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Palladium(II) Aryloxides of Pd(2,6-$(CH_2NMe_2)_2C_6H_3$)(OC_6H_4-X-*p*) (X = Me, NO_2): Synthesis, Property and Reactivity towards Diphenyliodium Chloride

Hyun Sang Jung, Yun Sik Park, Jung Min Seul, Jong Sook Kim, Ho Jin Lee, and Soonheum Park*

*Department of Chemistry, Dongguk University, Gyeongju 780-714, Korea. *E-mail: shpark@dongguk.ac.kr*
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para-Substituted phenoxide derivatives of Pd(II) having an NCN pincer, Pd(NCN)(OC_6H_4-*p*-X) (NCN = 2,6-$(CH_2NMe_2)_2C_6H_3$; X = NO_2 (**1**), Me (**2**)) were prepared by the reaction of Pd(NCN)(OSO_2CF_3) with equi-molar amount of $NaOC_6H_4$-*p*-X. Treatment of Pd(NCN)(OSO_2CF_3) with an excess amount of $NaOC_6H_4$-*p*-Me affords the hydrogen-bonding adduct complex **3** (**2**·HOC_6H_4-*p*-Me). Complex **3** can also be obtained from benzene solution of **2** in the presence of free HOC_6H_4-*p*-Me. Complex **1** does not undergo adduct formation with HOC_6H_4-*p*-NO_2 neither from metathesis reaction of Pd(NCN)(OSO_2CF_3) with an excess amount of $NaOC_6H_4$-*p*-NO_2 nor from treatment of **1** with free HOC_6H_4-*p*-NO_2. Complex **3** undergoes fast exchange of the coordinated *p*-cresolate with the hydrogen-bonding *p*-cresol. Complex **2** undergoes σ-ligand exchange reaction with HOC_6H_4-*p*-NO_2 to give **1**. The exchange reaction, however, is irreversible as readily anticipated from their respective pK_a values of the phenol derivatives. Reaction of **2** with diphenyliodium chloride quantitatively produced Pd(NCN)Cl and PhI along with liberation of *O*-phenylated product $PhOC_6H_4$-*p*-Me which was identified by GC/MS spectroscopy.

Key Words : Pd(II) aryloxides, NCN-pincer complex, σ-Ligand exchange, C-O Bond formation

Introduction

Late transition metal aryloxides are of interests because of their importance as intermediate species in the C-O bond formation reactions.[1] Related catalytic reactions involving aryloxide complexes are aryloxylation of aryl halides,[1c,2] oxidative carbonylation of aryl alcohols,[3] aryloxycarbonylation of aryl halides,[4] and hydroaryloxylation of olefins.[5] Of relevance to oxidative carbonylation of phenol to produce diphenyl carbonate, Pd(II)-diaryloxides with a chelating diamine ligand Pd(TMEDA)$(OAr)_2$ react with CO to yield the aryloxycarbonyl derivatives Pd(TMEDA)(C(O)OAr)(OAr) which undergo reductive elimination to generate diaryl carbonate ArOC(O)OAr.[6] In the reaction the latter step of the diaryl carbonate formation from Pd(TMEDA)(C(O)OAr)(OAr) is slower than the former step of carbonylation of the aryloxides complexes. Dimeric complexes having bridging aryloxides, $[Rh(\mu\text{-}OAr)(COD)]_2$[7] and $[NBu_4]_2[\{M(C_6F_5)_2(\mu\text{-}OAr)\}_2]$ (M = Pd, Pt),[8] readily undergo bridge cleavage reaction on the addition of tertiary phosphines such as PPh_3 to give more reactive monomeric species of aryloxides $Rh(OAr)(PPh_3)_3$ and $[NBu_4][M(C_6F_5)_2(PPh_3)(OAr)]$.[8,9] Carbonylation of electron deficient aryloxides complexes $Rh(OAr)(PPh_3)_3$ (Ar = OC_6Cl_5, OC_6F_5, OC_6H_4-*p*-NO_2) with CO gives ligand substitution products $Rh(OAr)(CO)(PPh_3)_2$ but not insertion derivatives.[9]

