



Synthesis and Characterization of Two New Imidazolylphosphine Hybrid Ligands and Their Ni (II), Co-(II) and-(III) Complexes

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ABSTRACT

Two new bidentate imidazolylphosphine P–N chelate ligands 2-(diisopropylphosphino-ethyl)-1-methylimidazole (PN^I) and 2-(diphenylphosphino-ethyl)-1-methylimidazole (PN^{II}) have been synthesized in good yields by treating R₂PCL (R = Prⁱ or Ph) with 1-methyl-2-trimethylsilylethylimidazole. Various types of nickel(II), cobalt-(II) and -(III) complexes have been prepared with these two ligands and characterized by physico chemical techniques. Complexes [NiX₂(PN^I)] (X = Cl and NCS) **1** and **2** are diamagnetic planar in the solid state and their chloride or thiocyanide are replaced by water or methanol giving diamagnetic yellow planar species. Two nickel(II) bis-ligand complexes, [Ni(PN^I)₂][BF₄]₂·H₂O **3** and [Ni(PN^{II})₂][BF₄]₂ **7**, take planar structures with different configurations. In **3** the two phosphorus atoms are in *cis* position whereas in **7** they are *trans* to each other. The structures of cobalt(II) complexes, [CoX₂(PN^I)] (where X = Cl or Br) **4** and **5** are tetrahedral whereas, cobalt(III) complexes, [Co(acac)₂(PN^I)]ClO₄ **6** and [Co(CN)₂(acac)(PN^{II})] **8** (where acac = acetylacetonate), are octahedral.

Keywords: P-N ligands; Hybrid ligands; Nickel complexes; Cobalt complexes; Catalysis

INTRODUCTION

Synthesis of new ligands for homogeneous catalysis is an active field of chemistry research. A huge effort has been devoted to the development of highly efficient transition metal catalyzed reactions using ligands based on P–P, P–N, or N–N coordination modes.¹ Of special interest are the P–N chelate ligands due to their unsymmetrical nature.² Nitrogen as a hard donor is capable of stabilizing metal ions in higher oxidation states whereas phosphorus as a soft donor is best suited to stabilize metals in lower to medium oxidation states. Hence, metal complexes of hybrid P–N chelate ligands have ability to act as “hemilabile” ligands.³ Therefore; effective catalysts may be generated from the complexes of hybrid chelate P–N ligands in which one donor atom is more loosely bound than another so that a reactive intermediate can be formed easily in the catalytic systems. They also can control the reactivity of metal sites owing to the different steric and electronic properties of the donor groups. This bifunctional character of hybrid ligands has proven to be very useful in homogeneous transition metal catalysis, activation of small molecules and stabilization of reactive transition metal species. Some important organic reactions catalyzed by transition metal complexes of P–N ligands are quite impressive in terms of both selectivity and reactivity.⁴ The

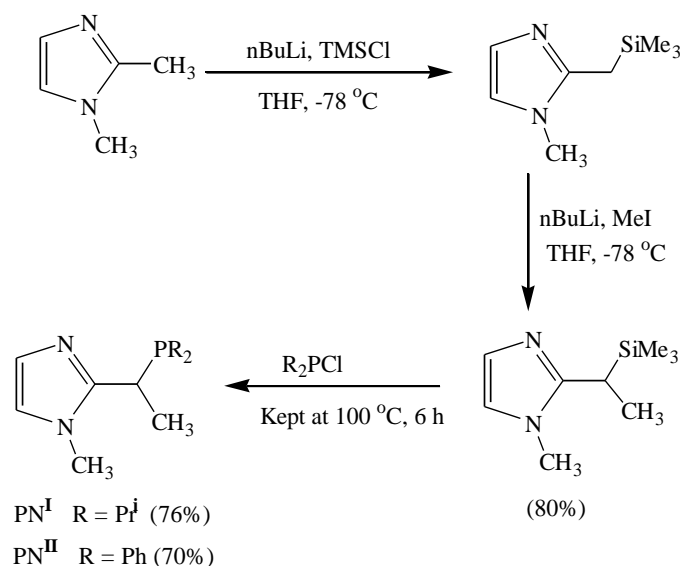
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incorporation of a chiral center into such ligands allows enantioselectivity in catalytic transformation mediated by complexes of these ligands.⁵ Recently we reported a new class of hybrid P–N ligands containing an imidazole nitrogen donor.⁶ Here we report the syntheses of two new imidazolylphosphine ligands resembled to our reported P–N ligands but having an additional methyl group in their backbone and their co-ordination behaviors toward nickel(II), cobalt-(II) and -(III) metal ions. Such modification of the P–N ligand is significant because we can tune the electronic and steric properties of the ligands which may have influence on a catalytic reaction.

