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Syntheses of new P–N ligands containing an imidazolyl group and their co-ordination behaviors toward nickel(II), cobalt-(II) and -(III)

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Two new bidentate imidazolylphosphine P–N chelate ligands 2-(diphenylphosphinomethyl)-1-methylimidazole (PN^I) and 2-(diisopropylphosphinomethyl)-1-methylimidazole (PN^{II}) have been synthesized in good yields by treating R_2PCl (R = Ph or Pr^i) with 1-methyl-2-trimethylsilylmethylimidazole. Various types of nickel(II), cobalt-(II) and -(III) complexes have been prepared with these two ligands and characterized by physico-chemical techniques. The structures of $PN^I \cdot HBr$ and two nickel(II) complexes, $[Ni(PN^I)_2][BF_4]_2$ **2** and $[Ni(PN^{II})_2][BF_4]_2 \cdot MeCN$ **4**·MeCN, have been studied by single crystal X-ray analyses. Both take planar structures with different configurations. In **2** the two phosphorus atoms are in *cis* position whereas in **4**·MeCN they are *trans* to each other. The complex $[NiCl_2(PN^I)]$ **1** adopts a five-co-ordinate dimeric structure with chloride bridges in the solid state and a monomeric square-planar structure, $[Ni(PN^I)(solv)_2]Cl_2$, in aqueous and in methanolic solutions. However, complex $[NiCl_2(PN^{II})]$ **3** is diamagnetic and takes square-planar geometry around the metal ions both in the solid and solution states. The structures of cobalt(II), $[CoX_2(L)]$ (where X = Cl or Br), and cobalt(III) complexes, $[Co(acac)_2(L)]ClO_4$ (where acac = acetylacetonate, L = PN^I or PN^{II}), are tetrahedral and octahedral, respectively. A variable temperature ^1H and ^{31}P NMR study of complexes **1** and **2** demonstrated the presence of dynamic motion of the PN-chelate ring(s). On the other hand, in the cobalt(III) complexes $[Co(acac)_2(PN^I)]ClO_4$ and $[Co(acac)_2(PN^{II})]ClO_4$ two protons of the backbone methylene group of the PN ligands are magnetically inequivalent.

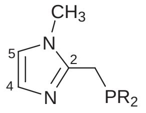
Introduction

Metal complexes with hybrid ligands containing P and N or O donor atoms are of increasing interest for their ability to act as "hemilabile" ligands.[1,2] Nitrogen or oxygen 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. Therefore, effective catalysts may be generated from the complexes of hybrid chelate 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.

In this context, pyridylphosphines and their metal complexes have received attention in view of their structural features, reactivity and catalytic applications.[2,3] Although a wide variety of pyridylphosphine ligands and their metal complexes has been extensively studied by many researchers, the other P–N ligand systems containing N-heterocycles have received less attention.[4–6]

Transition metal complexes containing imidazole and its derivatives play an important role in bioinorganic chemistry.[7] To the best of our knowledge imidazolylphosphine chelate (PN) ligands have not been reported yet. [Tris(imidazolyl)phosphine has been reported but does not act as a P–N chelate.[8]] Therefore, it is interesting to develop such new P–N chelate ligands containing both phosphorus and imidazolyl nitrogen as donor atoms.

Here we report the syntheses of two new imidazolylphosphine ligands PN^I and PN^{II} (Scheme 1) and their co-ordination behaviors toward nickel(II), cobalt-(II) and -(III) metal ions. The solid state structures of $PN^I \cdot HBr$ and complexes $[Ni(PN^I)_2][BF_4]_2$ and $[Ni(PN^{II})_2][BF_4]_2 \cdot MeCN$ have been established by single crystal X-ray analysis. Variable temperature ^1H and ^{31}P NMR spectra have also been investigated.



PN^I ; R = Ph

PN^{II} ; R = Pr^i

Results and discussion

Syntheses of ligands

For preparation of tertiary phosphines, R_3P, various synthetic methods have been developed. One facile method is the nucleophilic displacement on R_2PCl by organometallic reagents such as organolithium. Reaction of R_2PCl with $MeImCH_2Li$ generated by reaction of *n*-butyllithium with 1,2-dimethylimidazole,[9] however, afforded messy products. This is probably due to the unfavorable side reactions of $MeImCH_2Li$. In order to avoid such side reactions we used silylated methylimidazole, $MeImCH_2SiMe_3$, which provides an easy route to prepare imidazolylphosphine ligands. It readily reacted with R_2PCl (R = Ph or Pr^i) to give imidazolylphosphine in fairly good yields (≈75%). It should be noted here that the silylated compounds were successfully used to prepare some other phosphine ligands.[10]

The reaction conditions for silylation process are also very important. Very low temperature (−78 °C) is essential for selective silylation at the 2-methyl position of 1,2-dimethylimidazole. At 0 °C, however, the 5 position of imidazole was silylated. It was also found that disilylation mainly occurred at the 2-methyl position when $SiMe_3Cl$ was added to lithiated imidazole. This disilylation seems to proceed through monosilylation. Mono-

