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Water-soluble complexes MX_2L_2 (M = Pd, Pt; L = $PPh_2(C_6H_4$-*p*-$SO_3K)$): Synthesis, stereoisomerism, and catalytic activities for aromatic cyanation in *n*-heptane/water biphasic solution

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ABSTRACT

Reaction of (COD)MX_2 (M = Pd, Pt; X = Cl, I; COD = 1,5-cyclooctadiene) and $P(C_6H_5)_2(C_6H_4$-*p*-$SO_3K)$ afforded water-soluble complexes $MX_2\{P(C_6H_5)_2(C_6H_4$-*p*-$SO_3K)\}_2$ (M = Pd; X = Cl (**1**), M = Pt; X = Cl (**2**), I (**3**)) in high yields. Complexes **1**–**3** were fully characterized by various spectroscopic methods (IR, ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy) and elemental analyses. For **1** and **3**, a mixture of the *cis*- and *trans*-isomer was produced from the reaction. For **2**, however, only the *cis*-isomer was obtained. The stereochemistry of **1**–**3** can be assigned by the chemical shifts and the ^1J(Pt–P) values in ^{31}P{^{1}H}-NMR spectral data. The ratios of the *cis*/*trans* isomers of **1** and **3** obtained from reactions in a range of solvents with various dielectric constants resulted in a little variation. However, addition of aqueous potassium halide solution to a DMSO-d_6 solution of **1** and **3** considerably increased the ratio of the *cis*/*trans*, respectively, indicating a strong intramolecular interligand Coulombic repulsion between the ionic phosphine ligands is present. Catalytic cyanation of aromatic iodide with KCN/$ZnCl_2$ in *n*-heptane/water biphasic system has been tested in the presence of **1**–**3** with base.

1. Introduction

There has been a surge of interests in aqueous organometallic chemistry and catalysis due to the principal advantages of eco-friendly syntheses of fine chemicals along with relatively uncomplicated separation and regeneration of precious catalysts from reaction mixtures [1,2]. The extensively explored water-soluble complexes are those of tertiary phosphine derivatives of hydrophilic ion-pair substituents on the phenyl ring, such as sulfonate [3–6], carboxylate [7–9], phosphonate [10–12], or ammonium functionalities [13–15]. The best known precedents of water-soluble ligands are triphenylphosphine derivatives of sulfonate (SO_3^-) group at the *meta*-position on the phenyl ring: tris(*meta*-sulfonatophenyl) phosphine ($P(C_6H_4$-*m*-$SO_3M)_3$ (Na^+ or K^+ salt), mTPPTS) and diphenyl(*meta*-sulfonatophenyl)phosphine ($PPh_2(C_6H_4$-*m*-$SO_3M)$, mTPPMS) (Fig. 1) [3–6,16]. The monosulfonated phosphine ligand (mTPPMS) may offer a couple of merits over the trisubstituted one (mTPPTS) in relatively less demanding synthetic manipulation, and solubility toward reaction medium: phase-transfer property (ambiphilicity) in a water–organic biphasic system. For references, solubilities of mTPPMS and mTPPTS with sodium salt in water are 80 g dm^{-3} and 1100 g dm^{-3}, respectively [1,17]. Thus, the *meta*-substituted monosulfonated triphenylphosphine (mTPPMS) has been extensively utilized as a supporting ligand for the synthesis of water-soluble transition metal complexes [18–20]. In contrast, the *para*-substituted monosulfonated triphenylphosphine (pTPPMS) has attracted little attention as a supporting ligand in transition metal complexes. The *para*-isomer (pTPPMS), however, provides several advantages over the *meta*-isomer (mTPPMS), involving enhanced crystallinity of the ligand and its metal complexes, uncomplicated spectroscopic characteristics, and ease of preparation along with purification [21,22].

Reported in this paper are water-soluble palladium(II) and platinum(II) complexes of the *para*-substituted monosulfonated triphenylphosphine, $MX_2(PPh_2(C_6H_4$-*p*-$SO_3K))_2$ (M = Pd; X = Cl (**1**), M = Pt; X = Cl (**2**), I (**3**)). Catalytic cyanation of aromatic iodide in *n*-heptane/water biphasic system in the presence of the title complexes has been investigated. Catalytic yields and selectivity of aromatic cyanation largely varied depending not only on the employed substrates of aromatic iodide and a cyanide source but also on the applied base such as Zn-powder, $NaBH_4$, NaOAc or Na_2CO_3. The feasibility for catalytic cyanation of sterically demanding 1,3-dichloro-2-iodobenzene in a biphasic system is also described.