RESULTS AND DISCUSSION

Syntheses of ligands

One facile method for the preparation of tertiary phosphines, R_3P , is the nucleophilic displacement on R_2PCl by organometallic reagents such as organolithium. However, reaction of R_2PCl with organolithium containing imidazole moiety, $MeImCH_2Li$, afforded messy products. This is probably due to the unfavorable side reactions of $MeImCH_2Li$. In order to avoid such side reactions we reported an improved method where silylated methylimidazole, $MeImCH_2SiMe_3$, was used which provides an easy route to prepare imidazolylphosphine ligands.⁶ The present two ligands have prepared by similar fashion using two-pot, stepwise reactions as shown in Scheme 1.



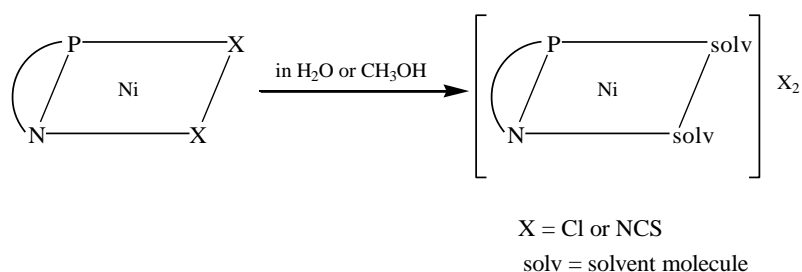
Scheme 1 Synthesis of ligands

Silyl and methyl groups were incorporated to methylimidazole by successive silylation and methylation of 1, 2-dimethylimidazole at its 2-methyl position. Silylation achieved by treating 1, 2-dimethylimidazole with *n*-BuLi followed by a reaction with trimethylsilylchloride in

THF at -78°C . The methylation step was performed similarly in the same reaction vessel without isolating the silylated imidazole by further lithiation and methylation of resultant product using $n\text{BuLi}$ and MeI respectively. The overall yield of $\text{MeImCH}(\text{CH}_3)(\text{SiMe}_3)$ is about 80% after distillation (b.p. 112°C at 15 mm Hg). The ligands were obtained by heating the mixture of $\text{MeImCH}(\text{CH}_3)(\text{SiMe}_3)$ and R_2PCl (Pr^i , Ph) (1:1 molar ratio) for 6 h and was isolated cleanly from the reaction mixture by distillation for PN^{I} (bp 82°C at 0.1 mmHg, yield 76%) and by formation of the hydrobromide salt for PN^{II} . The $\text{PN}^{\text{II}}\cdot\text{HBr}$ forms air stable colorless solid. The free PN^{II} was obtained by treating the ligand hydrobromide with K_2CO_3 in water and extracting into benzene. Evaporation of solvent left the free pure ligand as colorless oil.

Syntheses and characterization of complexes

The complexes investigated are listed in Table 1 along with their analytical data. Divalent metal complexes were readily prepared by reaction of the metal halides and thiocyanide with the ligands in ethanol. The cobalt(III) complexes were obtained by the ligand substitution of $[\text{Co}(\text{acac})_3]$ with PN^{I} and $[\text{Co}(\text{CN})_2(\text{acac})_2]$ with PN^{II} in methanol in the presence of active charcoal and separated from the reaction mixture in pure form by using alumina column chromatography. All the complexes are air stable in the crystalline state, whereas in solution nickel(II) and cobalt(II) complexes gradually decomposed in the air. The ^1H NMR spectra of complexes showed a downfield shift of the resonances compared to those of the “free” ligands. Those of the proton resonances appear to reflect the expected deshielding of these nuclei as a consequence of σ donation to the positively charged metal ions. Relatively large shifts observed for the 2-methene (CH) and imidazole- H_4 protons in complexes compared to the “free” ligands probably result from their proximity to the phosphorus and nitrogen donor atoms; these protons would be expected to experience the strongest σ effects. Complex **1** and **2** are diamagnetic planar in the solid state and their chloride or thiocyanide are replaced by water or methanol giving diamagnetic yellow planar species (Scheme 2). We have reported a same type of halide-co-ordinated planar structure in the solid state for a similar type of