Aryloxo complexes have strong affinity to undergo adduct formation with aryl alcohols through hydrogen-bonding.[10] In often cases this type of hydrogen-bonding is so strong; aryloxides complexes can be stabilized by association with free alcohols, leading to isolation of adducts in the solid state. Stability of adducts associated with free alcohols through intermolecular hydrogen-bonding are largely dependent upon not only the polarity developed on the M-O (phenoxide) but also σ-donor ability of the other ligands in the complexes; increasing the σ-donor strength of the ligand *trans* to the phenoxide improving a higher negative charge on the phenoxide.[11,12] A facile σ-ligand exchange of the coordinated aryoxides with the hydrogen-bonding aryl alcohols are commonly observed for adduct complexes in which a ligand with strong *trans*-effect enables fast exchange reactions.[13,14] Fundamental studies on catalytic formation of arylethers in aryloxylation of aryl halides mediated by palladium complexes demonstrated that arylpalladium(II)-aryloxo species involves in the catalytic cycle as an intermediate, from which reductive elimination leads to formation of arylethers. In the reductive elimination of the C-O bond from the Pd(II) complexes, the electron density of the oxygen on the aryloxo ligand was found to be one of crucial factors in driving the catalytic cycle; increasing electron density in the aryloxo ligand leading to enhancing reaction rates.[15]

In this paper, we report *para*-substituted phenoxides complexes of palladium(II) having a terdentate NCN pincer, Pd(2,6-$(CH_2NMe_2)_2C_6H_3$)(OC_6H_4-*p*-X) (X = NO_2, Me), in which the electron density on the oxygen in the phenoxide ligand could be tuned by employing methyl and nitro group at the *para*-position on the phenyl ring as electron donating and withdrawing functionality, respectively. Thereby the *para*-substituted phenoxide derivatives of Pd(II) with the same ligand framework of the rigid pincer would provide fundamental information on their properties for adduct formation with free aryl alcohol through hydrogen-bonding, σ-ligand exchange reaction, and reactivity of the title complexes to be probed.

Experimental Section

All preparations of air sensitive compounds were carried out on a standard Schlenk line or in an inert atmosphere glove box under argon. Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl under nitrogen, and then stored over molecular sieve. Benzene and *n*-hexane were distilled from sodium/benzophenone ketyl with tetraglyme (tetraethylene glycol dimethyl ether). $PdCl_2$ was supplied by Kojima Chemicals Co., Ltd., and used without purification. All other reagents were from various commercial companies. $Na(OC_6H_4$-*p*-Me) and $Na(OC_6H_4$-*p*-$NO_2)$ were prepared from the reaction of Na and the respective phenol derivative (HOC_6H_4-*p*-Me and HOC_6H_4-*p*-NO_2) in THF, and isolated from diethyl ether. $Pd_2(dba)_3$,[16] Pd(2,6-$(Me_2NCH_2)_2C_6H_3$)Br,[17] and Pd(2,6-$(Me_2NCH_2)_2C_6H_3$)(OTf)[18] were prepared as described in the literatures.

IR spectra were recorded on a Bomem FT-IR spectrometer (Michelson 100), as pressed KBr pellets. ^{1}H-NMR spectra were measured on a Varian Gemini-2000 spectrometer, using the deuterium signal of the solvent as an internal lock frequency. Chemical shifts for ^{1}H-NMR are reported in ppm (δ) relative to TMS. 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.