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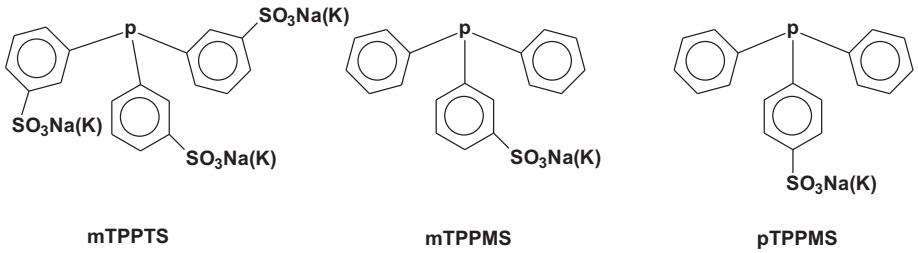


Fig. 1. Tri- and mono-sulfonated triphenylphosphines.

2. Experimental

2.1. General methods and materials

All preparations of air sensitive compounds were performed on a standard Schlenk line under nitrogen or argon atmosphere. THF and diethyl ether were distilled from sodium/benzophenone ketyl. *n*-Heptane was distilled from sodium/benzophenone ketyl in the presence of tetraglyme (tetraethylene glycol dimethyl ether) and stored on 4 Å molecular sieves under N_2. DMF and MeOH were distilled from $MgSO_4$, for DMF at reduced pressure of *ca.* 20 mmHg, and stored on 4 Å molecular sieves under N_2. The used water was doubly distilled under N_2, and had been adequately purged with N_2 prior to use. DMSO-d_6 was purchased from Aldrich Chemical Company, and used as supplied. $ZnCl_2$ was recrystallized from 1,4-dioxane [23]. $PdCl_2$ and K_2PtCl_4 were supplied by Kojima Chemicals Co., Ltd., and used without purification. PPh_2Cl, 4-fluorobenzenesulfonyl chloride, $KHCO_3$ and $NaBH_4$ were purchased from Aldrich Chemical Company or Strem Chemicals. All other chemicals were from various commercial companies. $PPh_2(C_6H_4$-*p*-$SO_3K)$ [22], $(COD)PdCl_2$ [24] and $(COD)PtCl_2$ [25] were synthesized according to the literature methods.

2.2. Physical measurements

IR spectra were recorded on a Bomem (Michelson 100) or a Bruker (Tensor 37) FT-IR spectrometer, as pressed KBr pellets. ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra were measured on a Varian Gemini-2000 spectrometer (^{1}H (199.975 MHz), ^{13}C{^{1}H} (50.288 MHz), ^{31}P{^{1}H} (80.950 MHz)), using the deuterium signal of the solvent as an internal lock frequency. Chemical shifts for ^{1}H- and ^{13}C{^{1}H}-NMR are reported in ppm (δ) relative to TMS. For ^{31}P{^{1}H}-NMR, chemical shifts were measured in ppm relative to external 85% H_3PO_4 (in a sealed capillary). GC/MS analyses were performed using an HP 6890 gas chromatograph equipped with an HP 5973 MSD and an HP-Ultra 1 column (Crosslinked Methyl Silicone Gum, 50 m × 0.2 mm, 0.33 μm film thickness). The injection temperature was 250 °C, and the column temperature ramped 10°/min from 40 °C to 250 °C. Elemental analyses were performed at Korea Basic Science Institute in Seoul, Korea.

2.3. Synthesis

2.3.1. $Pd(PPh_2(C_6H_4$-*p*-$SO_3K))_2Cl_2$ (**1**)

A mixture of $Pd(COD)Cl_2$ (50 mg, 0.175 mmol) and $PPh_2(C_6H_4$-*p*-$SO_3K)$ (166.5 mg, 0.438 mmol) in DMF (30 mL) was stirred for 4 h at ambient temperature. The volume of the solution was reduced to *ca.* 10 mL. Addition of diethyl ether (30 mL) on the concentrated solution gave deep yellow precipitates, which were isolated, washed with diethyl ether (3 × 10 mL), and then dried *in vacuo*. Yield 151 mg (92%). IR (KBr): $\nu(SO_3)$ = 1656, 1206, 1038 cm^{-1} (vs, br). ^{1}H NMR (DMSO-d_6): δ 7.42–7.97 *m* (Ph). ^{31}P{^{1}H}-NMR (DMSO-d_6): δ 33.0 s (*cis*-isomer, 22%), δ 24.2 s (*trans*-isomer, 78%). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ 126.1, 126.6, 129.2, 129.7, 131.7, 132.1, 134.8, 135.3. Anal. Calcd for $C_{36}H_{28}Cl_2K_2O_6P_2S_2Pd$: C, 46.1; H, 3.01; S, 6.84. Calcd for the monohydrate: C, 45.2; H, 3.16; S, 6.71. Found: C, 44.9; H, 3.45; S, 6.50.