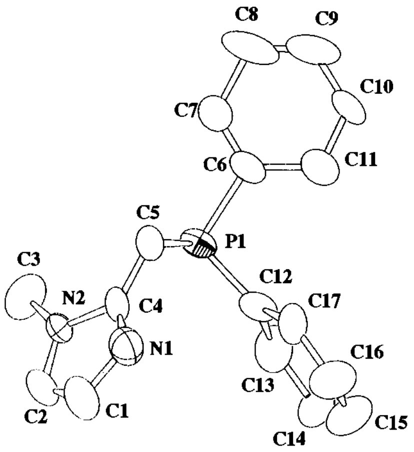


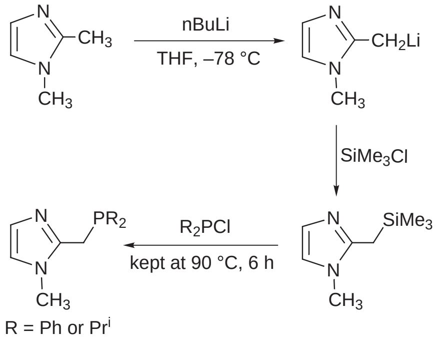
Fig. 1 An ORTEP drawing of the cation of PN$^{\rm I}$·HBr.

Table 1 Selected bond lengths (Å) and angles (°) of PN$^{\rm I}$·HBr

P1–C5	1.874(4)	C5–P1–C6	102.1(1)
P1–C6	1.832(3)	C5–P1–C12	96.0(1)
P1–C12	1.839(3)	C6–P1–C12	104.3(2)
N1–C1	1.385(4)	C1–N1–C4	109.7(3)
N1–C4	1.335(4)	C2–N2–C3	125.2(3)
N2–C2	1.385(4)	C2–N2–C4	108.6(3)
N2–C3	1.450(5)	C3–N2–C4	126.2(3)
N2–C4	1.340(4)	N1–C1–C2	106.6(3)
C1–C2	1.329(5)	N2–C2–C1	108.0(3)
C4–C5	1.473(4)	N1–C4–N2	107.1(3)

silylation makes the proton of the α-carbon more acidic, which is then readily deprotonated by remaining lithiated imidazole. Therefore, addition of $SiMe_3Cl$ to lithiated imidazole leads to formation of disilylated product. However, reverse addition gave chiefly monosilylated imidazole (yield ≈ 85%).

Purification of PN$^{\rm I}$ and PN$^{\rm II}$ was achieved by formation of the hydrobromide salt for PN$^{\rm I}$ and by distillation for PN$^{\rm II}$ (bp 80 °C at 1 mmHg). The PN$^{\rm I}$·HBr forms air stable colorless crystals. The synthetic procedure is given in Scheme 1. The free PN$^{\rm I}$ was obtained by treating the ligand hydrobromide with K_2CO_3 in water and extracting into benzene. Evaporation of solvent left free pure ligand as a colorless oil. The ^{31}P NMR peaks appear at δ −15.54 and 1.37 for PN$^{\rm I}$ and PN$^{\rm II}$ respectively.



Scheme 1

The structure of PN$^{\rm I}$·HBr was determined by single crystal X-ray analyses. An ORTEP[11] view of the cation is shown in Fig.1. Selected bond distances and angles are in Table 1.

Syntheses and characterization of complexes

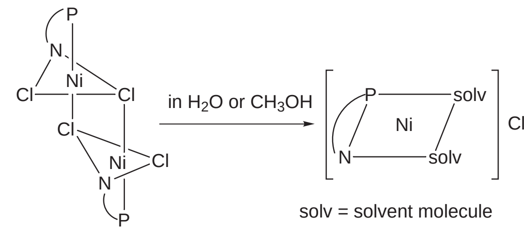
The complexes investigated are listed in Table 2 along with their analytical and ^{31}P NMR data. Divalent metal complexes were readily prepared by reaction of the metal halides with the ligands in ethanol. The cobalt(III) complexes were obtained by the ligand substitution of $[Co(acac)_3]$ with PN$^{\rm I}$ and PN$^{\rm II}$ 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 ^{1}H NMR spectra of all the 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 methylene (CH_2) 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.

The co-ordination of the tertiary phosphine in complexes is also evidenced from their ^{31}P NMR chemical shift (Δ) values. Upon co-ordination the peak shifted downfield (≈40–70 ppm) compared to those of the "free" ligands.

Complex **1** is high spin having an effective magnetic moment (24 °C) of 3.0 μ_B in the solid state. The solid state electronic spectrum is not as expected for either tetrahedral or spin free six-co-ordinated nickel(II) complex. It is instead very similar to the spectra of other high-spin nickel(II) complexes. The lower magnetic moment and the spectrum pattern indicate that this complex has an intermediate structure between the trigonal bipyramidal and square pyramidal.[12] A mass spectral analysis (FAB$^+$) of this complex in nitromethane showed several peaks in the range of *m*/*z* 600–800, which are higher than that expected for the monomer. Therefore, a dimeric structure involving bridging chlorides is proposed (Scheme 2). A similar bridging structure has also been proposed for some nickel(II) complexes of other P–N ligands.[13,14]

This complex is almost insoluble in non-polar solvents, however highly soluble in water and methanol. It underwent a dramatic change from purple to yellow when dissolved in water or methanol, which corresponds to dissociation of the dimer to a diamagnetic planar monomer. A planar structure was confirmed from its electronic spectra in water and methanol. The molar conductivity of a 10^{-3} mol dm^{-3} water solution shows 1:2 electrolyte behavior ($\Lambda_M = 211\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$). Therefore the planar species is ionic rather than neutral. The most probable form of the complex is [Ni(PN$^{\rm I}$)(solv)$_2$]Cl$_2$ (solv = solvent molecule) where the two solvent molecules are co-ordinated to the metal (Scheme 2) and the chloride ions acted as counter ions.