Scheme 2 Proposed structures of complexes **1** and **2** in solid state and in aqueous or methanolic solution.

imidazolyphosphine P–N ligand.⁶ The diamagnetic square-planar species **1** and **2** generated in water or methanol solution did not change on addition of an excess of tetrabutylammonium chloride. This unusual stability of planar species may be due to the presence of the strong imidazole N-donor.

Table 1 Analytical data of complexes

Complex	color	H	Analysis [#] (%)	
			C	N
1 [Ni(PN ^I)Cl ₂]	red	6.44(6.51)	40.41(40.50)	7.88(7.87)
2 [Ni(PN ^I)(NCS) ₂]	red	5.73(5.77)	41.77(41.92)	13.85(13.96)
3 [Ni(PN ^I) ₂](BF ₄) ₂ ·H ₂ O	orange	6.72(6.88)	40.76(41.01)	7.87(7.97)
4 [Co(PN ^I)Cl ₂]	blue	6.38(6.50)	40.20(40.47)	7.89(7.86)
5 [Co(PN ^I)Br ₂]	blue	5.20(5.21)	32.36(32.38)	6.30(6.29)
6 [Co(acac) ₂ (PN ^I)]ClO ₄	violet	6.53(6.40)	45.42(45.33)	4.96(4.81)
7 [Ni(PN ^{II}) ₂](BF ₄) ₂	yellow	4.62(4.80)	51.89(51.53)	6.67(6.67)
8 [Co(CN) ₂ (acac)(PN ^{II})]·H ₂ O	yellow	4.91(5.40)	57.06(57.47)	10.65(10.72)

calculated values in parentheses.

We found complex **3** and **7** is quite inert toward potassium cyanide (1: 2 molar ratio) under reflux in ethanol even after prolonged heating. A similar type of pyridylphosphine complex, [Ni-(PN)₂][ClO₄]₂ [where PN = 1-(diphenylphosphino)-2-(2-pyridyl)ethane], gave a dangling pyridine diamagnetic dicyano complex, [Ni(CN)₂(PN)₂], after refluxing for only 30 min with two molar ratios of potassium cyanide.⁷ This observation suggests that the donor ability of alkylated imidazole is stronger than that of pyridine. Previously we reported the structures of two bis-ligand complexes, [Ni(PN)₂](BF₄)₂, of two sterically different imidazolyl phosphine ligands having aryl and isopropyl substituted phosphorus atoms very similar to our present complexes **3** and **7**. The single crystal X-ray analysis of those two complexes revealed that Ph-substituted two phosphorus atoms occupied a *cis* configuration whereas Pr^I-substituted two phosphorus atoms occupied a *trans* configuration. Usually aryl substituted phosphines promote stabilization of *cis* isomers.⁸ This configuration avoids placing two ligands of high *trans* influence⁹ opposite to each other, and also prevents *trans* arrangements of strongly π-bonding ligands, where they would compete for use of the same metal d orbital. The *trans* configuration might be due to the steric bulkiness of the isopropyl group in the PN ligand. Based on our previous finding and comparing the spectroscopic data of complexes **3** and **7** we assigned the configuration of **3** as a *trans* and **7** as a *cis* (Figure 1).

