

Palladium(II) Aryloxides of Pd(2,6-(CH₂NMe₂)₂C₆H₃)(OC₆H₄-X-*p*) (X = Me, NO₂): Synthesis, Property and Reactivity towards Diphenyliodine Chloride

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para-Substituted phenoxide derivatives of Pd(II) having an NCN pincer, Pd(NCN)(OC₆H₄-*p*-X) (NCN = 2,6-(CH₂NMe₂)₂C₆H₃; X = NO₂ (**1**), Me (**2**)) were prepared by the reaction of Pd(NCN)(OSO₂CF₃) with equi-molar amount of NaOC₆H₄-*p*-X. Treatment of Pd(NCN)(OSO₂CF₃) with an excess amount of NaOC₆H₄-*p*-Me affords the hydrogen-bonding adduct complex **3** (2·HOC₆H₄-*p*-Me). Complex **3** can also be obtained from benzene solution of **2** in the presence of free HOC₆H₄-*p*-Me. Complex **1** does not undergo adduct formation with HOC₆H₄-*p*-NO₂ neither from metathesis reaction of Pd(NCN)(OSO₂CF₃) with an excess amount of NaOC₆H₄-*p*-NO₂ nor from treatment of **1** with free HOC₆H₄-*p*-NO₂. Complex **3** undergoes fast exchange of the coordinated *p*-cresolate with the hydrogen-bonding *p*-cresol. Complex **2** undergoes σ -ligand exchange reaction with HOC₆H₄-*p*-NO₂ to give **1**. The exchange reaction, however, is irreversible as readily anticipated from their respective p*K*_a values of the phenol derivatives. Reaction of **2** with diphenyliodine chloride quantitatively produced Pd(NCN)Cl and PhI along with liberation of *O*-phenylated product PhOC₆H₄-*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 aryloxy complexes are aryloxylation of aryl halides,^{1c,2} oxidative carbonylation of aryl alcohols,³ aryloxy carbonylation 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 aryloxy carbonyl 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(μ -OAr)(COD)]₂⁷ and [NBu₄]₂[M(C₆F₅)₂(μ -OAr)]₂ (M = Pd, Pt),⁸ readily undergo bridge cleavage reaction on the addition of tertiary phosphines such as PPh₃ to give more reactive monomeric species of aryloxides Rh(OAr)(PPh₃)₃ and [NBu₄][M(C₆F₅)₂(PPh₃)(OAr)].^{8,9} Carbonylation of electron deficient aryloxides complexes Rh(OAr)(PPh₃)₃ (Ar = OC₆Cl₅, OC₆F₅, OC₆H₄-*p*-NO₂) with CO gives ligand substitution products Rh(OAr)(CO)(PPh₃)₂ but not insertion derivatives.⁹

Aryloxy 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 aryloxides 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 aryloxy species in aryloxylation of aryl halides mediated by palladium complexes demonstrated that arylpalladium(II)-aryloxy species involves in the catalytic cycle as an intermediate, from which reductive elimination leads to formation of aryloxyethers. In the reductive elimination of the C-O bond from the Pd(II) complexes, the electron density of the oxygen on the aryloxy ligand was found to be one of crucial factors in driving the catalytic cycle; increasing electron density in the aryloxy 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-(CH₂NMe₂)₂C₆H₃)(OC₆H₄-*p*-X) (X = NO₂, 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). PdCl₂ was supplied by Kojima Chemicals Co., Ltd., and used without purification. All other reagents were from various commercial companies. Na(OC₆H₄-*p*-Me) and Na(OC₆H₄-*p*-NO₂) were prepared from the reaction of Na and the respective phenol derivative (HOC₆H₄-*p*-Me and HOC₆H₄-*p*-NO₂) in THF, and isolated from diethyl ether. Pd₂(dba)₃,¹⁶ Pd(2,6-(Me₂NCH₂)₂C₆H₃)Br,¹⁷ and Pd(2,6-(Me₂NCH₂)₂C₆H₃)(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. ¹H-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 ¹H-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-(CH₂NMe₂)₂C₆H₃)(OC₆H₄-*p*-NO₂) (1). To a THF (30 mL) solution of Pd(2,6-(CH₂NMe₂)₂C₆H₃)(OTf) (150 mg, 0.336 mmol) was added NaOC₆H₄-*p*-NO₂ (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 filtration and dried *in vacuo*. Yield 126 mg (86%). IR (KBr Pellet): ν(NO) = 1583, 1303 cm⁻¹ (sh, s). ¹H-NMR(C₆D₆): 2.17 s (12H, N-CH₃), 3.13 s (4H, CH₂N), 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, OC₆H₄-*p*-NO₂, ³J(HH) = 9.2 Hz), 8.34 d (2H, *m*-H, OC₆H₄-*p*-NO₂).