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

The phenomena of paramagnetic five-co-ordination in the solid state and diamagnetic planar four-co-ordination in the solution state are quite rare. To the best of our knowledge there is only one example, [NiCl$_2$(PNP)] [PNP = 2,6-bis-(2-diphenylphosphinoethyl)pyridine], which is five-co-ordinated in the solid state and four-co-ordinated diamagnetic planar in ethanol solution.[15]

On addition of diethyl ether to the methanolic solution of complex **1** a brownish precipitation was formed immediately. The isolated complex is highly unstable and is soon converted into an oil. When the precipitation was kept along with solvents

Table 2 Analytical and ^{31}P NMR data of complexes

Complex	Color	Analysis[a] (%) H	C	N	δ(^{31}P)
1 [NiCl$_2$(PN$^{\text{I}}$)]	Purple	4.29(4.18)	49.68(49.81)	6.70(6.83)	44.60[b]
2 [Ni(PN$^{\text{I}}$)$_2$][BF$_4$]$_2$·0.5H$_2$O	Yellow	4.37(4.39)	50.93(50.92)	6.83(6.98)	43.45[c]
3 [NiCl$_2$(PN$^{\text{II}}$)]	Red	6.11(6.19)	38.74(38.64)	8.30(8.19)	66.74[c]
4 [Ni(PN$^{\text{II}}$)$_2$][BF$_4$]$_2$·1.5H$_2$O	Orange	6.27(6.63)	38.62(38.64)	8.23(8.19)	57.83[c]
5 [CoCl$_2$(PN$^{\text{I}}$)]·H$_2$O	Blue	4.23(4.47)	48.11(47.69)	6.52(6.54)	—
6 [CoCl$_2$(PN$^{\text{II}}$)]	Blue	6.10(6.18)	38.51(38.61)	8.28(8.18)	—
7 [CoBr$_2$(PN$^{\text{II}}$)]	Blue	4.84(4.91)	30.70(30.65)	6.59(6.49)	—
8 [Co(acac)$_2$(PN$^{\text{I}}$)]ClO$_4$	Violet	4.86(4.90)	50.73(50.91)	4.40(4.39)	28.23[d]
9 [Co(acac)$_2$(PN$^{\text{II}}$)]ClO$_4$	Violet	6.12(6.20)	44.42(44.34)	5.00(4.92)	67.32[d]

[a] Calculated values in parentheses. [b] In CD$_3$OD. [c] In CD$_3$CN. [d] In CDCl$_3$.

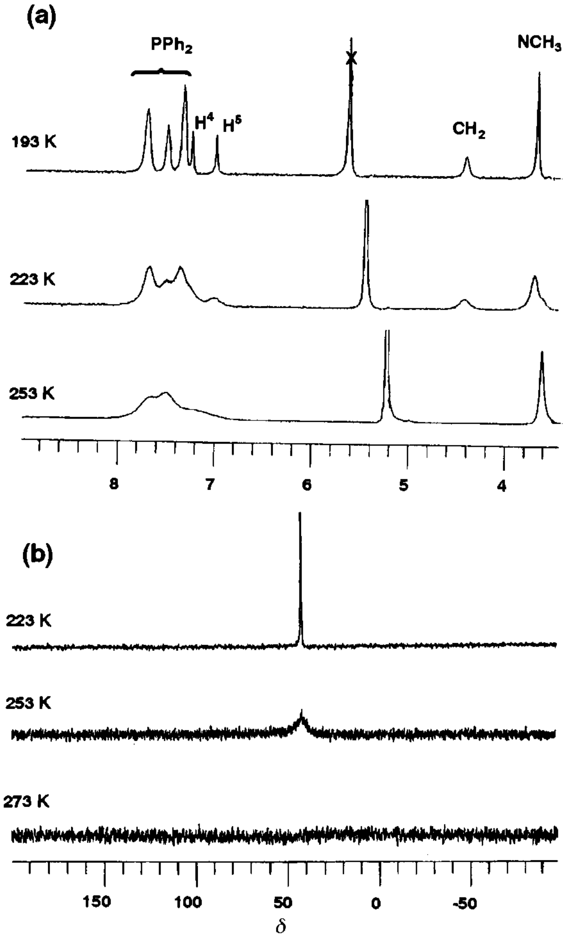


Fig. 2 Variable temperature (a) ^{1}H and (b) ^{31}P NMR spectra of complex **1** in CD$_3$OD.

it gradually returned to the original purple complex within a few minutes. This transformation process was more rapid upon vigorous shaking. However, when diethyl ether was added at solid CO$_2$ temperature a brownish orange precipitation occurred which did not change over a long period of time (3 h) when it was kept along with solvents at this temperature. If it was kept in a refrigerator at −10 °C the precipitation changed to black tarry masses. We believe this transient species contains two molecules of methanol in its co-ordination sphere. No further characterizations were made for this species. The conversion from a brownish into a purple complex seems to be an anation reaction which is highly dependent on temperature like that of [Co(NH$_3$)$_5$(H$_2$O)]Cl$_3$ to give [CoCl(NH$_3$)$_5$]Cl$_2$.

