å and N(2)-C(2) 1.376(2) Å lengths of free ligand are closed to C-N single bond length. The N1-N1# length (1.261(3) Å) is very similar to azo (-N=N-) length [46].

The nickel and palladium ion in each complexes are coordinated by one anionic ligand via the N, N, N atoms, producing a six membered chelate ring with the imino N and azo N atom and a five membered ring with amino N and azo N atoms. The fourth coordination site of both the complexes is occupied by the P atom of the triphenylphosphine ligand and  $[(HL)M(PPh_3)]^+$ (M=Ni, Pd) is satisfied by one perchlorate ion. The asymmetric unit of  $[(HL)Ni(PPh_3)]^+$  contains one methanol solvent. The tridentate monoanionic (HL)<sup>-</sup> ligand binds the metal (M=Ni and Pd) in N,N,N fashion. The structures of **2** and **3** adopt a near square planar geometry with N(1)–Ni–N(2), N(3)–Ni–P and N(1)–Pd1(1)–N(2), N(3)–Pd(1)–P(1) bond angles 170.72(15), 168.03(10) and 171.91(11), 174.31(7), respectively. The Ni–N(1), Ni–N(2), Ni–N(3) and Ni–P and Pd(1)–N(1),

Pd(1)–N(2),Pd(1)–N(3) and Pd(1)–P(1) bond lengths in **2** and **3** are 1.801(3), 1.945(3), 1.868(3), 2.2070(11) and 1.956(3), 2.057(3) and 2.007(2), 2.2952(7) Å, respectively, which are in agreement with the reported values for such distances [7,25,28,38,40,46,51,53,56-59]. The bond lengths within the ligand backbone (six membered rings) are suitably altered due to delocalization of the negative charge. The C(1)-N(1) length (~1.33Å) is shorter than the C-N single bond C(7)-N(3), (~1.42Å) in the same molecule (Ni(II) & Pd(II)) and is close to the imine distance. Due to delocalization the effect of imine formation is reflected in the adjacent phenyl ring. The quinonoid distortion in the phenyl ring (C1, C2, C3, C4, C5 and C6) adjacent to the chelate ring (six membered) with four longer (~1.42 Å) and two shorter bonds (~1.35Å) is consistent with the delocalization.

The geometry about Pt(II) is distorted square planar with N(1)–Pt(1)–N(2) and N(3)–Pt(1)– P(1) bond angles 170.6(3) and 177.19(19)Å where dinegative  $L^{2^{-}}$  binds tridentate (N,N,N) fashion, producing a six membered chelatering with the imino N and azo N atom and a five membered ring with another imino N and azo N atoms. The fourth coordination site of the complex is occupied by a P atom of the triphenylphosphine ligand. The Pt(1)-N(1), Pt(1)-N(2), Pt(1)-N(3) and Pt(1)-P(1) lengths 1.983(6), 1.963(6), 2.025(5) and 2.2549(14)Å are within the normal range [56, 58-62]. The bond lengths within the ligand backbone (six membered ring) are suitably altered due to delocalization of the negative charge. The C(12)-N(2) length (1.327(9) Å) is shorter than the C-N single bond C(6)-N(3), 1.431(9) Å in the same molecule and is close to the imine distance. The quinonoid distortion similar to Ni(II) and Pd(II) in the phenyl ring (C7, C8, C9, C10, C11 and C12) adjacent to the chelate ring (six membered) with four longer (~1.41 Å) and two shorter bonds (~1.34 Å) is also in accordance with the delocalization and imine formation.

#### 3.4. The Suzuki and Heck coupling reactions

The Suzuki cross-coupling is a widely used method for the production of biaryls, which is important in organic synthesis and a recurring functional group in several natural products [63-68]. Subsequently, many catalytic systems have been developed for the synthesis of biaryls derivatives. Therefore, the catalytic activity of the new palladium complex, [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>, in the Suzuki cross-coupling reaction (Eq 1) of a variety of aryl halides with phenyl boronic acid was investigated in refluxing THF solvent and K<sub>2</sub>CO<sub>3</sub> as base keeping reaction time constant (3h) and results were summarized in Table 6. All reactions were performed in presence of air and moisture. Isolated yields of the products varied from 82% to 96% depending upon variation of aryl halide substrate. After completion of the reaction the palladium catalyst was intact and isolated from the reaction mixture easily by column chromatography and the catalyst [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>, was reused for further reaction. This reusability of the catalyst was checked up to four times for a reaction, where the other condition intact.

#### Please insert Table 6 here

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The Heck cross-coupling reaction is an important method for carbon-carbon bond formation in synthetic organic chemistry where the palladium-catalyzed coupling of aryl halides with olefins [63-68]. In this case we perform the reactions using styrene and four aryl halides (bromide and iodide) in refluxing methanol (4h) and in presence of  $K_2CO_3$  as base in presence of air and moisture and results of conversions are given in Table 7. Isolated yields of the products varied from 75% to 94% depending upon variation of aryl halide. Similarly as mentioned in Suzuki coupling reactions, at the completion of the reaction the colour of the solution changed from pink-violet to light pink so the catalyst was not isolated indicating the fact that the catalyst may be a precatalyst in these reactions.