Pd(2,6-(CH₂NMe₂)₂C₆H₃)(OC₆H₄-*p*-Me) (2). A similar procedure as for complex 1 using Pd(2,6-(CH₂NMe₂)₂C₆H₃)(OTf) (150 mg, 0.336 mmol) and NaOC₆H₄-*p*-Me (56.8 mg, 0.437 mmol) gave complex 2. Yield 106 mg (78%). ¹H-NMR(C₆D₆): 2.40 s (12H, N-CH₃), 2.43 s (3H, OC₆H₄-*p*-CH₃), 3.23 s (4H, CH₂N), 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, OC₆H₄-*p*-CH₃, ³J(HH) = 8.4 Hz), 7.41 d (2H, *m*-H, OC₆H₄-*p*-CH₃).

2·HOC₆H₄-*p*-Me (3). Method A: To a stirred solution of 2 (50 mg, 0.124 mmol) in benzene (10 mL) was added

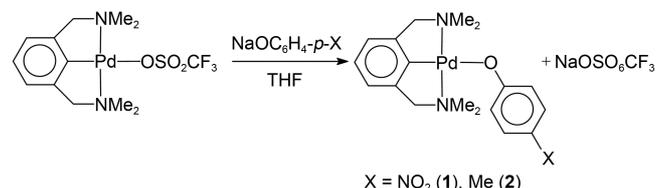
HOC₆H₄-*p*-Me (20 mg, 0.19 mmol). The mixture was stirred for 30 min. The solution volume was reduced to *ca.* 2 mL. Addition of *n*-hexane (*ca.* 10 mL) to the concentrated solution gave complex 3 (2·HOC₆H₄-*p*-Me). Method B: A similar procedure as for complex 2 using Pd(2,6-(CH₂NMe₂)₂C₆H₃)(OTf) (74 mg, 0.166 mmol) and an excess amount of NaOC₆H₄-*p*-Me (66 mg, 0.507 mmol), for 3 h reaction time, gave complex 3. ¹H-NMR(C₆D₆): 2.29 s (6H, PdOC₆H₄-*p*-CH₃·HOC₆H₄-*p*-CH₃), 2.37 s (12H, N-CH₃), 3.16 s (4H, CH₂N), 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, PdOC₆H₄-*p*-CH₃·HOC₆H₄-*p*-CH₃, ³J(HH) = 8.1 Hz), 7.45 d (4H, *m*-H, PdOC₆H₄-*p*-CH₃·HOC₆H₄-*p*-CH₃, ³J(HH) = 8.1 Hz), 12.8 br (1H, HOC₆H₄-*p*-CH₃).

Reaction of 2 and HOC₆H₄-*p*-NO₂ to Yield Complex 1 along with HOC₆H₄-*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 HOC₆H₄-*p*-NO₂ (*ca.* 7 mg). The formation of 1 and HOC₆H₄-*p*-Me in solution was supported by ¹H-NMR spectroscopy. Complex 1 was isolated from the reaction mixture.

Reaction of 2 and [Ph₂I]Cl to Yield Pd(2,6-(CH₂NMe₂)₂C₆H₃)Cl, PhI and PhOC₆H₄-*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 [Ph₂I]Cl (*ca.* 12 mg). The reaction immediately proceeded to produce Pd(2,6-(CH₂NMe₂)₂C₆H₃)Cl, PhI, and *O*-phenylated ether derivative PhOC₆H₄-*p*-Me as evidenced by ¹H-NMR and GC/MS spectroscopy. For PhOC₆H₄-*p*-Me: GC/MS: *m/z* = 184, 169, 107, 91, 77.

Results and Discussion

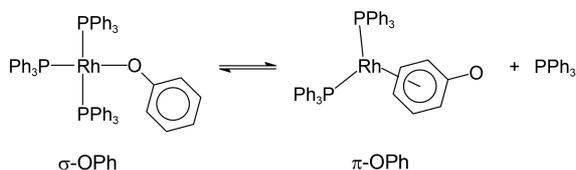
Preparation of the Palladium(II) Aryloxides. *para*-Functionalized phenoxide derivatives of palladium(II) having an NCN pincer, Pd(NCN)(OC₆H₄-*p*-X) (NCN = 2,6-(CH₂NMe₂)₂C₆H₃, X = NO₂ (1), Me (2)) were prepared by the reaction of Pd(NCN)(SO₃CF₃) with a slight excess molar amount of NaOC₆H₄-*p*-X in THF (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 ¹H-NMR spectroscopy, and microanalyses. In the ¹H-NMR spectrum of 1 in C₆D₆, the methyl (N(CH₃)₂) and methylene (CH₂N) 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 ($^3J(\text{HH}) = 9.2$ Hz), respectively. The respective magnetic equivalencies on the NMR time scale observed for each of the methyl ($\text{N}(\text{CH}_3)_2$) 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): $\Delta\delta = 0.89$ 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 $\nu(\text{NO})$ bands of the nitro group on *para*-position of the phenoxo ligand were observed at 1583 and 1303 cm^{-1} , respectively. In the $^1\text{H-NMR}$ 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 $\text{Rh}(\sigma\text{-OAr})(\text{PPh}_3)_3$