Complex **3** is diamagnetic planar in the solid state and its chloride ions are replaced by water or methanol giving diamagnetic planar species similar to that of complex **1** ($\Lambda_M = 244\ \Omega^{-1}$ cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} water solution). The same type of halide-co-ordinated planar structure in the solid state has also been reported for another P–N ligand.[16]

The diamagnetic square-planar species **1** and **3** 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 donor.

We found complex **2** 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)$_2$][ClO$_4$]$_2$ [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.[17] This observation suggests that the donor ability of alkylated imidazole is stronger than that of pyridine.

The ^{1}H NMR spectra of complexes **8** and **9** exhibit two signals with an intensity equal to one hydrogen for the methylene (CH$_2$) protons of the PN ligands (δ 4.18 and 4.62 for **8** and 3.66 and 3.81 for **9**), indicating that the two hydrogen atoms of methylene group are magnetically inequivalent.

Solution behaviors of complexes 1 and 2

The solution behaviors of complexes **1** and **2** were studied by ^{1}H and ^{31}P NMR spectroscopy in CD$_3$OD and CD$_3$CN respectively at various temperatures. The variable temperature NMR studies gave interesting information about the dynamic behavior of these two complexes in solution.

The ^{1}H NMR spectrum of complex **1** in the temperature range 323–253 K showed only broad signals for the NCH$_3$ and PPh$_2$ groups. The methylene (CH$_2$), H^4 and H^5 protons were not detectable. At 223 K, however, they appeared as broad signals. At 193 K distinct sharp signals appeared for all protons. In the case of the ^{31}P NMR spectrum at 273 K there is no signal for the phosphorus nucleus. At 253 K a very broad signal appeared and it became sharper at 223 K. The variable temperature ^{1}H and ^{31}P NMR spectra of **1** are presented in Fig. 2. The ^{1}H and ^{31}P NMR spectra of complex **2** in CD$_3$CN also showed similar behaviors. At 297 K the ^{1}H NMR spectrum exhibited only broad signals for NCH$_3$ and PPh$_2$ groups. At 263 K the three peaks for methylene (CH$_2$), H^4 and H^5 protons appeared as broad signals, which became considerably sharper at 243 K. In the ^{31}P NMR spectrum a very broad signal appeared at room temperature. On cooling the signal became sharp. The broad NMR signals have also been observed at higher than room temperature (323 K) for both complexes. These observations suggest the presence of dynamic motion in these two complexes on a timescale comparable to that of NMR.

The electronic spectra of these two complexes in MeOH and MeCN respectively at room temperature did not show any absorption bands for tetrahedral species. Therefore, we can rule

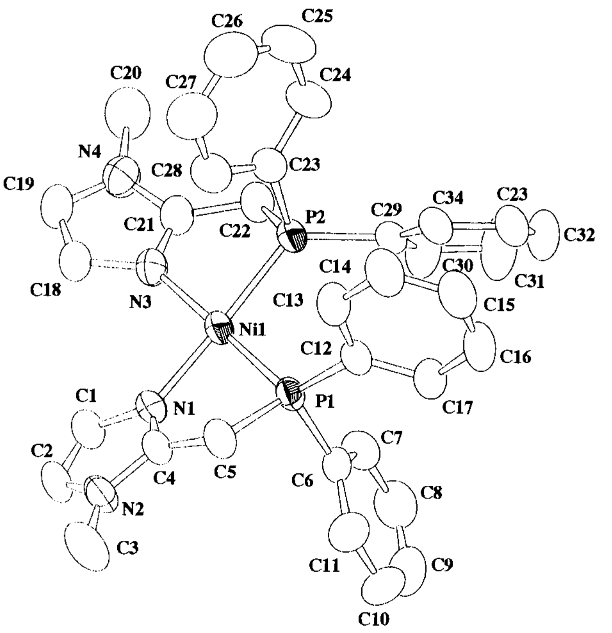


Fig. 3 An ORTEP drawing of the cation of the complex **2**.

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Ni1–P1	2.180(1)	P2–C22	1.834(5)
Ni1–P2	2.176(1)	P2–C23	1.800(5)
Ni1–N1	1.929(4)	P2–C29	1.804(4)
Ni1–N3	1.937(4)	N1–C4	1.332(6)
P1–C5	1.831(5)	N3–C21	1.321(7)
P1–C6	1.817(4)	C4–C5	1.475(7)
P1–C12	1.808(4)	C21–C22	1.481(7)
P1–Ni1–P2	99.12(5)	C5–P1–C6	106.3(2)
P1–Ni1–N1	83.0(1)	C5–P1–C12	105.6(2)
P1–Ni1–N3	175.7(1)	C6–P1–C12	107.1(2)
P2–Ni1–N1	177.7(1)	Ni1–P2–C22	100.4(2)
P2–Ni1–N3	81.9(1)	Ni1–P2–C23	109.9(2)
N1–Ni1–N3	96.0(2)	Ni1–P2–C29	126.7(2)
Ni1–P1–C5	99.0(2)	C22–P2–C23	103.7(2)
Ni1–P1–C6	112.9(1)	C22–P2–C29	105.8(2)
Ni1–P1–C12	124.0(2)	C23–P2–C29	107.7(2)

out the possibility of tetrahedral–square planar equilibria which are observed in some phosphine nickel(II) complexes.[18]

Therefore, the most probable dynamic motion is a δ and λ conformational change of five membered P–N chelate ring(s).