Pd(2,6-$(CH_2NMe_2)_2C_6H_3$)(OC_6H_4-*p*-NO_2) (1). To a THF (30 mL) solution of Pd(2,6-$(CH_2NMe_2)_2C_6H_3$)(OTf) (150 mg, 0.336 mmol) was added $NaOC_6H_4$-*p*-NO_2 (70.4 mg, 0.437 mmol). The reaction mixture was stirred for 1 h at ambient temperature, resulting in an orange solution. After filtering the reaction mixture, all volatiles were removed *in vacuo* to give a deep-orange residue. The resulting residue was extracted with benzene (3 × 5 mL) and filtered to give an orange solution. The solution volume was reduced to *ca*. 4 mL. Addition of *n*-hexane (*ca*. 15 mL) to the concentrated solution gave orange precipitates, which were isolated by vacuum filteration and dried *in vacuo*. Yield 126 mg (86%). IR (KBr Pellet): ν(NO) = 1583, 1303 cm^{-1} (sh, s). ^{1}H-NMR(C_6D_6): 2.17 s (12H, N-CH_3), 3.13 s (4H, CH_2N), 6.54 d (2H, *m*-*H*, aryl, ^3J(HH) = 7.5 Hz), 6.95 t (1H, *p*-*H*, aryl), 6.98 d (2H, *o*-*H*, OC_6H_4-*p*-NO_2, ^3J(HH) = 9.2 Hz), 8.34 d (2H, *m*-*H*, OC_6H_4-*p*-NO_2).

Pd(2,6-$(CH_2NMe_2)_2C_6H_3$)(OC_6H_4-*p*-Me) (2). A similar procedure as for complex **1** using Pd(2,6-$(CH_2NMe_2)_2C_6H_3$)(OTf) (150 mg, 0.336 mmol) and $NaOC_6H_4$-*p*-Me (56.8 mg, 0.437 mmol) gave complex **2**. Yield 106 mg (78%). ^{1}H-NMR(C_6D_6): 2.40 s (12H, N-CH_3), 2.43 s (3H, OC_6H_4-*p*-CH_3), 3.23 s (4H, CH_2N), 6.58 d (2H, *m*-*H*, aryl, ^3J(HH) = 7.5 Hz), 6.97 t (1H, *p*-*H*, aryl), 7.31 d (2H, *o*-*H*, OC_6H_4-*p*-CH_3, ^3J(HH) = 8.4 Hz), 7.41 d (2H, *m*-*H*, OC_6H_4-*p*-CH_3).

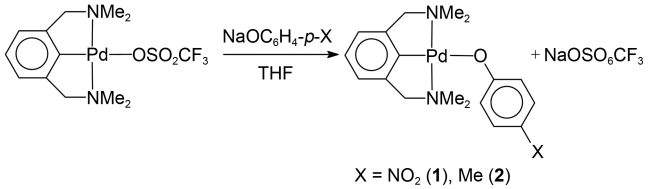
2·HOC_6H_4-*p*-Me (3). Method A: To a stirred solution of **2** (50 mg, 0.124 mmol) in benzene (10 mL) was added HOC_6H_4-*p*-Me (20 mg, 0.19 mmol). The mixture was stirred for 30 min. The solution volume was reduced to *ca*. 2 mL. Addition of *n*-hexane (*ca*. 10 mL) to the concentrated solution gave complex **3** (**2**·HOC_6H_4-*p*-Me). Method B: A similar procedure as for complex **2** using Pd(2,6-$(CH_2NMe_2)_2C_6H_3$)(OTf) (74 mg, 0.166 mmol) and an excess amount of $NaOC_6H_4$-*p*-Me (66 mg, 0.507 mmol), for 3 h reaction time, gave complex **3**. ^{1}H-NMR(C_6D_6): 2.29 s (6H, $PdOC_6H_4$-*p*-CH_3·HOC_6H_4-*p*-CH_3), 2.37 s (12H, N-CH_3), 3.16 s (4H, CH_2N), 6.52 d (2H, *m*-*H*, aryl, ^3J(HH) = 7.5 Hz), 6.94 t (1H, *p*-*H*, aryl), 7.16 d (4H, *o*-*H*, $PdOC_6H_4$-*p*-CH_3·HOC_6H_4-*p*-CH_3, ^3J(HH) = 8.1 Hz), 7.45 d (4H, *m*-*H*, $PdOC_6H_4$-*p*-CH_3·HOC_6H_4-*p*-CH_3, ^3J(HH) = 8.1 Hz), 12.8 br (1H, *H*OC_6H_4-*p*-CH_3).

