

Bis(imino)aryl Complex of Nickel(II): *N,C,N*-Pincer Type Complex, (2,6-(2,6-Et₂PhN=CH)₂C₆H₃)NiBr

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The synthesis of a novel *N,C,N*-type pincer, bis(*N*-aryl)-2-bromoisophthalaldimine 2,6-(2,6-Et₂PhN=CH)₂C₆H₃Br (**1**) and Ni(**1**)Br (**2**) is described. They were characterized by elemental analysis and spectroscopic techniques (IR and ¹H NMR). Attempted ethylene polymerization catalyzed by **2** has been futile, leading only to the formation of a small amount of oily oligomers.

Key Words : Bis(imino)aryl, *NCN*-Pincer, Ni(II) *NCN*-pincer complex, Oxidative addition, Catalyst

Introduction

Late transition metal complexes incorporating pincer type ligands are of great interest in not only homogeneous catalysis (aliphatic dehydrogenation,¹ Stille coupling,² Heck coupling,³ C-X (X = H, C, O) activation⁴) but materials chemistry.^{5,6}

The potential terdentate PCP or NCN ligands containing heteroatomic P- or N-donors on two *ortho*: *ortho* positions in the aryl ring undergo metallation with late transition (or platinum group) metals to provide square planar conformation consisting of two 5-membered metallacyclic rings (Figure 1).⁷ Thus the terdentate chelation in the complexes inhibits both dissociation of the phosphine (or nitrogen) groups and reductive elimination of the aryl group. Such a remarkably rigid framework provided by the pincer type ligands, therefore, enhances thermal stability of resulting complexes, and may have catalytic implication in a wide range of homogeneous catalysis.^{1-4,7-9}

We have recently reported Pd(II) and Pt(II) complexes of PCP pincers, in which reactive species (M-NHR) with a hard-base ligand can be stabilized by the presence of sterically demanding pincer ligands.¹⁰ We have also demonstrated that the metal-amide bond in the complexes are selectively involved in stoichiometric and catalytic reactions with various substrates.^{10a,c,d}

As a part of our ongoing studies on pincer complexes, herein we report the synthesis and characterization of a novel *N,C,N*-type pincer, bis(*N*-aryl)-2-bromoisophthalaldimine 2,6-(2,6-Et₂PhN=CH)₂C₆H₃Br (**1**) and Ni(**1**)Br (**2**). The Ni(II) complexes of NCN pincers are rare in contrast to

their Pd(II) and Pt(II) analogues.¹¹⁻¹³ We now put a new entry into a series of Ni complexes of NCN pincers.

Experimental Section

All operations for air sensitive compounds were performed on a standard Schlenk line or in an inert atmosphere glovebox under argon or nitrogen. All solvents were properly dried and deaerated by conventional manners.¹⁴ Bromo-*m*-xylene, NBS (*N*-bromosuccinimide), AIBN (azobisisobutyronitrile), NaOAc, CaCO₃, MgSO₄, Bu₄NBr, Ni(COD)₂, and CDCl₃ were purchased from Aldrich Chemical Co., and used as supplied. Argon and nitrogen gas were dried by passing through a column (Drierite gas-drying unit: Aldrich Z11287-9) filled with anhydrous CaSO₄ (a mixture of a color indicator). The compounds of 2,6-bis(dibromomethyl)-bromobenzene¹⁵ and 2-bromoisophthalaldehyde¹⁶ were prepared according to the literature methods.

Melting points were measured on a Gallenkamp Melting Point Apparatus under argon atmosphere. IR spectra were recorded on a Bomem FT-IR spectrometer (Michelson 100) in the 4000–600 cm⁻¹ region, as pressed KBr pellets. ¹H-NMR spectra were measured on an Urian Unity Inova FT-NMR spectrometer (500 MHz), using the deuterium signal of the solvent as an internal lock frequency. Chemical shifts for ¹H-NMR were reported in ppm relative to TMS. Elemental analyses for C, H, N were performed at Basic Science Institute (Dongguk University), and for Br at Analytical Laboratory (Georgia Institute of Technology).