The similar nickel(II) complexes **3** and **4** of the PN^{II} ligand did not show any dynamic motion over the temperature range 233–323 K.

Structures of complexes 2 and 4·MeCN

An ORTEP view of the cation of complex **2** is shown in Fig. 3. Selected bond distances and angles are given in Table 3. Both N and P atoms of the ligand are co-ordinated to the metal, forming a 5-membered chelate ring. The geometry of the nickel atom is approximately square planar with the two phosphorus atoms in a *cis* configuration and the bond angles around the nickel ranging from 81.9(1) to 99.12(5)° and summing to about 360°. Usually aryl substituted phosphines promote stabilization of *cis* isomers.[19] This configuration avoids placing two ligands of high *trans* influence[20] opposite to each other, and also prevents *trans* arrangments of strongly π-bonding ligands, where they would compete for use of the same metal d orbital. Steric repulsion between the two bulky *cis*-PPh$_2$ groups causes a significant deviation of the P1–Ni–P2 angle [99.12(5)°] from the ideal angle (90°).

An ORTEP view of the cation of complex **4**·MeCN is shown in Fig. 4. Selected bond lengths and angles are given in Table 4.

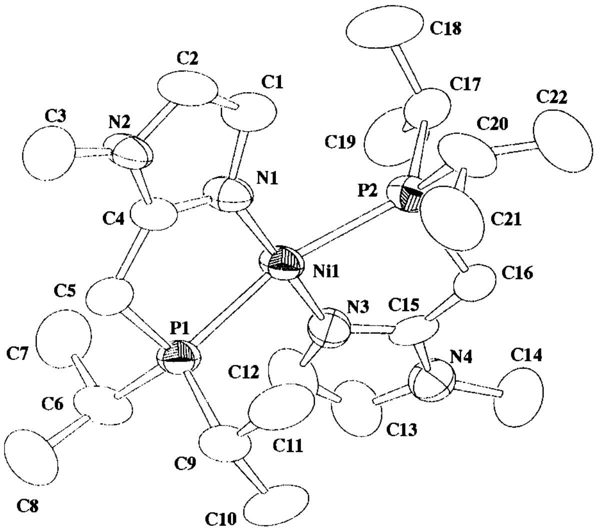


Fig. 4 An ORTEP drawing of the cation of the complex **4**·MeCN.

Table 4 Selected bond lengths (Å) and angles (°) for complex **4**·MeCN

Ni1–P1	2.249(4)	P2–C16	1.84(1)
Ni1–P2	2.266(4)	P2–C17	1.85(1)
Ni1–N1	1.897(8)	P2–C20	1.84(1)
Ni1–N3	1.877(9)	N1–C4	1.34(1)
P1–C5	1.85(1)	N3–C15	1.34(1)
P1–C6	1.83(1)	C4–C5	1.48(2)
P1–C9	1.82(1)	C15–C16	1.46(2)
P1–Ni1–N1	84.4(3)	C5–P1–C6	104.4(6)
P1–Ni1–N3	95.1(3)	C5–P1–C9	105.1(5)
P2–Ni1–N1	98.2(3)	C6–P1–C9	106.9(6)
P2–Ni1–N3	83.3(3)	Ni1–P2–C16	97.3(4)
P1–Ni1–P2	161.7(1)	Ni1–P2–C17	120.3(4)
N1–Ni1–N3	176.5(4)	Ni1–P2–C20	122.1(4)
Ni1–P1–C5	102.7(4)	C16–P2–C17	104.2(5)
Ni1–P1–C6	125.0(4)	C16–P2–C20	105.4(6)
Ni1–P1–C9	110.7(4)	C17–P2–C20	104.6(6)

The geometry of the nickel atom is approximately square planar with two phosphorus atoms in a *trans* configuration and the bond angles around nickel ranging from 83.3(3) to 98.2(3)° and summing to about 361°. This configuration might be due to the steric bulkiness of the isopropyl group in the PN^{II} ligand. Complexes [MX$_2$L$_2$] (L = phosphine ligand) with particularly bulky ligands[21] are usually only found as *trans* isomers.[22] Steric repulsion between a *cis*-imidazole ring and a PPr$^i_2$ group has also been observed and it causes a deviation of the P1–Ni1–N3 [95.1(3)°] and P2–Ni1–N1 [98.2(3)°] angles from the ideal angle (90°). To the best of our knowledge this is the first example of a [Ni(PN)$_2$]$^{2+}$ type complex containing a P–N ligand having a *trans* configuration as revealed by X-ray analyses.

The average M–P bond distance is 0.08 Å longer (2.26 *vs.* 2.18Å) in complex **4**·MeCN than in **2**. This is due to the *trans* effect of phosphine. For the same reason, in complex **2** the average Ni–N bond distance is 0.05 Å longer compared to that in **4**·MeCN.