2.3.2. *cis*-$Pt(PPh_2(C_6H_4$-*p*-$SO_3K))_2Cl_2$ (**2**)

A mixture of $Pt(COD)Cl_2$ (200 mg, 0.534 mmol) and $PPh_2(C_6H_4$-*p*-$SO_3K)$ (447.2 mg, 1.18 mmol) in DMF (30 mL) was refluxed in DMF at 60 °C for 4 h. After cooling the reaction mixture to ambient temperature, the solution volume was reduced to *ca.* 10 mL under high vacuum. Addition of diethyl ether (30 mL) on the concentrated solution gave off-white precipitates, which were isolated, washed with diethyl ether (3 × 10 mL), and then dried *in vacuo*. Recrystallization from MeOH/Et_2O gave satisfactory microanalytical data. Yield 521 mg (95%). IR (KBr): $\nu(SO_3)$ = 1656, 1206, 1037 cm^{-1} (vs, br). ^{1}H NMR (DMSO-d_6): δ 7.43–7.97 *m* (Ph). ^{31}P{^{1}H}-NMR (DMSO-d_6): δ 14.6 s (^1J(Pt–P) = 3688 Hz). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ 125.8, 128.7, 128.8, 129.0, 131.9, 134.5, 135.1, 135.2, 150.4. Anal. Calcd for $C_{36}H_{28}Cl_2K_2O_6P_2S_2Pt$: C, 42.1; H, 2.75; S, 6.25. Calcd for the monohydrate: C, 41.4; H, 2.89; S, 6.14. Found: C, 42.0; H, 3.21; S, 6.19.

2.3.3. $Pt(PPh_2(C_6H_4$-*p*-$SO_3K))_2I_2$ (**3**)

A similar procedure as for complex **2** using $Pt(COD)I_2$ (50 mg, 0.0896 mmol) and $PPh_2(C_6H_4$-*p*-$SO_3K)$ (75 mg, 0.1975 mmol) gave an orange complex **3** as an isomeric mixture (*trans*/*cis* = 1.3). Yield 98 mg (90%). IR (KBr): $\nu(SO_3)$ = 1656, 1206, 1038 cm^{-1} (vs, br). ^{1}H NMR (DMSO-d_6): δ 7.43–7.97 *m* (Ph). ^{31}P{^{1}H}-NMR (DMSO-d_6): δ 12.0 *s* (^1J(Pt–P) = 3494 Hz, *cis*-isomer (43%)), δ 12.6 s (^1J(Pt–P) = 2477 Hz, *trans*-isomer (57%)). ^{13}C{^{1}H}-NMR (DMSO-d_6): δ 125.7, 128.5, 128.6, 128.7, 129.0, 131.3, 131.6, 134.6, 135.0, 135.2, 135.6. Anal. Calcd for $C_{36}H_{28}I_2K_2O_6P_2S_2Pt$: C, 35.7; H, 2.33; S, 5.30. Calcd for the monohydrate: C, 35.2; H, 2.46; S, 5.22. Found: C, 35.3; H, 2.85; S, 4.96.

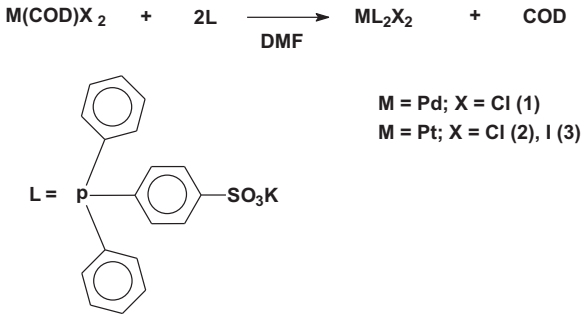
2.4. A typical procedure for catalytic cyanation of aromatic iodide in a biphasic system (*n*-heptane/H_2O)

To a stirred solution of complex **1** (10 mg, 0.0125 mmol) in a mixed solvent of *n*-heptane (1.5 mL) and water (1.5 mL) were added KCN (10.6 mg, 0.1625 mmol), $ZnCl_2$ (11.1 mg, 0.0825 mmol), $NaBH_4$ (0.5 mg, 0.0125 mmol), and iodobenzene (26 mg, 0.125 mmol). The reaction mixture was stirred at 100 °C for 1 h under nitrogen atmosphere. After cooling the reaction mixture in an ice-bath, aliquots of the organic layer were transferred to a vial with a Pasteur pipette. Eluting the aliquots with diethyl ether on a short glass-column (0.7 × 15 cm) packed with alumina (*ca.* 1 cm) resulted in a clear yellowish solution which was analyzed with GC/MS.