Reaction of 2 and HOC_6H_4-*p*-NO_2 to Yield Complex 1 along with HOC_6H_4-*p*-Me. To a d_6-benzene solution of complex **2** (*ca*. 5 mg) in a 5-mm screw-capped NMR tube (Wilmad, 528-TR) was added an excess amount of HOC_6H_4-*p*-NO_2 (*ca*. 7 mg). The formation of **1** and HOC_6H_4-*p*-Me in solution was supported by ^{1}H-NMR spectroscopy. Complex **1** was isolated from the reaction mixture.

Reaction of 2 and $[Ph_2I]Cl$ to Yield Pd(2,6-$(CH_2NMe_2)_2C_6H_3$)Cl, PhI and $PhOC_6H_4$-*p*-Me. To a d_6-benzene solution of complex **2** (*ca*. 5 mg) in a 5-mm screw-capped NMR tube was added 3 equivalents of $[Ph_2I]Cl$ (*ca*. 12 mg). The reaction immediately proceeded to produce Pd(2,6-$(CH_2NMe_2)_2C_6H_3$)Cl, PhI, and *O*-phenylated ether derivative $PhOC_6H_4$-*p*-Me as evidenced by ^{1}H-NMR and GC/MS spectroscopy. For $PhOC_6H_4$-*p*-Me: GC/MS: *m/z* = 184, 169, 107, 91, 77.

Results and Discussion

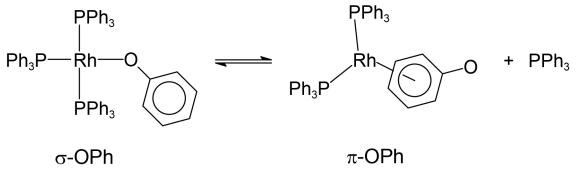
Preparation of the Palladium(II) Aryloxides. *para*-Functionalized phenoxide derivatives of palladium(II) having an NCN pincer, Pd(NCN)(OC_6H_4-*p*-X) (NCN = 2,6-$(CH_2NMe_2)_2C_6H_3$, X = NO_2 (**1**), Me (**2**)) were prepared by the reaction of Pd(NCN)(SO_3CF_3) with a slight excess molar amount of $NaOC_6H_4$-*p*-X in THF (Scheme 1). Complexes **1** and **2** were isolated as orange crystalline solids in 86% and 78% yield, respectively, after purification processes. The complexes were characterized by IR and ^{1}H-NMR spectroscopy, and microanalyses. In the ^{1}H-NMR spectrum of **1** in C_6D_6, the methyl ($N(CH_3)_2$) and methylene (CH_2N) resonances of the NCN ligand display at δ 2.17 and 3.13 as a single peak, respectively, with a peak integration ratio of 12/4. The *meta*-H and *para*-H resonances on the σ-bonding aryl moiety of the pincer ligand exhibit δ 6.54 and 6.95 as a doublet (^3J(HH) = 7.5 Hz) and a triplet, respectively. The