Bis(*N*-2,6-diethylphenyl)-2-bromoisophthalaldimine (1). A 90 mL methanolic solution of 2-bromoisophthalaldehyde (1.5 g, 7.1 mmol) and 2,6-diethylaniline (2.2 g, 14.5 mmol) was stirred for 3 h at refluxing temperature, resulting in a yellow solution. After cooling the reaction mixture at ambient temperature, all volatiles were removed *in vacuo* to give a deep-orange residue. The resulting residue was dissolved in hot methanol (*ca.* 50 mL) to give an orange solution. Recrystallization by slow cooling of the hot methanolic solution afforded compound **1** as yellow crystalline

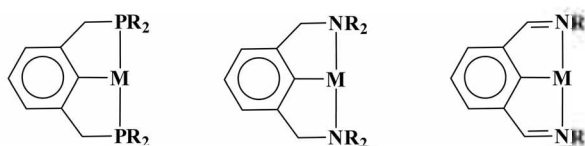


Figure 1. Late transition metal complexes having PCP- and NCN-pincer type ligands.

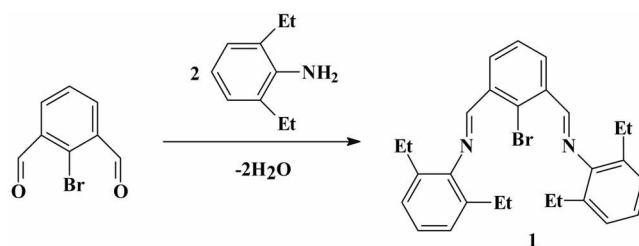
solids. Yield 2.67 g (79%). M.P.: 135 °C. IR (KBr, cm^{-1}): $\nu(\text{CN}) = 1626$. $^1\text{H-NMR}$ (CDCl_3): δ 1.18 t (12H, CH_3CH_2 , $J = 7.5$ Hz), 2.53 q (8H, CH_3CH_2 , $J = 7.5$ Hz), 7.07 t (2H, $J = 7.5$ Hz), 7.14 d (4H, $J = 7.5$ Hz), 7.58 t (1H, $J = 7.5$ Hz), 8.40 d (2H, $J = 7.5$ Hz), 8.74 s (2H, $\text{CH}=\text{N}$). Anal. calcd for $\text{C}_{28}\text{H}_{31}\text{N}_2\text{Br}$: C, 70.77; H, 6.52; N, 5.89; Br, 16.81; found: C, 70.68; H, 6.58; N, 5.77; Br, 16.88%.

Bis(*N*-2,6-diethylphenyl)isophthalaldimin-2-yl nickel(II) bromide (2). To a mixture of $\text{Ni}(\text{COD})_2$ (0.25 g, 0.91 mmol) and bis(*N*-2,6-diethylphenyl)-2-bromoisophthalaldimine (0.43 g, 0.91 mmol) was added 20 mL of THF pre-cooled in a liquid nitrogen bath. The solution was slowly warmed to ambient temperature. The reaction mixture was stirred for 2 h, resulting in a deep brownish solution. The solution volume was reduced to ca. 3 mL under high vacuum. Addition of *n*-pentane (ca. 15 mL) to the concentrated solution gave tan precipitates, which were isolated by vacuum filtration and dried *in vacuo*. Complex 2 for satisfactory microanalysis can be obtained by column chromatography on alumina (Al_2O_3) with an eluant of THF to give tan crystals from *n*-pentane. The isolated yield of complex 2 after column chromatography was 68% (0.33 g). M.P.: 237 °C. IR (KBr, cm^{-1}): $\nu(\text{CN}) = 1532$. $^1\text{H-NMR}$ (CDCl_3): δ 0.55 t (6H, CH_2CH_3 , $J = 7.7$ Hz), 0.64 t (6H, CH_2CH_3 , $J = 7.7$ Hz), 2.11 q (4H, CH_2CH_3 , $J = 7.7$ Hz), 2.20 q (4H, CH_2CH_3 , $J = 7.7$ Hz), 6.38-6.62 m (6H), 6.95 t (1H, $J = 7.4$ Hz), 7.76 d (2H, $J = 7.4$ Hz), 8.07 s (2H, $\text{CH}=\text{N}$). Anal. calcd for $\text{C}_{28}\text{H}_{31}\text{N}_2\text{BrNi}$: C, 63.13; H, 5.82; N, 5.24; found: C, 63.38; H, 5.94; N, 5.03%.