Scheme 2

converts into the π -bonding aryloxides $\text{Rh}(\pi\text{-OAr})(\text{PPh}_3)_2$ 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 $^1\text{H-NMR}$ 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**: $\text{HOC}_6\text{H}_4\text{-}p\text{-Me}$, *vide infra*) gave satisfactory microanalytical data for C, H, and N. The selected $^1\text{H-NMR}$ and analytical data of **1-3** are shown in Table 1.

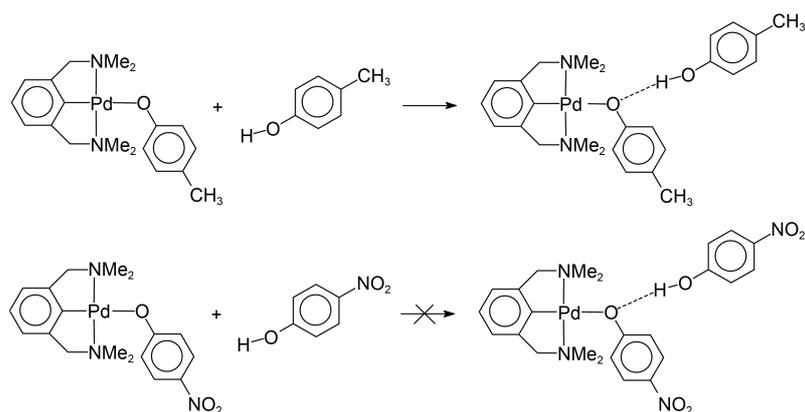
Adduct Formation, σ -ligand Exchange and Reactivity of the Palladium(II) Aryloxides. Complex **2** undergoes adduct formation with $\text{HOC}_6\text{H}_4\text{-}p\text{-Me}$ through hydrogen-bonding (Scheme 3). The adduct complex **3** (**2**: $\text{HOC}_6\text{H}_4\text{-}p\text{-Me}$) can readily be prepared by treatment of a benzene solution of **2** with $\text{HOC}_6\text{H}_4\text{-}p\text{-Me}$, and has been isolated from the solution. Treatment of $\text{Pd}(\text{NCN})(\text{OSO}_2\text{CF}_3)$ with an excess amount of $\text{NaOC}_6\text{H}_4\text{-}p\text{-Me}$ (> 3 equivalents) also affords the hydrogen-bonding adduct. In the reaction, $\text{HOC}_6\text{H}_4\text{-}p\text{-Me}$ is likely arisen from hydrolysis of $\text{NaOC}_6\text{H}_4\text{-}p\text{-Me}$ with an infinitesimal amount of water present in the solvent. However complex **1** with $\text{HOC}_6\text{H}_4\text{-}p\text{-NO}_2$ does not form adduct neither from treatment of **1** with free $\text{HOC}_6\text{H}_4\text{-}p\text{-NO}_2$ nor from metathesis reaction of $\text{Pd}(\text{NCN})(\text{OSO}_2\text{CF}_3)$ with an excess amount of $\text{NaOC}_6\text{H}_4\text{-}p\text{-NO}_2$.

In the $^1\text{H-NMR}$ spectrum of **3** in d_6 -benzene, the hydroxy proton in the $\text{Pd-O}\cdots\text{HO}$ resonates at δ 12.8 which is shifted to far downfield in comparison with that of free $\text{HOC}_6\text{H}_4\text{-}p\text{-Me}$ 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 $\text{Pd-OC}_6\text{H}_4\text{-}p\text{-Me}$ 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 $\text{HOC}_6\text{H}_4\text{-}p\text{-Me}$ 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 $^1\text{H-NMR}$ and analytical data of **1**, **2** and **3** (**2**: $\text{HOC}_6\text{H}_4\text{-}p\text{-Me}$)

Comp.	$^1\text{H-NMR}$ (δ) ^a				Analytical data (%) ^b		
	N-CH ₃	-NCH ₂	<i>o</i> -H, ^c <i>m</i> -H, ^c <i>p</i> -CH ₃ ^c	$^3J(\text{HH})$ ^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, OH)	8.1	61.3 (60.9)	6.93 (6.68)	5.14 (5.46)

^aIn C_6D_6 . ^bCalculated values in parentheses. ^cCoordinated *p*-X-phenoxide. ^d J in Hz. ^eCombined with the hydrogen-bonding *p*-cresol.