Scheme 1

ortho- and *meta*-protons on the *p*-nitrophenoxide ligand resonate at δ 6.98 and 8.34 as two doublets (^3J(HH) = 9.2 Hz), respectively. The respective magnetic equivalencies on the NMR time scale observed for each of the methyl ($N(CH_3)_2$) and methylene (CH_2N) in the NCN pincer, and for each of the *ortho*- and *meta*-protons on the *p*-nitrophenoxide indicate rapid rotation around the Pd-O and the O-C bond in solution, resulting from little steric hindrance around both linkages.[12,14,19] These proton-resonances on the *p*-nitrophenoxide ligand are significantly shifted to the downfield upon ligation to the palladium(II) center as compared to those of free *p*-nitrophenol (or *p*-nitrophenoxide anion): Δδ = 0.89 and 0.53 for *ortho*- and *meta*-protons, respectively. Relative large-shifts to the downfield for the phenoxide proton-resonances, especially for the *ortho*-protons, observed for square planar d^8-metal complexes are well documented.[11-14,20] The magnetic anisotropy of the metal center in a square planar geometry impinges on deshielding of protons positioned on above or below the coordination plane.[21,22] Crystal structures reported for Pd(II) and Pt(II) phenoxides reveal that the M-O-Ph units are bent to be about 120°, showing the *ortho*-protons of the phenolate are located above the coordination plane, in the proximity of the metal center.[14,23] Thus the significant downfield shifts observed for the *ortho*-protons imply that these protons stay further time on above or below the coordination plane during fast rotation around the Pd-O bond in solution.[14] In the IR spectrum of **1**, the characteristic symmetric and *anti*-symmetric ν(NO) bands of the nitro group on *para*-position of the phenoxo ligand were observed at 1583 and 1303 cm^{-1}, respectively. In the ^{1}H-NMR spectrum of complex **2**, corresponding proton-resonance signals of the ligand-moieties were observed as similar to those in **1**, along with the *para*-methyl peak in the *p*-methylphenoxide ligand exhibiting at δ 2.43 as a single peak.

Previous study demonstrated that the Wilkinson type complexes of the σ-bonding aryloxides Rh(σ-OAr)$(PPh_3)_3$ converts into the π-bonding aryloxides Rh(π-OAr)$(PPh_3)_2$ *via* the phosphine ligand dissociation (Scheme 2).[24] The dissociative conversion from the σ-OAr to the π-OAr is facilitated by either an electron-rich phenolate or a less basic tertiary phosphine such as PPh_3 in the complexes.[9,24] The phenolic proton-resonances of the π-bonding aryloxide complexes were reported to appear fairly upfield-shifted in the region of δ 4.4-5.5 in stark contrast to those of σ-bonding aryloxide complexes.[24] The observed chemical shifts, spin-spin couplings and peak-integration ratios in the ^{1}H-NMR spectra of complexes **1** and **2** are well consistent with those of corresponding σ-bonding aryloxo complexes in four-coordinated square planar geometry.[12-14] Complexes **1**, **2** and **3** (**2**·HOC_6H_4-*p*-Me, *vide infra*) gave satisfactory microanalytical data for C, H, and N. The selected ^{1}H-NMR and analytical data of **1-3** are shown in Table 1.



Scheme 2

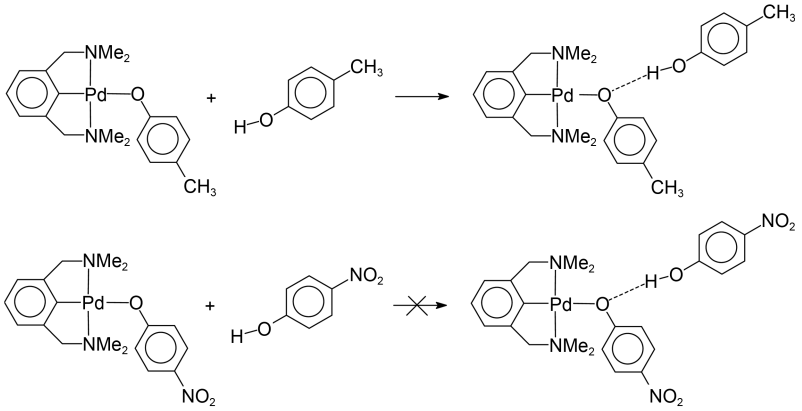
Adduct Formation, σ-ligand Exchange and Reactivity of the Palladium(II) Aryloxides. Complex **2** undergoes adduct formation with HOC_6H_4-*p*-Me through hydrogen-bonding (Scheme 3). The adduct complex **3** (**2**·HOC_6H_4-*p*-Me) can readily be prepared by treatment of a benzene solution of **2** with HOC_6H_4-*p*-Me, and has been isolated from the solution. Treatment of Pd(NCN)(OSO_2CF_3) with an excess amount of $NaOC_6H_4$-*p*-Me (> 3 equivalents) also affords the hydrogen-bonding adduct. In the reaction, HOC_6H_4-*p*-Me is likely arisen from hydrolysis of $NaOC_6H_4$-*p*-Me with an infinitesimal amount of water present in the solvent. However complex **1** with HOC_6H_4-*p*-NO_2 does not form adduct neither from treatment of **1** with free HOC_6H_4-*p*-NO_2 nor from metathesis reaction of Pd(NCN)(OSO_2CF_3) with an excess amount of $NaOC_6H_4$-*p*-NO_2.