3. Results and discussion

3.1. Synthesis of water-soluble complexes MX_2L_2

The ligand $PPh_2(C_6H_4$-*p*-$SO_3K)$ was synthesized by the reaction of potassium 4-fluorobenzenesulfonate with $KPPh_2$ in THF



Scheme 1.

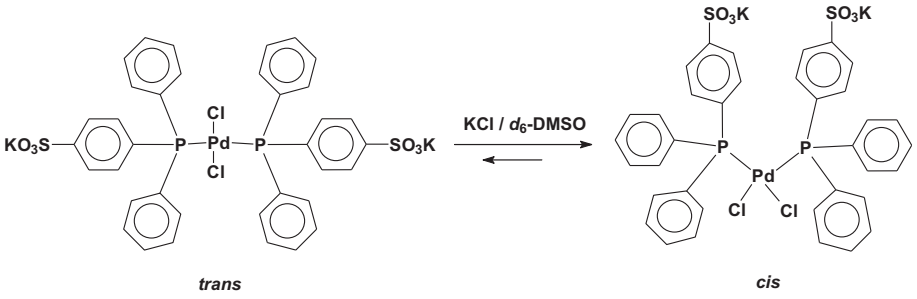
according to the reported method [22]. The purity of the ligand was confirmed by $^{31}P\{^{1}H\}$-NMR (δ −6.52 s, DMSO-d_6), revealing no phosphine oxide present [26]. Water-soluble complexes of Pd(II) and Pt(II), ML_2X_2 (L = $PPh_2(C_6H_4$-*p*-$SO_3K)$, M = Pd; X = Cl (**1**), M = Pt; X = Cl (**2**), I (**3**)) were prepared by the reaction of $M(COD)X_2$ with 2 equivalents of $PPh_2(C_6H_4$-*p*-$SO_3K)$ in DMF (Scheme 1). Complexes **1**–**3** were isolated as yellow crystalline solids in high yields (90–95%), and fully characterized by IR and NMR(^{1}H, $^{31}P\{^{1}H\}$, $^{13}C\{^{1}H\}$) spectroscopy, and microanalyses. The complexes are fairly soluble in DMF, DMSO and H_2O but sparingly soluble in benzene, acetone, THF, and chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. All complexes **1**–**3** gave satisfactory microanalytical data for C, H, and N (see Experimental). In the IR spectra of **1**–**3**, the characteristic symmetric and *anti*-symmetric $\nu(SO_3)$ bands of the sulfonate group on *para*-position of the phenyl substituent were observed at 1656, 1206, 1038 cm^{-1} [27,28]. In the ^{1}H NMR spectra of **1**–**3** in DMSO-d_6, phenyl protons resonate at δ 7.43–7.97 as multiplets, respectively. The $^{13}C\{^{1}H\}$-NMR spectral data for **1**–**3** were obtained, though the fine structure patterns of ^{13}C resonances (J(C–P)) for assignments of stereoisomers were not well resolved due to a low signal/noise ratio [29]. For complexes **1** and **3**, a mixture of the *cis*- and *trans*-isomers was obtained, while for complex **2**, the *cis*-isomer was exclusively formed. The stereochemistry of **1**–**3** can be assigned from the respective $^{31}P\{^{1}H\}$-NMR chemical shift value for the palladium complex, and the spin–spin coupling constants (^{1}J(Pt–P)) for the platinum complexes.