Electronic spectra

The electronic spectral data are in the Experimental section. The electronic spectrum of complex **1** in water or methanol solution showed an absorption band around 405 nm (log ε ≈ 2.25). Other nickel(II) complexes **2**, **3** and **4** also showed similar absorption bands around 400–500 nm, which is typical of those of low-spin square planar nickel(II) complexes. It is assigned to the d–d transition $^1A_1 \longrightarrow {}^1B_2$ for a square-planar d^8 complex.

The spectra of cobalt(II) complexes **5**, **6** and **7** showed intense bands around 500–700 nm (log ε ≈ 2.7), which are characteristic of tetrahedral cobalt(II) complexes. These have their origin in the $^4A_2 \longrightarrow {}^4T_1$ (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.[23]

The spectra of the cobalt(III) complexes showed a d–d transition in the visible region. Those of **8** and **9** appeared around 500–540 nm. The spectral features confirmed the octahedral geometry of these complexes. Comparison of the electronic spectra of complexes **8** and **9** with that of a complex of ethylenediamine,[24] $[Co(acac)_2(en)]^+$, leads the relative position of these two ligands in the spectrochemical series, PN^{II} (19500) > PN^I (18700) ≈ en (18600 cm^{-1}).

Conclusion

Two new bidentate P–N chelate ligands containing an imidazolyl group have been successfully 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 $[NiL_2]^{2+}$ type complexes. The present study also shows that alkylated imidazolylphosphine ligands have better donor abilities than related pyridylphosphine ligands. Variable temperature NMR studies of the nickel(II) complexes **1** and **2** showed the presence of dynamic motions of their P–N chelate ring(s) in solution.

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 $[Co(acac)_3]$ was prepared according to literature procedures.[25]

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 and sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) for D_2O and ^{31}P to 85% H_3PO_4 sealed in a melting point capillary tube. 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. Molar conductivity was measured by a TOA CM-30V conductivity meter. Elemental analyses were performed by the Faculty of Pharmaceutical Science, Kanazawa University. X-Ray measurements were made on a Rigaku AFC7R diffractometer or Rigaku Raxis-IV imaging plate area detector.

Preparations

$MeImCH_2SiMe_3$. To a stirred solution of 1,2-dimethylimidazole (100 mmol, 9.6 g) in THF (300 ml) was added 2.5 M *n*-butyllithium in hexane (100 mmol, 40 ml) at −78 °C. After 3 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. After 1 h the mixture was warmed slowly to 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 110 °C at 15 mmHg). Yield 14.30 g (85%). ^1H NMR ($CDCl_3$): δ 0.0 (s, 9 H, $SiMe_3$), 2.02 (s, 2 H, CH_2), 3.41 (s, 3 H, NCH_3), 6.62 (d, 1 H, H^5) and 6.78 (d, 1 H, H^4). If the reaction was carried out at 0 °C the 5 position of the imidazole ring was silylated. ^1H NMR ($CDCl_3$): δ 0.00 (s, 9 H, $SiMe_3$), 2.10 (s, 3 H, CH_3), 3.29 (s, 3 H, NCH_3) and 6.68 (d, 1 H, H^4).

$MeImCH_2PPh_2{\cdot}HBr$ ($PN^I{\cdot}HBr$). To $MeImCH_2SiMe_3$ (20 mmol, 3.36 g) 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 −5 °C to give colorless crystals, which were filtered off, washed with ethanol–ether (1 : 4) and dried *in vacuo*. Yield 5.34 g (74%) (Found: C, 56.22; H, 5.08; N, 7.63. Calc. for $C_{17}H_{18}BrN_2P$: C, 56.52; H, 5.02; N, 7.75%). ^1H NMR (D_2O): δ 3.37 (s, 3 H, NCH_3), 3.74 (d, 2 H, CH_2), 7.07 (d, 1 H, H^5), 7.10 (d, 1 H, H^4) and 7.32–7.41 (m, 10 H, Ph).

Free PN^I 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^I as a colorless oil. ^1H NMR ($CDCl_3$): δ 3.30 (s, 3 H, NCH_3), 3.43 (d, 2 H, CH_2), 6.65 (d, 1 H, H^5), 6.88 (d, 1 H, H^4) and 7.27–7.44 (m, 10 H, Ph). ^{31}P NMR ($CDCl_3$): δ −15.54 (s).

$MeImCH_2PPr^i_2$ (PN^{II}). To $MeImCH_2SiMe_3$ (20 mmol, 3.36 g) 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 100 °C. The pure product was obtained by distillation of the remaining oil, bp 80 °C at 1 mmHg. Yield 3.22 g (76%). ^1H NMR ($CDCl_3$): δ 0.76–0.91 (m, 12 H, CH_3 of Pr^i), 1.45–1.57 (m, 2 H, CH of Pr^i), 2.59 (d, 2 H, CH_2), 2.96 (s, 3 H, NCH_3), 6.28 (d, 1 H, H^5) and 6.86 (d, 1 H, H^4). ^{31}P NMR ($CDCl_3$): δ 1.37 (s).