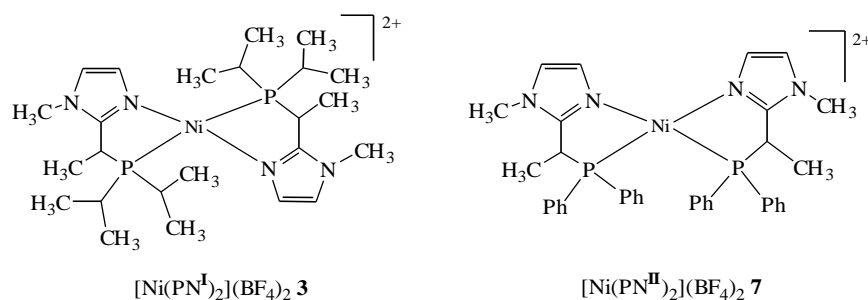


Figure 1 proposed structure of complexes **3** and **7**

Electronic spectra

The electronic spectral data are in the Experimental section. The electronic spectrum of all Ni(II) complexes **1**, **2**, **3**, and **7** in water or methanol solution showed absorption bands around 400–500 nm ($\log \epsilon \approx 2.5$), which is typical of those of low-spin square planar nickel(II) complexes. It is assigned to the d–d transition ${}^1\text{A}_1 \longrightarrow \square {}^1\text{B}_2$ for a square-planar d^8 complex. The spectra of cobalt (II) complexes **4** and **5** showed intense bands around 500–700 nm ($\log \epsilon \approx 2.7$), which are characteristic of tetrahedral cobalt(II) complexes. These have their origin in the ${}^4\text{A}_2 \longrightarrow {}^4\text{T}_1(\text{P})$ transition, in T_d symmetry. The absorptions move to lower frequencies in the sequence Cl^- , Br^- as expected from the position of these ligands in the spectrochemical series. The splitting is an expected consequence of spin–orbit coupling and low-symmetry components of the field.¹⁰ The spectra of the cobalt(III) complex **6** showed a d–d transition in the visible region that appeared 530 nm whereas, in complex **8** the band moved to higher energy at 428 nm which is due to the presence of two strong CN^- groups in the coordination sphere. The spectral features confirmed the octahedral geometry of these two complexes.

Conclusion

Two new bidentate P–N chelate ligands containing an imidazolyl moiety have been synthesized in fairly good yields and their co-ordination behaviors toward nickel(II), cobalt(II) and cobalt(III) metal ions investigated. Steric bulkiness and the electronic nature of the substituents on the phosphorus atom of the ligand have influences on the stereochemistry of $[\text{NiL}_2]^{2+}$ type complexes. The study shows that imidazolylphosphine ligands have better donor abilities than related pyridylphosphine ligands.

Experimental Methods

All reactions were run in oven-dried glassware under an atmosphere of N_2 gas. Anhydrous solvents used in reactions either were purchased in anhydrous form (methanol) or distilled prior to use (THF from sodium–benzophenone). All chemicals were reagent grade used as received. The complex $[\text{Co}(\text{acac})_3]$ was prepared according to literature procedures.¹¹ The organic phase from all liquid–liquid extractions was dried over anhydrous Na_2SO_4 . Column chromatography was performed on 150–250 mesh alumina. **CAUTION:** perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled only in small quantities with appropriate precautions.

Instruments

All NMR spectra were recorded with a JEOL JMTC 400/54 or 300/54 spectrometer, ^1H referenced to SiMe_4 for organic solvent. The IR spectra were recorded with the KBr disc method on a Horiba FT-300 spectrometer, electronic spectra on a Jasco U-best 50 or Hitachi U-3400 spectrophotometer. Elemental analyses were performed by the Faculty of Pharmaceutical Science, Kanazawa University.

Preparations

MeImCH(CH₃)SiMe₃. To a stirred solution of 1, 2-dimethylimidazole (100 mmol) in THF (300 ml) was added 2.5 M *n*-butyllithium in hexane (100 mmol, 40 ml) at -78°C . After 2 h the reaction mixture was transferred slowly *via* a cannula to another flask which was previously charged by SiMe_3Cl (100 mmol, 9.30 ml) in THF (20 ml) whilst the temperature was kept at -78°C and the reaction mixture was stirred for further 1 h at ambient temperature. Then the reaction mixture was again cooled to -78°C and 2.5 M *n*-BuLi (100 mmol, 40 ml) was added slowly. After 2 h MeI (100 mmol) was added and the reaction mixture was stirred for 2 h at ambient temperature. The THF was removed, benzene and water were added and the organic layer was collected. Removal of the solvent by evaporation followed by distillation of residual oil gave pure compound (bp 112°C at 15 mmHg). Yield 80%. ^1H NMR (CDCl_3): δ 0.0 (s, 9 H, SiMe_3), 1.36 (d, 3H, CH_3), 2.27 (q, 1 H, CH), 3.47 (s, 3 H, NCH_3), 6.67 (d, 1 H, H_5) and 6.89 (d, 1 H, H_4).