In the ^{1}H-NMR spectrum of **3** in d_6-benzene, the hydroxy proton in the Pd-O···*H*O resonates at δ 12.8 which is shifted to far downfield in comparison with that of free HOC_6H_4-*p*-Me at δ 4.3, implying that the *p*-cresol is very strongly hydrogen-bonded. This hydroxyl proton resonance is getting shifted to upfield by elevating temperature of the d_6-benzene solution of **3** up to 70 °C, indicating weakening the hydrogen-bonding between the Pd-OC_6H_4-*p*-Me and *p*-cresol. The associated *p*-cresol in the isolated adduct can hardly be removed by washing with diethyl ether or hexane. The adduct formation of **2** with HOC_6H_4-*p*-Me through strong hydrogen-bonding is readily explained by high electron density of the *O*-atom in the phenoxide ligand developed by electron donating methyl at the *para*-position on the phenyl

Table 1. Selected ^{1}H-NMR and analytical data of **1**, **2** and **3** (**2**·HOC_6H_4-*p*-Me)

Comp.	^{1}H-NMR (δ)[a]				Analytical data (%)[b]		
	N-C*H*$_3$	-NC*H*$_2$	*o-H*,[c] *m-H*,[c] *p*-C*H*$_3$[c]	^3J(HH)[d]	C	H	N
1	2.17	3.13	6.98, 8.34	9.2	50.1 (49.6)	5.72 (5.32)	9.98 (9.64)
2	2.40	3.23	7.31, 7.41, 2.43	8.4	56.7 (56.4)	6.67 (6.47)	6.52 (6.92)
3	2.37	3.16	7.16,[e] 7.45,[e] 2.29,[e] 12.8 (br, O*H*)	8.1	61.3 (60.9)	6.93 (6.68)	5.14 (5.46)

[a]In C_6D_6. [b]Calculated values in parentheses. [c]Coordinated *p*-X-phenoxide. [d]*J* in Hz. [e]Combined with the hydrogen-bonding *p*-cresol.



Scheme 3

ring. HOC_6H_4-*p*-Me is much weaker acid than HOC_6H_4-*p*-NO_2 (pK_a = 10.3 (*p*-cresol), 7.15 (*p*-nitrophenol)).[25] The high stability of **3** caused by intermolecular strong hydrogen-bonding may be arisen from functionality of the phenoxide ligand rather than from the σ-donor ability of the aryl ligand coordinated *trans* to the phenoxide ligand in the palladium(II) complex. Previous studies for *trans*-PdMe(OPh)$(PMe_3)_2$ and *cis*-PdMe(OPh)(DMPE) suggested that increasing the σ-donor strength of the ligand *trans* to the phenoxide may effect a higher negative charge on the entire phenoxide ligand but not inevitably develop the negative charge on the oxygen atom.[13] Bergman and co-workers suggested that the Rh-O aryloxide bond in $[Rh(OC_6H_4$-*p*-Me$)L_3]\cdot(HOC_6H_4$-*p*-Me) (L = PMe_3, $PPhMe_2$) is strongly polarized with high negative charge on the *O*-atom in the phenoxide and high positive charge on the Rh atom affecting HOC_6H_4-*p*-Me to be very strongly bonded to the *O*-atom of the Rh-aryloxide bond, being supported by the very high enthalpies (ΔH = −10 ~ −14 kcal/mol) of the adduct formation.[11] For references, typical enthalpy values for intermolecular hydrogen-bonding between phenols and electron-donors are in the range of −3 ~ −6 kcal/mol.[26] It is also interesting to note that the π-bonding aryloxides Rh(π-OAr)$(PPh_3)_2$ can be stabilized through hydrogen-bonding on the addition of 2 equivalents of free phenol.[24]