$[NiCl_2(PN^I)]$ 1. An ethanolic solution (10 ml) of PN^I (1 mmol, 0.28 g) was added with stirring to a solution of $NiCl_2{\cdot}6H_2O$ (1 mmol, 0.23 g) in ethanol (20 ml) at ambient temperature. After 20 min ethanol was removed by evaporator and acetone added. The purple crystals precipitated were filtered off, washed with cold ethanol and dried *in vacuo*. Yield 0.30 g (74%). ^1H NMR (CD_3OD): δ 3.70 (s, 3 H, NCH_3), 4.45 (br, 2 H, CH_2), 7.03 (s, 1 H, H^5), 7.28 (s, 1 H, H^4) and 7.37–7.74 (m, 10 H, Ph). λ_{max}/nm (water) 402 (log ε 2.25) and (MeOH) 406 (log ε 2.20).

$[Ni(PN^I)_2][BF_4]_2{\cdot}0.5H_2O$ 2·$0.5H_2O$. An ethanolic solution (20 ml) of $Ni(BF_4)_2{\cdot}6H_2O$ (1 mmol, 0.31 g) was added with stirring to an ethanolic solution (10 ml) of PN^I (2 mmol, 0.56 g) at ambient temperature. The complex precipitated after 20 min, was filtered off, washed with ethanol and dried *in vacuo*. Yield 0.77 g (96%). ^1H NMR (CD_3CN): δ 3.60 (s, 3 H, NCH_3), 4.07 (br, 2 H, CH_2), 6.90 (br, 1 H, H^5), 7.17 (br, 1 H, H^4) and 7.38–8.06 (m, 10 H, Ph). λ_{max}/nm (MeCN) 412 (log ε 2.43).

$[NiCl_2(PN^{II})]$ 3. This complex was prepared in a similar manner to that of **1** using metal salts $NiCl_2{\cdot}6H_2O$ (1 mmol, 0.23 g) and PN^{II} (1 mmol, 0.21 g). The complex precipitated from the concentrated ethanolic solution. Yield 0.276 g (81%). ^1H NMR (CD_3CN): δ 1.40 (m, 6 H, CH_3 of Pr^i), 1.60 (m, 6 H, CH_3

Table 5 Crystallographic data of PN^{I}·HBr and complexes **2** and **4**·MeCN

	PN^{I}·HBr	**2**	**4**·MeCN
Empirical formula	$C_{17}H_{18}BrN_2P$	$C_{34}H_{34}B_2F_8N_4NiP_2$	$C_{24}H_{45}B_2F_8N_5NiP_2$
M	361.22	792.92	697.91
Crystal dimensions/mm	0.20 × 0.20 × 0.50	0.46 × 0.21 × 0.43	0.1 × 0.25 × 0.25
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a/Å	8.599(3)	13.674(5)	20.688(8)
b/Å	21.030(4)	16.03(1)	9.975(2)
c/Å	9.690(3)	9.405(7)	17.100(4)
α/°	—	104.21(6)	—
β/°	95.16(3)	109.78(4)	104.70(4)
γ/°	—	89.68(4)	—
U/Å^3	1745.2(9)	1874(2)	3413(1)
Z	4	2	4
μ(Mo-Kα)/cm^{-1}	24.49	6.73	7.29
T/°C	23.0	24.0	24.0
Number of reflections (total)	4395	8912	4293
(unique)	4133	8604	—
R_{int}	0.021	0.038	—
R, R'	0.031, 0.052	0.072, 0.109	0.059, 0.072

of Pr^i), 2.73 (m, 2 H, CH of Pr^i), 2.87 (d, 2 H, CH_2), 3.54 (s, 3 H, NCH_3), 6.99 (d, 1 H, H^5) and 7.23 (d, 1 H, H^4). λ_{max}/nm (CH_2Cl_2) 506 and 322 (log ε 2.62 and 3.52).

[Ni(PN^{II})$_2$][BF$_4$]$_2$·1.5H$_2$O 4·1.5H$_2$O. A solution of Ni(BF_4)$_2$·6H_2O (1 mmol, 0.31 g) in ethanol (20 ml) was added with stirring to a solution of PN^{II} (2 mmol, 0.42 g) in ethanol (10 ml). The crystals separated during addition. After filtration they were washed with ethanol and dried *in vacuo*. Yield 0.635 g (93%). ^{1}H NMR (CD_3CN): δ 1.26 (m, 12 H, CH_3 of Pr^i), 2.45 (m, 2 H, CH of Pr^i), 3.22 (d, 2 H, CH_2), 3.67 (br, 3 H, NCH_3), 6.53 (br, 1 H, H^5) and 7.08 (br, 1 H, H^4). λ_{max}/nm (MeCN) 432 and 323 (log ε 2.86 and 3.77).

[CoCl$_2$(PN^I)]·H$_2$O 5. An ethanolic solution (10 ml) of PN^I (1 mmol, 0.28 g) was added with stirring to a solution of $CoCl_2$·6H_2O (1 mmol, 0.24 g) 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 0.40 g (94%). λ_{max}/nm (CH_2Cl_2) 660, 575 and 332 (log ε 2.5, 2.14 and 2.27).