3.2. Stereoisomerism of MX_2L_2

It is well documented that in square planar d^8-Pd(II) complexes, a type of PdL_2X_2, the ^{31}P chemical shift (δ) of the *trans*-isomer generally appears upfield from that of the *cis*-isomer [30,31]. In the $^{31}P\{^{1}H\}$-NMR spectrum of **1** in DMSO-d_6, two resonances display at δ 24.2 and 33.0 as a single peak, assignable to *trans*- and *cis*-$PdCl_2\{PPh_2(C_6H_4$-*p*-$SO_3K)\}_2$, respectively. In DMF solution the *trans*-isomer was predominantly formed from the reaction (the *trans*:*cis* ratio being about 78:22). The respective ^{31}P NMR chemical shift values observed for complex **1** are in good comparison with the reported values of Pd(II) complexes with the ion-paired phosphine ligands, for $PdCl_2(mTPPTS)_2$ [32] at δ 25.3 (*trans*) and δ 34.3 (*cis*), and for $PdCl_2\{PPh(C_6H_4$-*m*-$NHCNH_2NMe_2Cl)_2\}_2$ [33] at δ 28.8 (*trans*) and δ 35.9 (*cis*). For platinum complexes of the type PtL_2X_2, the *cis*- and *trans*-isomers can be unambiguously assigned from the respective ^{1}J(Pt–P) value due to considerable variation of the *trans*-influence of the ligands, halide and phosphine [34]. The observed $^{1}J(Pt-P_{cis})$ value is significantly larger than that of the $^{1}J(Pt-P_{trans})$. For the chloro complex **2**, the reaction yields exclusively the *cis*-isomer judged from the $^{31}P\{^{1}H\}$ NMR resonance at δ 14.6 flanked with the ^{195}Pt satellites (^{1}J(Pt–P) = 3688 Hz). However, for the iodo complex **3**, a mixture of the *cis*- and *trans*-isomers was formed from the reaction (*cis* (43%): δ 12.0 *s*, ^{1}J(Pt–P) = 3494 Hz, *trans* (57%): δ 12.6 s, ^{1}J(Pt–P) = 2477 Hz). The observed ^{1}J(Pt–P) values for **2** and **3** compare well with those of PtX_2L_2 having neutral or ion-paired phosphine ligands [35].

Stereoisomerism in bisphosphine complexes of the type of ML_2X_2 comprises a complicated combination of factors [36–40]. The *trans*/*cis* ratio varies depending not only on electronic and steric features of constituents of metal complexes including phosphine and halide ligands, and metal but also on reaction mediums. For complexes with ion-paired phosphine ligands, contributions arising from either attractive or repulsive interactions between the ionic functionalities have to be incorporated with the factors [41]. The ratio of the *cis*/*trans* isomers of MX_2L_2 complexes generally increases as the dielectric constant or the dipole moment of the solvent increases [42,43]. Thus, on reactions for $PdCl_2\{PPh_2(C_6H_4$-*p*-$SO_3K)\}_2$, various solvents such as CH_3CN, MeOH, DMF, DMSO and H_2O were employed, resulting in a little variation of the *cis*/*trans* ratio. The formation of the *cis*-isomer barely increased from 19% (in CH_3CN) to 28% (in H_2O) but was not predominant. For the Pt(II) iodide **3**, the *cis*/*trans* ratios are practically not much different from the employed solvent, DMF to MeOH. These results are incompatible with the previous studies for the type of $PdCl_2L_2$, on which the *cis*/*trans* ratio considerably increases with the dielectric constant of the employed solvent increases [33,41–43]. For sterical parameters effecting the *cis*/*trans* ratio, the cone angle of the ligand $PPh_2(C_6H_4$-*p*-$SO_3K)$ (θ = 137.7°) [28], comparing with those of other tertiary arylphosphines (PPh_3 (141.5°) [44], mTPPMS (177.6°) [45], mTPPTS (170.0°)) [46,47] seems to be not responsible for the observed results.

For complexes of ion-paired phosphines, intramolecular interligand Coulombic interaction or repulsion has strong effect on the thermodynamic stability of the respective isomers [36–39,48]. Since intramolecular interligand Coulombic repulsion is diminished at higher ionic strengths due to shielding of the charges [41,49], further experiments on the stereoisomers were performed in potassium halide solution of DMSO. Treatment of DMSO-d_6 solution of $PdCl_2\{PPh_2(C_6H_4$-*p*-$SO_3K)\}_2$ (the *trans*/*cis* = *ca.* 8/2) with



Scheme 2.

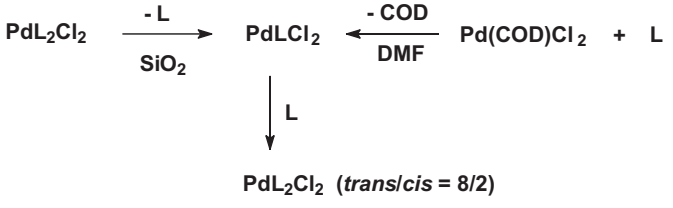
a saturated aqueous KCl solution gave the *trans*/*cis* ratio of *ca.* 2/8 in a short period of time (30 min) (Scheme 2). For $PtI_2\{PPh_2(C_6H_4$-*p*-$SO_3K)\}_2$ with KI, the *trans*/*cis* ratio considerably changed from 6/5 to 3/7. These results are consistent with the recent report that the *trans*/*cis* ratio decreases with increasing the ionic strength of solution [49]. Thus the observed results for the stereoisomeric ratio may be attributed to a strong intramolecular interligand Coulombic repulsion between the ionic phosphine ligands, which disfavors the *cis*-isomer. In the title complexes, intramolecular interligand interaction and repulsion are likely to be finely balanced, except for the Pt(II) chloride in which the two ionic phosphine ligands occupy a *cis* configuration with respect to each other.

