Synthesis of New Imidazole-based P,N-Ligands and Properties of Their Metal Complexes

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学 位 論 文 要 旨

Abstract

Various convenient and efficient synthetic methods for the preparation of new imidazole-based P,N chelating and bridging ligands have been developed. A good number of transition metal complexes of these ligands have been synthesized and characterized by various physico-chemical techniques including single crystal X-ray analyses. General observations arising from comparisons of these complexes indicate that the imidazolphosphine ligands are well suited to stabilizing all octahedral, tetrahedral and square-planar complexes with a variety of metal oxidation states. Steric properties of ligands have significant effect on the structure of the metal complexes. Some of these complexes also exhibit very unusual structures and properties. The experiment on the carbonyl insertion reactions of organopalladium complexes indicates that the insertion of CO to M-C bonds is highly influenced by the nature of the 3rd ligand that occupied at the *cis* position with respect to the coordinated organic ligand. The study also shows that the organic ligand always occupied the *trans* position with respect to the imidazole N-donor of the P-N ligands and afforded only a single product. A very convenient method for modification of the P-N ligands has been developed. In these method $Mo(0)(CO)_4$ complex of the P-N ligand has been used instead of the free ligand. Various functional as well as alkyl or aryl groups have been successfully introduced at the backbone of the P-N ligand. The two synthesized bridging ligands have been found to be very effective to bind two metal ions into close proximity and in some cases afforded complexes with unusual structures.

Introduction

Metal complexes with hybrid ligands containing P and N donor atoms are of increasing interest for their ability to act as hemilabile ligands. They also can give rise to selective metal-ligand interactions that may control the reactivity at the metal site owing to the different electronic properties of the donor atoms. These particular objectives are driven by the potential application of these species in catalysis.

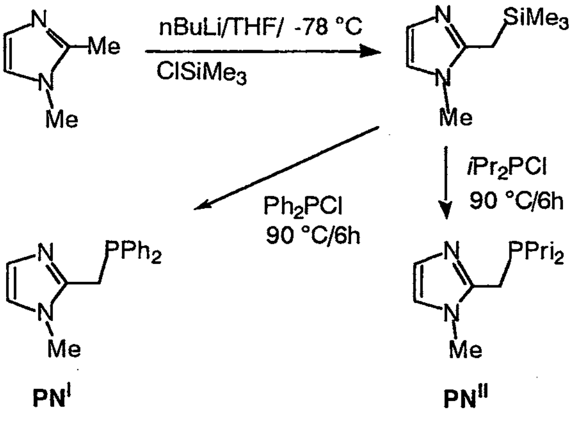
On the other hand, bridging P-N ligands are excellent candidates for the preparation of bimetallic complexes. Complexes comprised of more than one metal center in close proximity might exhibit different properties, compared to the monometallic fragments that constitute them: cooperative reactivity patterns, stabilization of unusual ligands coordination modes, higher catalytic activity or different selectivity than the corresponding mononuclear moieties.

Various P-N ligands containing different N-donor groups have been reported but the imidazole-based P-N ligands have not been reported yet. Therefore we have taken plan to develop this new P-N ligand system. Imidazoles are both interesting ligands and biochemical molecules. Thus, it is of great value to develop such imidazole-based P-N ligand system and examine their coordination behaviors and catalytic properties.

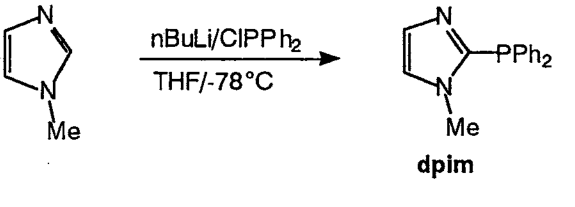
Results and discussion

The synthetic methods for the preparation of chelating and bridging imidazolylphosphine ligands are depicted in Scheme 1-4.