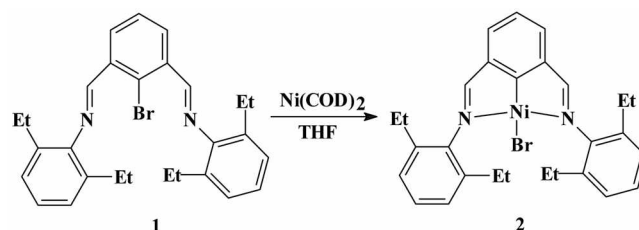
Results and Discussion

Ligand synthesis. A new NCN pincer, 2,6-(2,6-Et₂PhN=CH)₂C₆H₃Br (1) was prepared from Schiff-Base condensation of 2-bromoisophthalaldehyde with 2,6-diethylaniline. The starting compound, 2-bromoisophthalaldehyde was synthesized according to the literature.¹⁶ It is worth noting that much longer reaction time (~3 days) than reported in the literature (9 h) was required for the synthesis of the starting compound in the presence of a large excess of the phase-transfer reagent, Bu_4NBr . The reaction of 2-bromoisophthalaldehyde and 2 equivalent of 2,6-diethylaniline in a methanolic solution for 3 h at refluxing temperature readily produced compound 1 (Scheme 1). The compound has been isolated as yellow crystalline solids in a moderately high yield of 79% after purification processes. Compound 1 has been fully characterized by IR and NMR spectroscopy, and microanalyses.

In the IR spectrum of 1, the characteristic $\nu(\text{C}=\text{N})$ band of the imino group was observed at 1626 cm^{-1} . In the $^1\text{H-NMR}$ spectrum in CDCl_3 , the methyl (CH_3CH_2 , $^3J(\text{HH}) = 7.5$ Hz) and methylene (CH_3CH_2) protons resonances of the ethyl group on 2,6-position of *N*-aryl ring displayed at δ 1.18 and 2.53 as a triplet and a quartet, respectively. The resonance for the imine proton ($\text{N}=\text{CH}$) has been observed at δ 8.74, expectedly. The aryl protons on *N*-aryl and *Br*-aryl rings are observed in the region of δ 7.07-8.40 along with their



Scheme 1



Scheme 2

appropriate spin-spin couplings. All the $^1\text{H-NMR}$ spectral data are well consistent with those of reported other derivatives of bis(*N*-aryl)-2-bromoisophthalaldimine, recently.¹² Compound 1 gave satisfactory microanalytical data for C, H, N, and Br (see Experimental Section). 1 is moderately stable in air and moisture in the solid state. However it is noteworthy that partial hydrolysis of bis(imino)aryl derivatives to the mono(imino)benzaldehyde slowly takes place over a period of time in ethanolic solution.^{12c}

Complex formation. Scheme 2 shows the formation of the nickel complex of the type $\text{Ni}(\text{I})\text{Br}$ (2) through oxidative addition of 1 to $\text{Ni}(\text{COD})_2$ ($\text{COD} = 1,5\text{-cyclooctadiene}$). The oxidative addition of 1 to the low valent nickel complex $\text{Ni}(\text{COD})_2$ was quite facile to form a tridentate $\eta^3\text{-N,C,N}$ -pincer type complex. No evidence of $\eta^1\text{-C}$ -bonded or $\eta^2\text{-N,C}$ -bonded complex formation was observed. Very recently, van Koten has reported a series of $\text{Ni}(\text{II})$ complexes with ketimines and oxazoloxazolines such as [bis(ketimine)phenyl]NiBr and (Phebox)NiBr (Figure 2).¹³ These nickel complexes can be prepared either from transmetalation of $\text{Ni}(\text{II})$ bromide with lithiated aryl derivatives or from oxidative addition of Ar-Br to $\text{Ni}(0)$. However, it is worth noting that oxidative addition gives the pincer type complexes exclusively, while transmetalation produces a mixture of $\eta^3\text{-N,C,N}$ - and $\eta^1\text{-C}$ -bonded complexes. The complex 2 is closely related to the Ni-ketimine complex.

Complex 2 is moderately stable in air in the solid state.

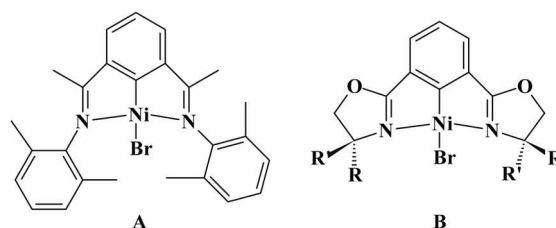


Figure 2. (bis(ketimine)phenyl)NiBr (A) and (Phebox)NiBr (B).