3.3. Three-coordinated palladium(II) species $PdCl_2L$

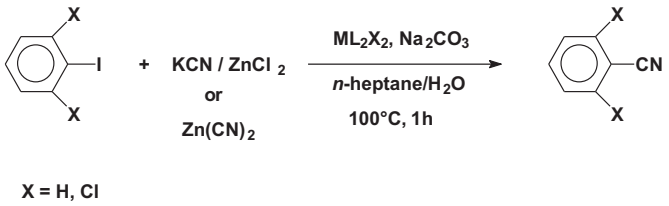
Separation of the *trans*- and *cis*-isomers from an isomeric mixture of $PdCl_2\{PPh_2(C_6H_4$-*p*-$SO_3K)\}_2$ from column chromatography on silica gel with various eluents was attempted without success, resulting in the practically same ratio (*trans*/*cis* = *ca.* 7/3) of the *trans*- and *cis*-isomers along with an additional complex which shows a broad signal at δ 31.2 in the $^{31}P\{^1H\}$-NMR spectrum. Since the amount of the complex resulted from column chromatography was significant (43%), we conducted further investigation on the complex. This complex is verified as a three-coordinated Pd(II) species $PdCl_2\{PPh_2(C_6H_4$-*p*-$SO_3K)\}$ by its independent synthesis from the reaction of $Pd(COD)Cl_2$ with one equivalent of $PPh_2(C_6H_4$-*p*-$SO_3K)$ (Scheme 3). Thus the formation of $PdCl_2\{PPh_2(C_6H_4$-*p*-$SO_3K)\}$ resulted from column chromatography can be apparently explained by a strong intermolecular dissociative interaction between the ion-paired phosphine ligand and silica, liberating one of the coordinated phosphine ligands from the palladium center. When an excess amount of $PPh_2(C_6H_4$-*p*-$SO_3K)$ was added into a DMSO-d_6 solution of $PdCl_2\{PPh_2(C_6H_4$-*p*-$SO_3K)\}$, the monophosphine complex converts into the bisphosphine complex **1**, being supported by observation of disappearing the broad peak at δ 31.2 and appearing two sharp peaks at δ 24.2 and 33.0 in the $^{31}P\{^1H\}$-NMR spectrum, corresponding to *trans*- and *cis*-$PdCl_2\{PPh_2(C_6H_4$-*p*-$SO_3K)\}_2$ (*trans*/*cis* = 83/17), respectively. It is noteworthy that in the reaction, no significant variation of the isomeric ratio (*trans*/*cis* = *ca.* 8/2) was observed in the presence of excess $PPh_2(C_6H_4$-*p*-$SO_3K)$, even for a prolong period of time (48 h).

3.4. Aromatic cyanation in n-heptane/water biphasic system

The title complexes **1**–**3** have been tested for catalytic cyanation of aromatic iodide with a number of cyanide source (KCN, KCN/$ZnCl_2$ or $Zn(CN)_2$) in *n*-heptane/water biphasic system (Scheme 4). An additive base such as Zn-powder, $NaBH_4$, Na_2CO_3 or NaOAc has been varied for the best results. In Table 1, the obtained results for catalytic cyanation of iodobenzene to produce benzonitrile are summarized. The palladium complex **1** shows higher catalytic activity than the analogous platinum complexes **2** and **3**. When $ZnCl_2$ was employed as a supporting agent along with KCN, the catalytic activity was considerably enhanced [50]. $Zn(CN)_2$ displays



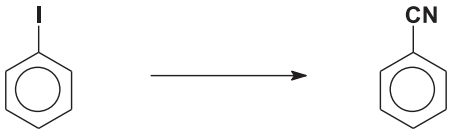
Scheme 3.