[CoCl$_2$(PN^{II})] 6. This complex was prepared from $CoCl_2$·6H_2O (1 mmol, 0.23 g) and PN^{II} (1 mmol, 0.21 g) in a similar manner to that described for **5**. The blue crystals were separated during addition. After filtration they were washed with ethanol and dried *in vacuo*. Yield 0.29 g (89%). λ_{max}/nm (CH_2Cl_2) 680, 648 and 554 (log ε 2.72, 2.59 and 2.38).

[CoBr$_2$(PN^{II})] 7. This complex was prepared from $CoBr_2$·6H_2O (1 mmol, 0.32 g) and PN^{II} (1 mmol, 0.21 g) in a similar manner to that described for **5**. The blue crystals separated during mixing. After filtration they were washed with ethanol and dried *in vacuo*. Yield 0.365 g (85%). λ_{max}/nm (CH_2Cl_2) 693, 668, 582 and 314 (log ε 2.76, 2.71, 2.45 and 3.37).

[Co(acac)$_2$(PN^I)]ClO$_4$ 8. The complex [Co(acac)$_3$] (2 mmol, 0.71 g) and PN^I·HBr (2 mmol, 0.72 g) were dissolved in methanol (100 ml) to which Et_3N (2 mmol, 0.30 ml) was added and stirred for 8 h in the presence of charcoal at 0 °C. A violet solution formed. Then 70% perchloric acid (2.2 mmol, 0.2 ml) was added followed by stirring for 30 min. Charcoal was filtered off and the methanol evaporated. The residue was then chromatographed on alumina. Gradient elution with acetone gave a violet band which was collected and concentrated. The desired complex was obtained by addition of ether. Yield 0.86 g (68%). ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 3 H, CH_3 of acac), 1.74 (s, 3 H, CH_3 of acac), 1.99 (s, 3 H, CH_3 of acac), 2.40 (s, 3 H, CH_3 of acac), 4.05 (s, 3 H, NCH_3), 4.18 (m, 1 H, CH_2), 4.62 (m, 1 H, CH_2), 5.01 (s, 1 H, CH of acac), 5.50 (s, 1 H, CH of acac), 6.81 (d, 1 H, H^5), 7.00 (d, 1 H, H^4), 7.53–7.64 (m, 8 H, Ph) and 8.03–8.09 (m, 2 H, Ph). λ_{max}/nm (Me_2CO) 536 (log ε 2.7).

[Co(acac)$_2$(PN^{II})]ClO$_4$ 9. The compound PN^{II} (2 mmol, 0.42 g) was added to a stirring solution of [Co(acac)$_3$] (2 mmol, 0.71 g) in methanol (100 ml) at 0 °C containing some charcoal and allowed to react for 8 h. Then 70% perchloric acid (2 mmol, 0.2 ml) 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 0.82 g (72%). ^{1}H NMR ($CDCl_3$): δ 0.95 (m, 6 H, CH_3 of Pr^i), 1.35 (m, 6 H, CH_3 of Pr^i), 1.6 (s, 3 H, CH_3 of acac), 1.8 (s, 3 H, CH_3 of acac), 1.9 (s, 3 H, CH_3 of acac), 2.2 (s, 3 H, CH_3 of acac), 3.80 (s, 3 H, NCH_3), 3.66 (m, 1 H, CH_2), 3.81 (m, 1 H, CH_2) 5.4 (s, 1 H, CH of acac), 5.5 (s, 1 H, CH of acac), 6.7 (d, 1 H, H^5) and 7.1 (d, 1 H, H^4). λ_{max}/nm (Me_2CO) 513 (log ε 2.47).

X-Ray crystallographic studies

Crystals of complexes **2** and **4**·MeCN suitable for X-ray diffraction study were grown by slow diffusion of diethyl ether into acetonitrile solutions of these complexes at −5 °C. All crystallographic data are summarized in Table **5**. Measurements of PN^I·HBr and **2** were performed on a Rigaku AFC7R diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å) at room temperature. Single crystals of them were mounted on glass fibers. The data were collected using an ω–2θ scan technique to a maximum 2θ value of 55° for PN^I·HBr and **2** at a scan speed of 16.0° min^{-1} (in ω). The weak reflections [$I < 10.0\sigma$(I)] were rescanned (maximum of 5 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection.

The crystal of complex **4**·MeCN readily lost its transparency when separated from the mother-liquor. Therefore, a single crystal was sealed in a capillary tube together with the mother-liquor and the measurement carried out by a Rigaku Raxis IV imaging plate area detector using graphite monochromated Mo-Kα radiation at room temperature. Crystal to detector distance 120 mm. In order to determine the cell constants and orientation matrix, three oscillation photographs were taken with oscillation angle 2° and exposure time 8 min for each frame. Intensity data were collected by taking oscillation photographs (total oscillation range 90°; 30 frames; oscillation angle 3°; exposure time 11 min).

The structures of PN^I·HBr and complex **2** were solved by a direct method[26] and that of **4**·MeCN by heavy-atom Patterson methods[27] and expanded using Fourier techniques.[28] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation but not refined. All calculations were performed using the TEXSAN[29] crystallographic software package. Complex neutral atom scattering factors were taken from ref. 30.

CCDC reference number 186/1379.

See http://www.rsc.org/suppdata/dt/1999/1655/ for crystallographic files in .cif format.

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