#### Please insert Table 7 here

#### 4. Conclusion

In conclusion, we have reported convenient syntheses and comprehensive characterization of nickel(II), palladium(II) and platinum(II) complexes (2-4) containing newly synthesized azoimine based tridentate ligand  $H_2L$  and triphenylphosphine. The solid state structures of complexes 2-4 were determined by X-ray crystallography. The complexes showed the expected square planar geometry about the metal center. The new  $[(HL)Pd(PPh_3)]ClO_4$  complex has been used as catalyst for Suzuki and Heck coupling reactions in ambient condition. The [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub> complex is stable under the condition of Suzuki coupling, indicating the catalytic activity of the molecular nA complex itself.

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#### Appendix A. Supplementary data

Figures S1–S4 shows the IR spectra and Figs. S5-S8 <sup>1</sup>H NMR spectra of the ligand HL, 1 and complexes 2-4. CCDC 1418054, 1418055, 1418056 and 1418057 contains the supplementary crystallographic data for compounds H<sub>2</sub>L, 1, [(HL)Ni(PPh<sub>3</sub>)]ClO<sub>4</sub>, 2, [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>, 3 and [(L)Pt(PPh<sub>3</sub>)], 4. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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### Synthesis of 2,2'-diaminoazobenzene



Scheme 1.Synthesis of 2,2'-diaminoazobenzene and metal complexes.

Equation 1



### Table 1

Chemical formula	$C_{12}H_{12}N_4$	C <sub>30</sub> H <sub>26</sub> N <sub>4</sub> PNi,ClO <sub>4</sub> , CH <sub>3</sub> OH	$C_{30}H_{26}N_4PPd$ , ClO <sub>4</sub>	C <sub>30</sub> H <sub>25</sub> N <sub>4</sub> PPt
Formula weight	212.26	663.72	679.37	667.60
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
space group	C2/c	$P2_1/n$	$P2_{I}/c$	$P2_{1}2_{1}2_{1}$
a/Å	22.285(2)	8.9005(4)	11.8856(5)	10.4172(1)
b/Å	5.8593(6)	16.2489(7)	14.2644(6)	13.2278(1)
c/Å	8.2532(7)	20.4720(9)	16.7476(6)	18.2993(2)
α/deg	90	90	90	90
β/deg	106.404(4)	94.926(3)	97.405(2)	90
⁄/deg	90	90	90	90
λ/Å	0.71073	0.71073	0.71073	0.71073
$V/\text{\AA}^3$	1033.80(17)	2949.8(2)	2815.7(2)	2521.58(4)
F(000)	448	1376	1376	1310
Crystal Size [mm]	0.02x0.02x0.20	0.2x0.10x0.02	0.20x0.20x0.20	0.08x0.18x0.20
Ζ	4	4	4	4
T/K	120(2)	150(2)	295(2)	100(2)
$D/mg/m^{-3}$	1.364	1.495	1.603	1.759
$\mu$ /mm <sup>-1</sup>	0.087	0.851	0.855	5.655
Theta Min-Max [deg]	3.606 -27.115	1.602, 29.253	1.728, 28.328	1.900, 28.295
reflections measured	3276	31419	27192	25517
unique reflections (Rint)	1137, 0.0315	7993, 0.0769	6986, 0.0384	6200, 0.0606
No. of reflections used $[I > 2\sigma(I)]$	826	4875	5046	5038
R1,wR2(all data)	0.0691, 0.1207	0.1267, 0.1678	0.0653, 0.0892	0.0526, 0.0536
R1, wR2[ <i>I</i> > 2σ( <i>I</i> )]	0.0464, 0.1097	0.0664, 0.1437	0.0389, 0.0792	0.0342, 0.0487
GOF	1.062	1.023	1.023	0.972

### Table 2

Selected Bond Distances (Å) and Angles (deg) for Compound H<sub>2</sub>L.

1.397(2)
1.378(2)
1.395(2)
1.379(2)
6
5
2 114.81(14)

### Table 3

Selected Bond Distances (Å) and Angles (deg) for Compound [(HL)Ni(PPh<sub>3</sub>)]ClO<sub>4</sub>.