MeImCH(CH₃)PPrⁱ₂ (PN^I). To MeImCH(CH₃)SiMe₃ (20 mmol) chlorodiisopropylphosphine (20 mmol, 3.2 ml) was added slowly *via* a syringe. The mixture was stirred at 100°C for 6 h. All volatile components were removed *in vacuo* (15 mmHg) at 120°C . The pure product was obtained by distillation of the remaining oil, bp 82°C at 0.1 mmHg. Yield (76%). ^1H NMR (CDCl_3): δ 0.8–1.0 (m, 12 H, CH_3 of Pr^i), 1.4 (t, 3H, CH_3), 1.6 (m, 1 H, CH of Pr^i), 1.8 (m, 1 H, CH), 3.0 (s, 3 H, NCH_3), 6.3 (d, 1 H, H_5) and 6.9 (d, 1 H, H_4).

MeImCH(CH₃)PPh₂·HBr (PN^{II}·HBr). To MeImCH(CH₃)SiMe₃ (20 mmol) chlorodiphenylphosphine (20 mmol, 3.60 ml) was added slowly *via* a syringe. The mixture was stirred at 100°C for 6 h. Then all volatile components were removed *in vacuo* (15 mmHg) at 120°C , and 47% HBr aqueous solution (20 mmol, 2.35 ml) was added followed by stirring for 2 h at room temperature. Water was removed by evaporation and the reaction mixture dissolved in ethanol (10 ml) to which diethyl ether was added slowly with shaking until it just turned cloudy. The resultant solution was then cooled to 25°C to give colorless crystals, which were filtered off, washed with ethanol–ether (1: 4) and dried *in vacuo*. Yield (70%) (Found: C, 57.18; H, 5.38; N, 7.29. Calc. for $\text{C}_{18}\text{H}_{20}\text{BrN}_2\text{P}$: C, 57.61; H, 5.37; N, 7.46%). ^1H NMR (D_2O): δ 1.44 (dd, 3H, CH_3), 3.06 (s, 3 H, NCH_3), 4.12 (m, H, CH), 6.99 (d, 1 H, H_5), 7.01 (d, 1 H, H_4) and 7.03–7.68 (m, 10 H, Ph). Free PN^{II} was obtained by treating the ligand hydrobromide with K_2CO_3 (1:2) in water and extracting with benzene. Evaporation of solvent left free pure PN^{II} as a colorless oil.

[NiCl₂(PN^I)] 1. An ethanolic solution (10 ml) of PN^{I} (1 mmol) was added with stirring to a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) in ethanol (20 ml) at ambient temperature. The complex precipitated from the concentrated ethanolic solution. The crystals precipitated were filtered

off, washed with cold ethanol and dried *in vacuo*. Yield (84%). $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2) 504 (log ϵ 2.64) and 320 (log ϵ 3.49).

[Ni(NCS)₂(PN^I)] 2. This complex was prepared in a similar manner to that of **1** using metal salts Ni(NCS)₂·6H₂O (1 mmol) and PN^I (1 mmol). The complex precipitated from the concentrated ethanolic solution. The crystals precipitated were filtered off, washed with cold ethanol and dried *in vacuo*. Yield (85%). $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2) 460 (log ϵ 2.96), 314 (log ϵ 3.34) and 268 (log ϵ 4.13)

[Ni(PN^I)₂][BF₄]₂·H₂O 3·H₂O. A solution of Ni(BF₄)₂·6H₂O (1 mmol) in ethanol (20 ml) was added with stirring to a solution of PN^I (2 mmol) in ethanol (10 ml). The crystals separated during addition. After filtration they were washed with ethanol and dried *in vacuo*. Yield (93%). $\lambda_{\text{max}}/\text{nm}$ (CH_3COCH_3) 425 (log ϵ 2.88).