Scheme 1



Scheme 2

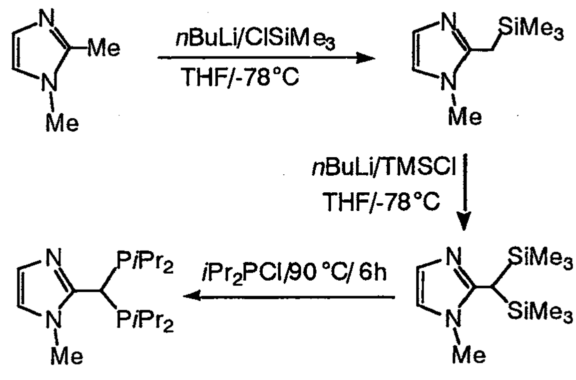


We found that the use of silylated-methylimidazole has an advantage in the preparations of chelating PN^{I} and PN^{II} ligands. When the lithiated-imidazole and chlorophosphine were allowed to react directly by escaping the silylation step, a messy product was obtained. This is due to the susceptibility of the heterocyclic organometalics to side reactions. However, the silylation does not have significant effect in the preparation of the bridging 'dpim' ligand where the phosphine donor directly bonded to the imidazole ring.

We also have developed a very facile one pot reaction for the preparation of chelating P-N ligands by using diols as the starting materials (Scheme 4). This method also allowed us to prepare chiral P-N ligands by simply using the optically active diols. The coordination and catalytic properties of these ligands are presently being investigated.

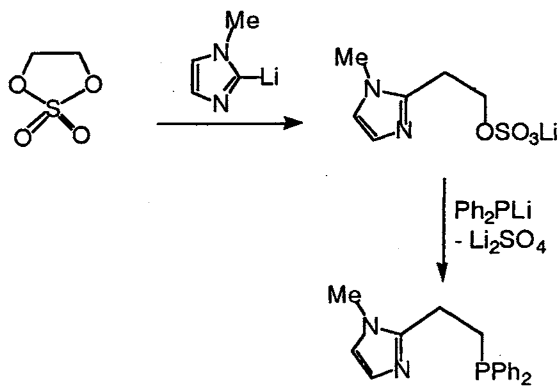
We have prepared a variety of new 1st transition metal complexes by using these chelating PN[I] and PN[II] ligands. Crystallographic studies have amassed a body of structural data. General observations arising from comparisons of these complexes indicate that these chelating P-N ligands are well suited to stabilizing all octahedral, tetrahedral and square-planar complexes with a variety of metal oxidation states and their sizes. The structures of the metal complexes are highly influenced by the steric and electronic properties of the ligands. For instance, the structures of the two nickel complexes of PN[I] and PN[II], $[Ni(PN^I)_2](BF_4)_2$ **1** and $[Ni(PN^{II})_2](BF_4)_2$ **2**, are similar but their configurations are quite different. In the first one, the two phosphorus atoms occupied the *cis*-position whereas, in the latter one, the two phosphorus atoms occupied the *trans* position (Figure 1). Some complexes of these imidazolphosphine ligands exhibited very unusual and interesting properties which have not been observed previously in the complexes of other P-N ligands. For instance, the complex $[Ni(PN^I)Cl_2]$ **3** adopts a five coordinate dimeric structure with chloride bridges in solid state and a monomeric square-planar structure in water and in methanole (Scheme 5). It underwent a dramatic color change from purple to yellow when dissolved in water or methanol, which corresponds to dissociation of dimer to diamagnetic planar monomer. The phenomenon paramagnetic penta coodination in solid state and diamagnetic planar four coordination in solution state is quite rare.

Scheme 3



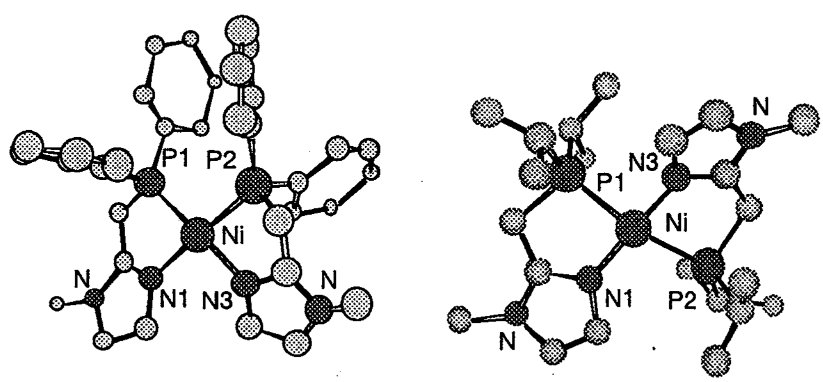
PPN

Scheme 4



PN[III]