Scheme 4.

an alternative cyanide source comparable with $KCN/ZnCl_2$ [51–54]. Our results are consistent with earlier studies that excess cyanide anions released from KCN deactivate the palladium catalyst, forming inactive palladium species of cyanide [55,56]. As the applied base, $NaBH_4$ or Na_2CO_3 was found to be more effective than Zn-powder. In the absence of base, no conversion of iodobenzene to benzonitrile was observed. The base apparently involves in the formation of reactive Pd(0) species. However, high concentration of $NaBH_4$ (40 mol %) diminished the catalytic activity, generating hydrodehalogenation product. In an immiscible biphasic solvent, complete conversion of iodobenzene to benzonitrile by utilizing $KCN/ZnCl_2$ or $Zn(CN)_2$ as a cyanide source was observed in the presence of catalytic amount of **1** along with base such as Na_2CO_3 or $NaBH_4$. Although catalytic efficiency with the title complex is comparable with precedents of lipophilic catalysis [56], the present protocol has an advantage of uncomplicated separation of organic product from catalyst and reactants soluble in water-phase. Our results compare well with earlier investigation on catalytic cyanation of aromatic iodide in a biphasic system with water-soluble catalysts [50]. The complexes with the monosulfonated ligands pTPPMS and mTPPMS revealed higher catalytic activity than those with the carboxylate and ammonium derivatives $PPh_2(C_6H_4$-*m*-$CO_2Na)$ and $PPh_2(C_6H_4$-*m*-$CH_2NMe_3Cl)$, respectively. The higher catalytic efficiency with the complexes of the monosulfonated ligands is likely attributed to advantageous counter phase-transfer property in a biphasic system.

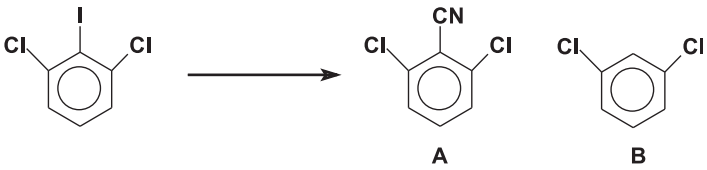
Table 1
Catalytic cyanation of iodobenzene with MX_2L_2.[a]



Comp.	CN Source	$ZnCl_2$ (equiv)[b]	Base (equiv)[c]	Conversion (%)[d]
1	KCN	–	Zn (1)	<4
1	KCN	0.5	Zn (1)	14
1	KCN	0.5	$NaBH_4$ (1)	32
1	KCN	0.5	$NaBH_4$ (4)	16
1	KCN	0.6	Na_2CO_3 (4)	35
1	KCN[e]	0.6	Na_2CO_3 (4)	100[f]
1	$Zn(CN)_2$	–	$NaBH_4$ (1)	100[f]
2	$Zn(CN)_2$	–	$NaBH_4$ (1)	3
2	KCN	0.5	Na_2CO_3 (4)	4
2	KCN	0.5	$NaBH_4$ (1)	3
3	KCN	0.5	$NaBH_4$ (1)	5
3	$Zn(CN)_2$	–	$NaBH_4$ (1)	4

[a] Reaction conditions: iodobenzene (0.125 mmol), KCN (0.163 mmol), $Zn(CN)_2$ (0.0815 mmol), MX_2L_2 (0.0125 mmol).
[b] Molar equivalent to KCN.
[c] Molar equivalent to MX_2L_2.
[d] GC-based yield for 1 h at 100 °C.
[e] 0.250 mmol of KCN was employed.
[f] Conversion obtained after 24 h.

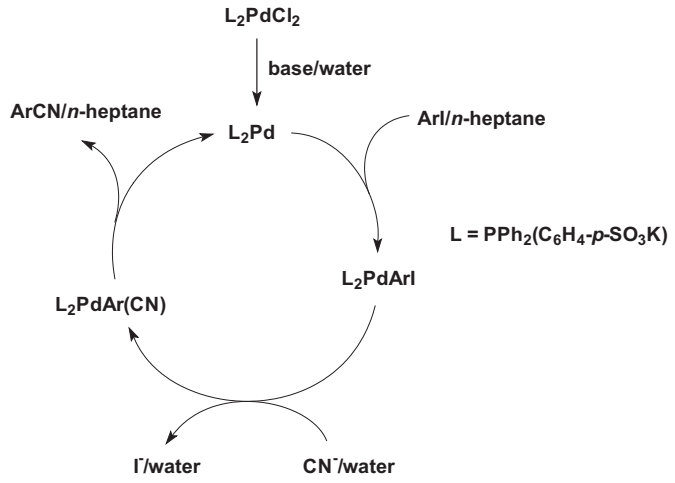
Table 2
Catalytic cyanation of 1,3-dichloro-2-iodobenzene in the presence of **1**.[a]