The ^{1}H-NMR spectrum of **3** in d_6-benzene shows that the adduct undergoes fast exchange of the coordinated *p*-cresolate with the hydrogen-bonding *p*-cresol (Figure 1, Scheme 4). As shown in Figure 1, the phenolic proton-signals of the coordinated *p*-cresolate and the hydrogen-bonding *p*-cresol are not separated each other; the respective resonances of the *ortho*-H, the *meta*-H and the *para*-CH_3 of the phenoxide ligand OC_6H_4-*p*-CH_3 are magnetically equivalent with corresponding proton-resonances of the hydrogen-bonding HOC_6H_4-*p*-CH_3, exhibiting at δ 7.16, 7.45 and 2.29 with peak intensities of 4/4/6, respectively. The combined signals are little broad compared with other peaks of the pincer ligand, representing fast exchange of the coordinated OC_6H_4-*p*-Me with the hydrogen-bonding HOC_6H_4-*p*-Me taking place at ambient temperature on the NMR time scale. The observed line-width ($\Delta\nu_{1/2}$) of the signals is in the range of

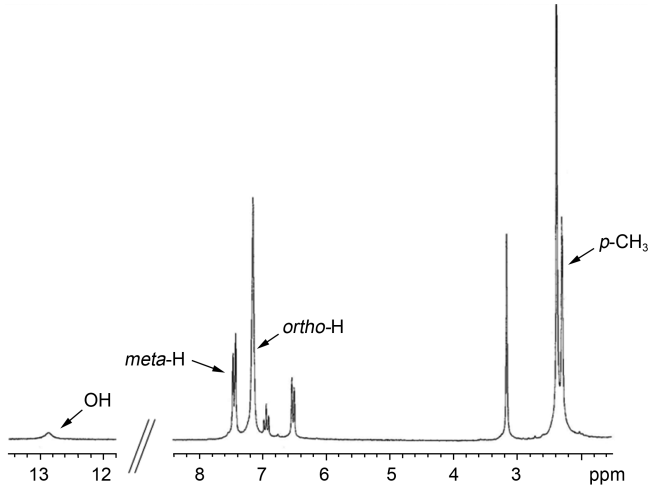
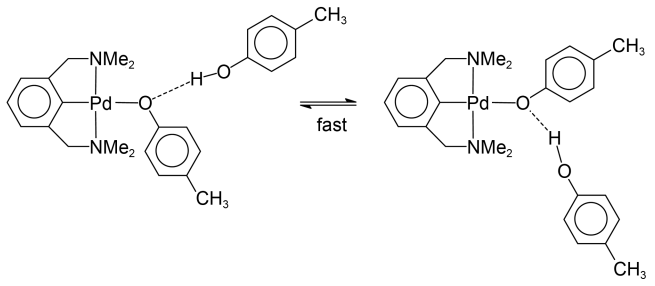
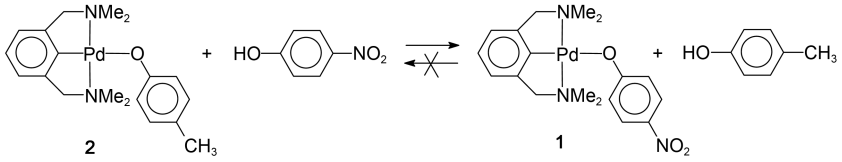


Figure 1. The ^{1}H-NMR spectrum of **3** (**2**·HOC_6H_4-*p*-Me) shows that fast exchange undergoes between the coordinated *p*-cresolate and the hydrogen-bonding *p*-cresol (marked with arrows). The resonance signal of the *ortho*-H is overlapped with that of the protio-benzene.