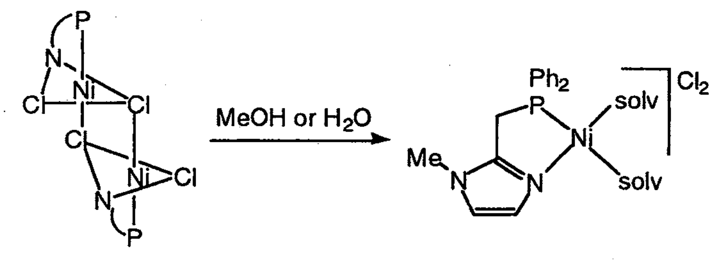
Figure 1



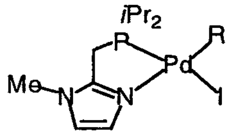
1 **2**

We also have prepared several neutral and cationic organopalladium complexes containing PN^{II} ligand and checked the feasibility of the carbonylation which is the first necessary step in many catalytic transformations. Neutral organopalladium complexes, [(PN^{II})PdPhI] **4** and [(PN^{II})PdMeI] **5** have been synthesized by oxidative addition of PhI and MeI respectively to [Pd(dba)$_2$] in presence the ligand. However, the cationic complexes [(PN^{II})PdPh(PPh$_3$)]BF$_4$ **6** and [(PN^{II})PdMe(PPh$_3$)]BF$_4$ **7** are obtained by adding an acetone solution of AgBF$_4$/PPh$_3$ to the corresponding neutral precursor **4** and **5** respectively. A cationic allyl complex, [(PN^{II})Pd(η^3-C$_3$H$_5$)]Br **8**, has also been prepared by an oxidative addition of 3-bromopropene to Pd(dba)$_2$ in presence of the ligand. In all complexes the organic ligands (phenyl or methyl) occupied the *trans* position in respect to the imidazole N-donor. The X-ray structures of **4** and **7** are depicted in Figures 2 and **8** is depicted in Figure 3. All the Pd-N bond distances are considerably shorter compared to those reported for P-N ligands complexes such as amino- and iminophosphine complexes.

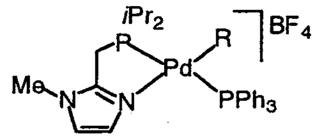
Scheme 5



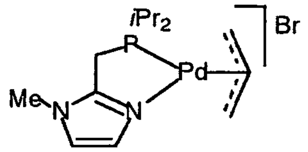
Purple (solid) orange (solution)



4 R = Ph
5 R = Me



6 R = Ph
7 R = Me



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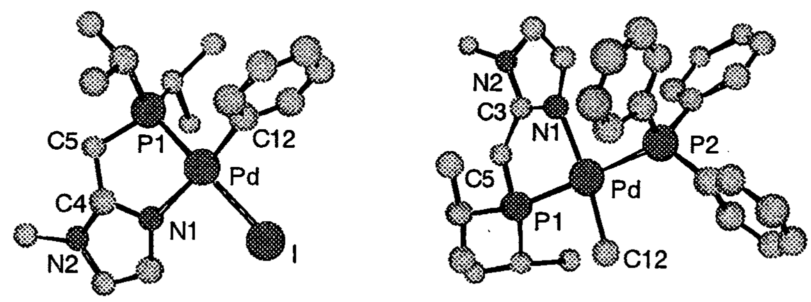
We found that the CO insertion to M-C bonds is highly influenced by the nature of the 3rd ligand that occupied at the *cis* position with respect to the coordinated organic ligand. The carbonyl insertion reaction for neutral complexes **4** is completed within about 4 h whereas it takes only 15 min for complex **5** and afford the corresponding carbonylated products [(PN^{II})Pd(C(O)Ph)I] **9** and [(PN^{II})Pd(C(O)Me)I] **10** respectively (eqn. 1).