Table 1. ¹H-NMR, IR and Analytical data of **1** and **2**

Comp.	¹ H-NMR (δ)		IR (cm ⁻¹)	Analytical Data (%) ^a			
	-CH=N	-CH ₂ CH ₃ , -CH ₂ CH ₂	ν(C=N)	C	H	N	Br
1	8.74	2.53 1.18	1626	70.77 (70.68)	6.52 (6.58)	5.89 (5.77)	16.81 (16.88)
2	8.07	2.11, 2.20 0.55, 0.64	1532	63.13 (63.38)	5.82 (5.94)	5.24 (5.03)	

^aCalculated values in parentheses

Elemental analysis is in good agreement with those of the calculated values. A significant blue shift in the ν(C=N) band is observed upon complexation: namely the band for the free ligand appears at 1626 cm⁻¹ moves to 1532 cm⁻¹. This is ascribed to π-back donation, and has recently been observed in the related iridium(III) complexes of 2,6-bis-(aldimine)phenyl derivatives.^{12c} Numerous other examples are also available with Pd-, Pt-, Rh-, and Ir-complexes incorporating 2,6-bis(aldimine)phenyls.¹² To the best of our knowledge, however, nickel analog of bis(aldimine)phenyl complexes has proved elusive.¹⁷

In the ¹H-NMR spectrum of **2** in CDCl₃, the ethyl groups on 2,6-position of *N*-aryl rings show magnetically inequivalent two resonances. These resonance peaks displayed at δ 0.55 t (6H, CH₂CH₃, *J* = 7.7 Hz) and 0.64 t (6H, CH₂CH₃) for the methyl protons, and at 2.11 q (4H, CH₂CH₃, *J* = 7.7 Hz) and 2.20 q (4H, CH₂CH₃) for the methylene, respectively, that are considerably shifted to upfield upon coordination.¹² For the free ligand, the ethyl groups give one resonance set for the methyl and methylene protons at δ 1.18 and 2.53, respectively (see Table 1). This resonance observation for complex **2** clearly indicates that the *N,C,N* pincer type ligand is coordinated to nickel through η³-*N,C,N*-chelation, exhibiting diastereotopically two different ethyl resonances. The imine proton (N=CH) resonance displays at δ 8.07 as a singlet peak, which is significantly shielded upon coordination through *N*-donor, being compared to that of the free ligand observed at δ 8.74. This resonance shift for the imine proton in complex **2** is in good accordance with those of analogous complexes Rh(III)-,^{11a} Ir(III)-,^{12c} and Pt(II)-pincer.^{12a} previously observed. The phenyl protons attached to 3,4,5-position on *N*-aryl rings exhibit in the region of δ 6.38-6.62 as multiplets and *C*-coordinated aryl protons on 3,4- and 5- positions displays at 7.76 d (2H, *J* = 7.4 Hz) and 6.95 t (1H), respectively. The selected ¹H-NMR, IR and Analytical data of **1** and **2** are shown in Table 1.

The catalytic activity of complex **2** in ethylene polymerization has been tested. In a high pressure vessel, 200 psi of ethylene gas was charged in toluene in the presence of catalytic amount of **2** along with 1,000 equivalents of MAO (methylaluminoxane) as a co-catalyst. After stirring the reaction mixture for 3 h at 60 °C, the reaction was quenched in a cold water-bath, resulting in a yellow solution but no evidence of polyethylene formation (white precipitates). The solution was concentrated under high vacuum. Addition of methanol to the concentrated solution gave a tiny amount of

oily material which has been identified as ethylene oligomers. Preliminary results indicate that the pincer complex was found to be inactive as a catalyst in ethylene polymerization. This is presumably ascribed to lability of the imino groups, thereby being readily susceptible to electrophile species, not providing a crucial condition for subsequent reaction. The stability and conformation of Pt-acetylenide and Pt-methyl complexes of *N,C,N* pincer system are largely dependent upon the steric congestion of the ligand framework, in which one of the imino group is dangling off the metal center.^{12a,b} Synthetic derivatives of *N,C,N*-pincer type nickel complexes having a hard-base ligand and their application to catalytic hydroamination of olefins is currently under investigation.

We have demonstrated a facile synthetic route to *N,C,N*-pincer complex of nickel(II) bromide through oxidative addition of a novel derivative of 2-bromoisophthalaldimine 2,6-(2,6-Et₂PhN=CH)₂C₆H₃Br to Ni(COD)₂. The complex is both air and moisture stable, providing a useful precursor in preparation of a new series of nickel pincer type complexes for studying stoichiometric and catalytic reactions.

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