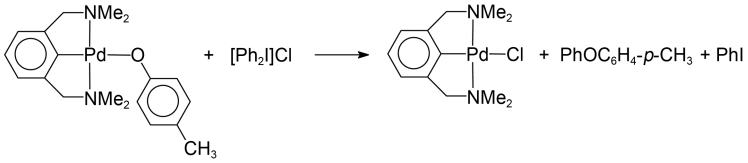


Scheme 4

3.3-4.4 Hz. Kinetic experiments demonstrated that the exchange process is intramolecular.[13] The exchange rates have been found to be largely dependent upon the *trans* ligand with respect to the phenoxide ligand in the complexes. Strong *trans*-influence ligands such as a methyl and an aryl facilitate fast exchange of the coordinated phenoxide with the hydrogen-bonding phenol.[13,14] The reported free energy of activation ($\Delta G^{\ddagger}$) for *trans*-Pd(Me)$(PMe_3)_2(OC_6H_4$-*p*-X) and Pd(NCN)



Scheme 5



Scheme 6

(OPh) is in the range of 12.7-14.8 kcal/mol. Interestingly, for the complexes of *trans*-[Pd(pyrrolidine)$_2$(OPh)$_2$]·HOPh and [Rh(NN'N)(OPh)]·HOPh (NN'N = bis(imino)pyridine ligand) in which the strong σ-donor ligands are positioned *trans* to the phenoxides, the exchange rates have been discovered to be slow.[12,14] The ^{1}H-NMR data reported for the pyrrolidine and pyridine complexes demonstrated that the proton-resonances for the coordinated phenoxides and the associated phenols were shown to be sharp and separated each other. It is also noted that the palladium phenoxides undergo the exchange reaction more facile than the platinum analogs in which the hydrogen-bonding phenol is even strongly associated.[14]

Complex **2** undergoes σ-ligand exchange reaction with free HOC_6H_4-*p*-NO_2 to give **1** (Scheme 5). However the exchange reaction is irreversible as readily anticipated from the pK_a values of the respective phenol (*vide supra*). Treatment of **2** with diphenyliodium chloride ([Ph$_2$I]Cl) quantitatively affords Pd(NCN)Cl[27] and PhI along with release of *O*-phenylated product $PhOC_6H_4$-*p*-Me which were identified by ^{1}H-NMR and GC/MS spectroscopy (Scheme 6). The fragmentation pattern of the liberated phenyl *p*-tolyl ether is in good agreement with that of an authentic sample (*m*/*z* = 184, 169, 107, 91, 77). In the reaction, *O*-phenylation to produce $PhOC_6H_4$-*p*-Me likely proceeds *via* facile oxidative addition of [Ph$_2$I]Cl to the Pd(II) phenoxide leading to a transient Pd(IV) species followed by the C-O bond reductive elimination. On the contrary, no reaction of **1** with [Ph$_2$I]Cl has been observed for 24 h. The Rh(I)-phenoxide of bis(imino)pyridine Rh(NN'N)(OPh) was reported to undergo oxidative addition of acetyl chloride to give the acetyl Rh(III)-phenoxide Rh(NN'N)(OPh)(MeCO)Cl, which thermally converts to the Rh(I) chloride Rh(NN'N)Cl by reductive elimination of phenylacetate.[12] Complexes **1** and **2** undergo no reaction with Me_3SiCF_3 for 3 days either at ambient temperature or at elevated temperature of 60 °C. The catalytic activity of the Pd(II) aryloxides on hydroaryloxylation of acrylonitrile with phenol derivatives has been tested, resulting in no expected products.

In summary, we have prepared the *para*-substituted phenoxides complexes of Pd(II) having the NCN pincer Pd(NCN)(OC_6H_4-*p*-X) (X = NO_2 (**1**), Me (**2**)). Our studies on the phenoxides complexes demonstrated that the electron density on the oxygen in the phenoxide derivatives strongly impinges on adduct formation, σ-ligand exchange and nucleophility of the title complexes. Complex **1** in which the strong *trans*-influence aryl is nonetheless positioned to the electron deficient *p*-nitrophenoxide ligand undergoes no facile σ-ligand exchange reaction. Further studies on new derivatives of palladium(II) species which would drive the catalytic hydroaryloxylation of olefins are currently under investigation.

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