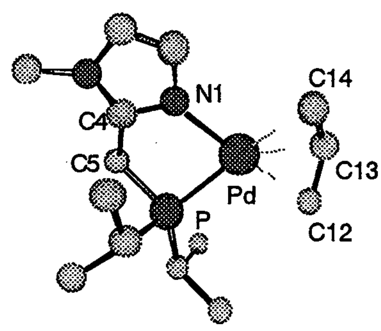
Figure 2



4 **7**

On the other hand, the carbonyl insertions into Pd-C bonds are not observed for cationic complexes **6** and **7** at normal condition even after prolonged reaction time. However, it is evident from the spectroscopic data that the imidazole N-donor of **6** is replaced by CO and afforded P-coordinated complex [(P-N)PdPh(PPh_3)(CO)]BF_4 **11** after keeping its CO-bubbled CD_2Cl_2 solution for about a week at -10 °C (eqn. 2). The relactance of these two complexes to carbonyl insertions is that of the strong binding nature of the PPh_3 ligand. It is well established that the cationic organopalladium complexes show enhanced reactivities toward carbonyl insertion when the *cis* position with respect to alkyl or aryl ligand is occupied by a weakly coordinating ligand.

Figure 3



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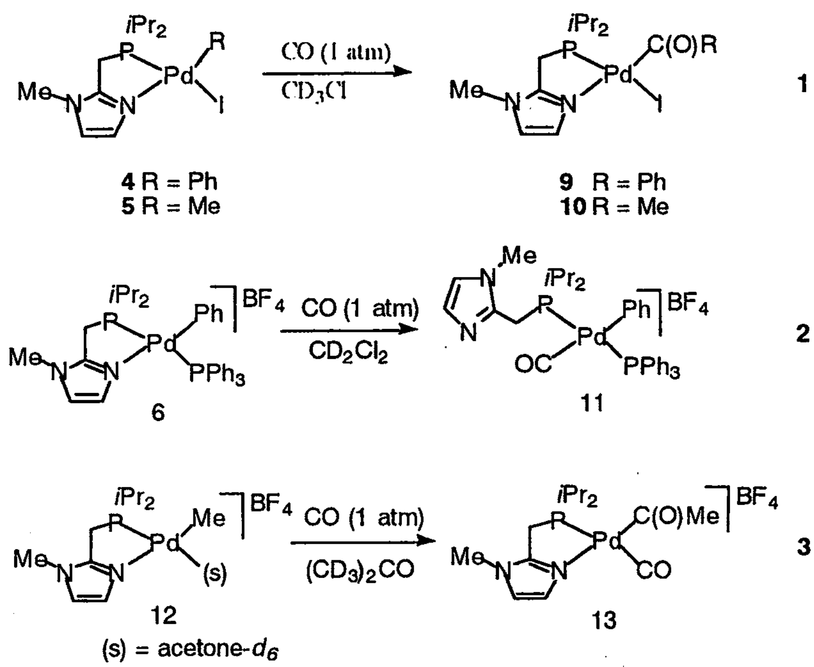
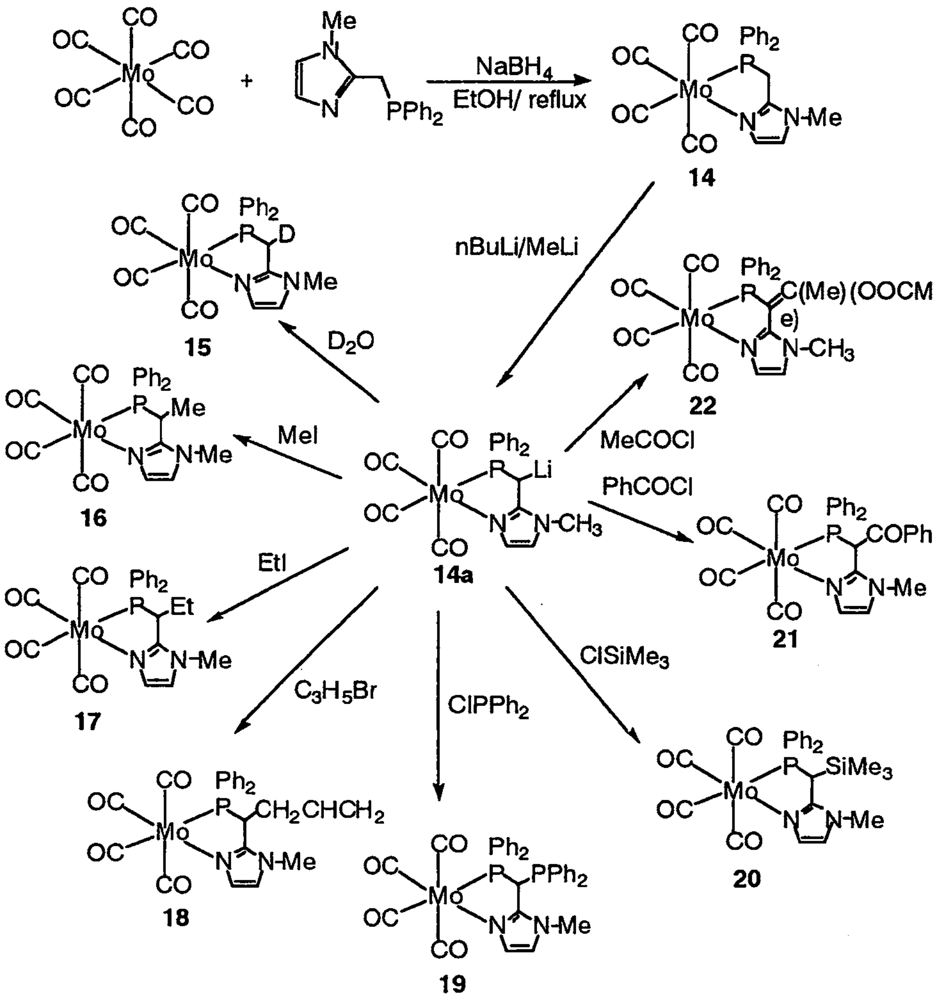
In order to clarify this choice of ligands for the carbonylation reaction we also prepared an acetone coordinated cationic complex [(PN^{II})PdMe{$(CD_3)_2CO$}]BF_4 **12** in an NMR tube by addition of equimolar or little excess $AgBF_4$ to an acetone-d_6 solution of complex **5**. The complex **5** reacts very fast with CO and affords acetyl derivative [(P-N)Pd{MeC(O)}(CO)]BF_4 **13** (eqn. 3).