CN Source	$ZnCl_2$ (equiv)[b]	Base (equiv)[c]	A (%)[d]	B (%)[d]
KCN	–	Zn (1)	–	38
KCN	–	Na_2CO_3 (1)	–	–
KCN	–	NaOAc (1)	–	–
KCN	0.5	$NaBH_4$ (1)	<1.4	16
KCN	0.5	Na_2CO_3 (1)	9	<0.1
KCN	0.5	NaOAc (1)	7	<0.1
KCN[e]	0.5	Na_2CO_3 (4)	8[f]	–
$Zn(CN)_2$	–	Na_2CO_3 (1)	11[f]	<0.1

[a] Reaction conditions: $PdCl_2L_2$ (0.0125 mmol), 1,3-dichloro-2-iodobenzene (0.125 mmol), KCN (0.163 mmol), $Zn(CN)_2$ (0.0815 mmol).
[b] Molar equivalent to KCN.
[c] Molar equivalent to $PdCl_2L_2$.
[d] GC-based yield for 1 h at 100 °C.
[e] 0.250 mmol of KCN was employed.
[f] Conversion obtained after 24 h.

Selective cyanation of 1,3-dichloro-2-iodobenzene was also investigated in the presence of complex **1**. As shown in Table 2, no cyanation reaction proceeded in the absence of the additive $ZnCl_2$. When Zn-powder was applied as a reducing agent, a considerable amount of hydrodeiodination derivative 1,3-dichlorobenzene was exclusively produced. The hydride source may be attributed to H_2O generating molecular hydrogen by the reaction with Zn catalyzed by Pd species [57,58]. For sterically hindered 1,3-dichloro-2-iodobenzene, catalytic cyanation remarkably retarded at the same reaction condition, comparing with that of iodobenzene. No significant increase of the cyanation product was observed with increasing amount of KCN or $Zn(CN)_2$ even for a prolonged reaction time (>48 h). An excess amount of cyanide source or base rather decreases the reactivity. The restricted catalytic activity of complex **1** for aromatic cyanation of 1,3-dichloro-2-iodobenzene could be ascribed to a limited thermal barrier in an aqueous biphasic system and decomposition of palladium species, generating metal particles which could be inactive for catalysis. The observation of black particles formed from the reaction mixture after 48 h reaction time could be conspicuous for decomposed catalysts.



Scheme 5. A plausible reaction pathway for catalytic cyanation of aromatic iodide in *n*-heptane/water biphasic system.

In the present catalytic reaction, the mechanism may follow the typical cycle for a palladium-catalyzed cross-coupling reaction with oxidative addition and reductive elimination [56]. Reactive Pd(0) species $Pd\{PPh_2(C_6H_4\text{-}p\text{-}SO_3K)\}_2$ presumably generated from reduction of $PdCl_2\{PPh_2(C_6H_4\text{-}p\text{-}SO_3K)\}_2$ in the presence of base would drive the catalytic reaction *via* facile oxidative addition of aryl iodide and followed by ligand substitution with cyanide to lead $PdAr(CN)\{PPh_2(C_6H_4\text{-}p\text{-}SO_3K)\}_2$, finally undergoing reductive elimination to produce aromatic nitrile along with regeneration of active palladium(0) species. A plausible reaction pathway is depicted in Scheme 5.

4. Conclusion

We have prepared water-soluble complexes of Pd(II) and Pt(II), MX_2L_2 (L = $PPh_2(C_6H_4\text{-}p\text{-}SO_3K$), X = Cl, I). For $PdCl_2L_2$ and PtI_2L_2, a mixture of the *cis*- and *trans*-isomer was obtained while for $PtCl_2L_2$, the *cis*-isomer was produced, exclusively. The ratios of the *cis*/*trans* isomers of **1** and **3** obtained from reactions in a range of solvents with various dielectric constants resulted in a little variation. However, addition of aqueous potassium halide solution to a DMSO-d_6 solution of **1** and **3**, respectively, resulted in a significant increase of the ratio of the *cis*/*trans*, indicating a strong intramolecular interligand Coulombic repulsion between the ionic phosphine ligands is present. The title complexes were tested for catalytic cyanation of aromatic iodide in *n*-heptane/water biphasic system. The palladium complex revealed better catalytic activity than the platinum complexes for aromatic cyanation of iodobenzene to benzonitrile. However, catalytic cyanation of sterically restrained 1,3-dichloro-2-iodobenzene was found to be considerably retarded, leading to motif for alteration of the ligand-framework of catalysts to overcome the limited catalytic activity for steric tolerance of substrates.

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