111-1	2.2070(11)	C2-C3	1.346(7)		
Ni-N1	1.801(3)	C3-C4	1.411(7)		
Ni-N3	1.868(3)	C4-C5	1.368(7)		
Ni-N2	1.945(3)	945(3) C5-C6			
N1-C1	1.346(5)	C1-C6	1.418(6)		
N2-C12	1.463(5)	P-C19	1.813(4)		
N3-N4	1.287(4)	Cl1-O1	1.372(4)		
N3-C7	1.433(5)	Cl1-O2	1.370(4)		
N4-C6	1.355(5)	Cl1-O3	1.383(5)		
C1-C2	1.426(6)	Cl1-O4	1.447(6)		
	A	Angles			
N2-Ni-P	91.64(10)	N1-Ni-N3	91.47(15)		
N3-Ni-P	168.03(10)	C12-C7-N3	114.1(3)		
N3-Ni-N2	85.78(14)	C7-C12-N2	115.3(3)		
C12-N2-Ni	109.1(2)	02-Cl1-O1	113.9(3)		
N4-N3-Ni	132.4(3)	O2-Cl1-O3	110.1(3)		
N4-N3-C7	113.6(3)	O1-Cl1-O3	114.3(3)		
C7-N3-Ni	113.9(3)	O2-Cl1-O4	110.9(5)		
N3-N4-C6	120.0(3)	01-Cl1-O4	109.1(4)		
N1-C1-C6	121.8(4)	O3-Cl1-O4	97.3(5)		

### Table 4

Selected Bond Distances (Å) and Angles (deg) for Compound [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>.

Distances							
Pd1-P1	2.2952(7)		C4-C5	1.349	(5)		
Pd1-N1	1.956(3)		C5-C6	1.427	(4)		
Pd1-N2	2.057(3)		C7-C8	1.395	1.395(4)		
Pd1-N3	2.007(2)		C7-C12	1.376(4)			
N3-N4	1.274(3)		P1-C13	1.817	1.817(3)		
C1-C6	1.435(4)		N1-C1	1.329	1.329(4)		
C1-C2	1.424(4)		N2-C12	1.458	1.458(4)		
C2-C3	1.352(4)		Cl1-O1	1.408	1.408(3)		
N3-C7	1.421(4)		Cl1-O3	1.375	(3)		
N4-C6	1.351(4)		Cl1-O2	1.392	(3)		
C3-C4	1.402(5)		Cl1-O4	1.402	(4)		
Angles							
N1-Pd1-P1		94.51(8)	N1-C1-C6		123.4(3)		
N2-Pd1-P1		93.54(8)	N1-Pd1-N3		89.86(10)		
N3-Pd1-P1		174.31(7)	N3-Pd1-N2		82.15(10)		
N1-Pd1-N2		171.91(11)	O3-Cl1-O2		113.5(2)		
N4-N3-C7		115.3(2)	O3-Cl1-O4		108.5(3)		
N4-C6-C1		128.1(3)	O2-Cl1-O4		106.6(2)		
C12-C7-N3		116.2(2)	O3-Cl1-O1		107.7(2)		
N4-N3-Pd1		130.69(19)	O2-Cl1-O1		112.7(2)		
C1-N1-Pd1		126.6(2)	04-Cl1-O1		107.7(3)		
C12-N2-Pd1		110.4(2)	C7-N3-Pd1		113.93(18)		
C7-C12-N2		117.2(3)	N3-N4-C6		121.3(2)		
PC	,		1		1		

### Table 5

Selected Bond Distances (Å) and Angles (deg) for Compound [(L)Pt(PPh<sub>3</sub>)].

### Table 6

Suzuki cross coupling reaction with the catalyst [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>.



### Table 7

Heck reaction with the catalyst [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub>.





**Fig. 1** UV-Vis spectra of  $H_2L$  (—), [(HL)Ni(PPh<sub>3</sub>)]ClO<sub>4</sub> (—), [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub> (—) & [(L)Pt(PPh<sub>3</sub>)] (—) in dichloromethane



Fig. 2 Molecular structure of  $H_2L$  (40% probability ellipsoids) with atom numbering scheme

R



Fig. 3 Molecular structure of  $[(HL)Ni(PPh_3)]ClO_4$  (40% probability ellipsoids) with atom numbering scheme. The hydrogen atoms, except those of the amino groups, have been omitted for clarity.

6



Fig. 4 Molecular structure of  $[(HL)Pd(PPh_3)]ClO_4$  (40% probability ellipsoids) with atom numbering scheme. The hydrogen atoms, except those of the amino groups, have been omitted for clarity.

6



Fig. 5 Molecular structure of  $[(L)Pt(PPh_3)]$  (40% probability ellipsoids) with atom numbering scheme. The hydrogen atoms, except those of the amino groups, have been omitted for clarity.

### **Graphical Synopsis**

Synthesis, characterization, structure and catalytic activity of (NNN) tridentate azo-imine nickel(II), palladium(II) and platinum(II) complexes

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Synthesis of newly designed tridentate ligand, 2,2'-(bisdiamino)azobenzene, and Ni(II), Pd(II) and Pt(II) complexes. Complex [(HL)Pd(PPh<sub>3</sub>)]ClO<sub>4</sub> acts as potential catalyst towards C-C bond formation.