Scheme 3

ring. HOC₆H₄-*p*-Me is much weaker acid than HOC₆H₄-*p*-NO₂ ($pK_a = 10.3$ (*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)(PMe₃)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(OC₆H₄-*p*-Me)L₃](HOC₆H₄-*p*-Me) (L = PMe₃, PPhMe₂) is strongly polarized with high negative charge on the *O*-atom in the phenoxide and high positive charge on the Rh atom affecting HOC₆H₄-*p*-Me to be very strongly bonded to the *O*-atom of the Rh-aryloxide bond, being supported by the very high enthalpies ($\Delta H = -10 \sim -14$ 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 $-3 \sim -6$ kcal/mol.²⁶ It is also interesting to note that the π -bonding aryloxides Rh(π -OAr)(PPh₃)₂ can be stabilized through hydrogen-bonding on the addition of 2 equivalents of free phenol.²⁴

The ¹H-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*-CH₃ of the phenoxide ligand OC₆H₄-*p*-CH₃ are magnetically equivalent with corresponding proton-resonances of the hydrogen-bonding HOC₆H₄-*p*-CH₃, 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 OC₆H₄-*p*-Me with the hydrogen-bonding HOC₆H₄-*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

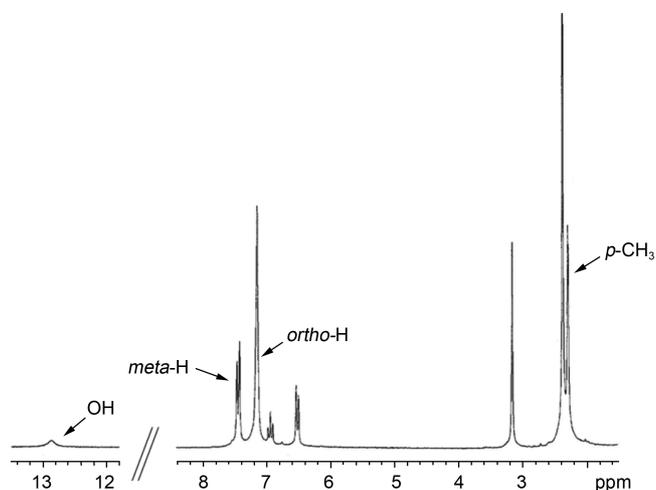
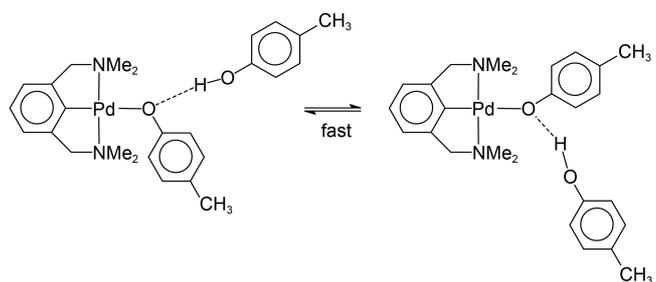
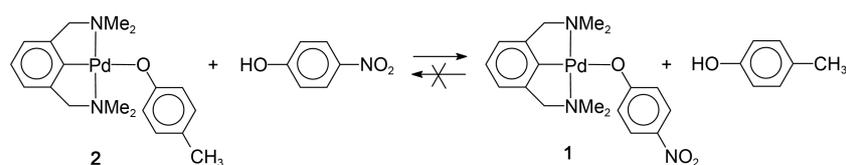


Figure 1. The ¹H-NMR spectrum of **3** (2-HOC₆H₄-*p*-Me) shows that fast exchange undergoes between the coordinated *p*-cresolate and the hydrogen-bonding *p*-cresol (marked with arrows). The resonance signal of the *ortho*-H is overlapped with that of the protio-benzene.

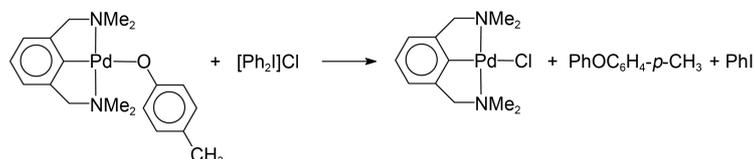


Scheme 4

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 (ΔG^\ddagger) for *trans*-Pd(Me)(PMe₃)₂(OC₆H₄-*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(pyrrrolidine)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 ¹H-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 HOC₆H₄-*p*-NO₂ 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 diphenyliodine chloride ([Ph₂I]Cl) quantitatively affords Pd(NCN)Cl²⁷ and PhI along with release of *O*-phenylated product PhOC₆H₄-*p*-Me which were identified by ¹H-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 PhOC₆H₄-*p*-Me likely proceeds *via* facile oxidative addition of [Ph₂I]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 [Ph₂I]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 Me₃SiCF₃ 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)(OC₆H₄-*p*-X) (X = NO₂ (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 nucleophilicity 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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