[CoCl₂(PN^I)] 4. An ethanolic solution (10 ml) of PN^I (1 mmol) was added with stirring to a solution of CoCl₂·6H₂O (1 mmol) in ethanol (20 ml) at ambient temperature. The complex was precipitated during addition of ligand solution. It was filtered off, washed with ethanol and dried *in vacuo*. Yield (94%). $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2) 680 (log ϵ 2.70), 645 (log ϵ 2.57) and 560 (log ϵ 2.38) 312 (log ϵ 2.38)

[CoBr₂(PN^I)] 5. This complex was prepared from CoBr₂·6H₂O (1 mmol) and PN^I (1 mmol) in a similar manner to that described for **4**. The blue crystals separated during mixing. After filtration they were washed with ethanol and dried *in vacuo*. Yield (85%). $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2) 690 (log ϵ 2.77), 668 (log ϵ 2.72) and 655 (log ϵ 2.71) 585 (log ϵ 2.48), 307 (log ϵ 3.39).

[Co(acac)₂(PN^I)ClO₄] 6. The ligand PN^I (2 mmol) was added to a stirring solution of [Co(acac)₃] (2 mmol) in methanol (100 ml) at 0 °C containing some charcoal and allowed to react for 8 h. Then 70% perchloric acid (2 mmol) was added. The resulting violet solution was filtered and concentrated. The residue was chromatographed on alumina. Gradient elution of acetone gave a violet band which was collected and concentrated. The desired complex was obtained by addition of ether. Yield (72%). ¹H NMR (CDCl_3): δ 0.84 (dd, 3H, CH₃ of Prⁱ), 1.01 (dd, 3H, CH₃ of Prⁱ), 1.54 (m, 6 H, CH₃ of Prⁱ), 1.82 (s, 3 H, CH₃ of acac), 1.86 (s, 3 H, CH₃ of acac), 1.99 (s, 3 H, CH₃ of acac), 2.34 (s, 3 H, CH₃ of acac), 3.95 (s, 3 H, NCH₃), 5.42 (s, 1 H, CH of acac), 5.48 (s, 1 H, CH of acac), 6.83 (d, 1 H, H₅) and 6.90 (d, 1 H, H₄). $\lambda_{\text{max}}/\text{nm}$ (CH_3COCH_3) 530 (log ϵ 2.50).

[Ni(PN^{II})₂][BF₄]₂·H₂O 7·H₂O. An ethanolic solution (20 ml) of Ni(BF₄)₂·6H₂O (1 mmol) was added with stirring to an ethanolic solution (10 ml) of PN^{II} (2 mmol) at ambient temperature. The complex precipitated after 20 min, was filtered off, washed with ethanol and dried *in vacuo*. Yield (95%). $\lambda_{\text{max}}/\text{nm}$ (CH_3CN) 425 (log ϵ 2.58).

[Co(CN)₂(acac)(PN^{II})]·H₂O 8·H₂O. The complex K[Co(acac)₂(CN)₂] (1 mmol) and PN^{II}·HBr (1 mmol) were dissolved in methanol (100 ml) to which Et₃N (1 mmol) was added and stirred for 8 h in the presence of charcoal at ambient temperature. A yellow solution formed. Charcoal was filtered off and the methanol evaporated. The residue was then chromatographed on alumina. Gradient elution with benzene-acetone gave a yellow band which was collected and concentrated. The desired complex was obtained by addition of

ether. Yield (70%). $^1\text{H NMR}$ (CDCl_3): δ 1.10 (s, 3 H, CH_3 of acac), 1.46 (dd, 3H, CH_3), 2.22 (s, 3 H, CH_3 of acac), 3.93 (s, 3 H, NCH_3), 4.11 (m, 1 H, 2-CH), 5.32 (s, 1 H, CH of acac), 6.62 (d, 1 H, H_5), 7.01 (d, 1 H, H_4), and 7.30–8.20 (m, 10 H, Ph) 8.03–8.09 (m, 2 H, Ph). $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2) 428 (log ϵ 2.76).

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