Modification of phosphine ligands is very important for catalytic point of view because one can tune the electronic and steric properties of the ligand by choosing an appropriate substituents and may able to design the ligands for catalytic uses with maximum efficiencies. We developed a very facile method for modifications of our P-N ligand system where metal complexes have been used for reactions instead of free ligands. The advantage in using the metal complexes is that the reaction is very selective and mild. In some cases, this metal mediated reaction afforded the unexpected substituted products which could not be achieved by simple substitution reaction of the free ligands.

We used [$Mo(CO)_4(PN^I)$] **14** as a parent complex which was prepared in high yield by

Scheme 6

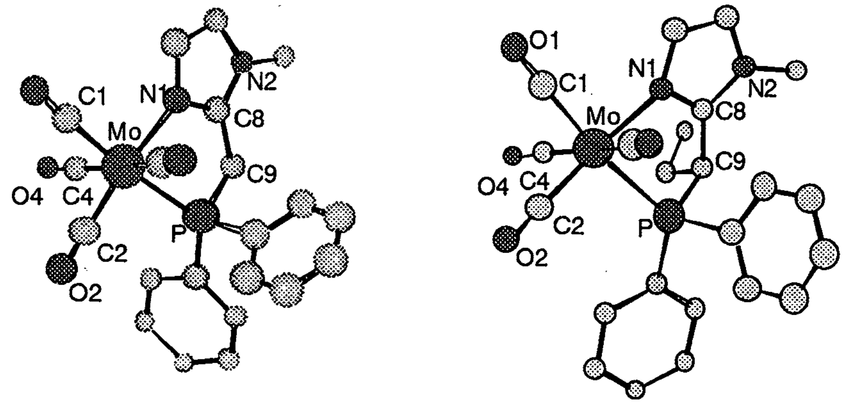


refluxing molybdenum hexacarbonyl, $Mo(CO)_6$, with the PN[I] ligand in ethanol in the presence of sodium borohydride. In the complex $[Mo(CO)_4(PN^I)]$ **14**, the PN[I] ligand is selectively deprotonated at its backbone methylene carbon by the action of n-butyllithium or methyllithium at room temperature to give the carbanion $[Mo(CO)_4(MeImCHPPh_2)]^-$ **14a**. The co-ordinated carbanion **14a** can react with various electrophiles to give selectively substituted derivatives in high yields (Scheme 6).

The carbanion **14a** readily reacted with deuterium oxide, methyl iodide, ethyl iodide, allyl bromide, and trimethylsilyl chloride to give $[Mo(CO)_4(MeImCHRPPh_2)]$ (R = D, **15**; Me, **16**; Et, **17**; $CH_2{=}CHCH_2$, **18** and $SiMe_3$, **20**). The crystal structures of the parent and the ethyl-substituted complexes are depicted in Figures 9 and 10. The structural differences of **14** from **16** can be ascribed to the larger steric bulk of the ethyl substituted PN[I] ligand. To minimize the steric interactions between the substituted ethyl group and the other parts of the ligand, the Mo-P and P-C bond distances slightly increased relative to those found for **14**.

We also have attached a variety of functional groups to the backbone carbon atom using this

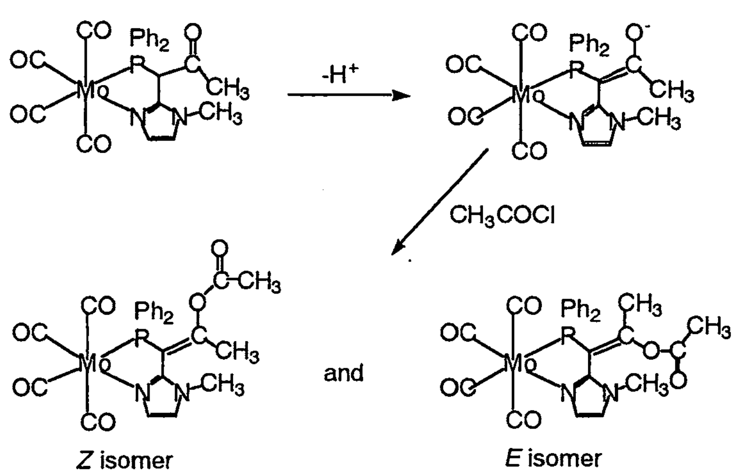
Figure 4



14 16

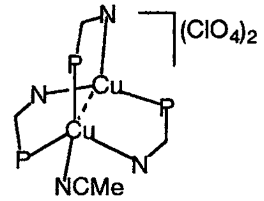
coordinated carbanion. When a solution of the carbanion **14a** was treated with chlorodiphenylphosphine the corresponding derivative **19** was obtained. For the preparation of the benzoyl derivative **21**, the carbanion **14a** should be reversibly added to benzoyl chloride. Normal addition of benzoyl chloride to the carbanion **14a** gave a mixture of complexes which we were unable to separate in pure form. We observed the formation of the O-acetyl enolate derivative **22** in 37% yield instead of an acetyl derivative when acetyl chloride was added slowly to a tetrahydrofuran solution of the carbanion **14a**. This reaction proceeds through an intermediate acetyl derivative. Therefore, slow addition of acetyl chloride to the carbanion **14a** afforded first an acetyl derivative, which readily converted to the enolate ion in the presence of excess unreacted carbanion **14a** in the reaction bulk. This enolate ion reacted with additional acetyl chloride to give the complex **22** (Scheme 7). The spectroscopic data show that the complex **22** exhibits in Z and E isomers (Scheme 7).

Scheme 7



The two bridging dpim and PPN ligands are very effective to hold two metal into very short proximity and afford a wide variety of dinuclear complexes. The structural feature of the ligand dpim is very similar to that of the 2-diphenylphosphinopyridine (dppy) but the steric and electronic properties are considerably different from those of the dppy. Imidazole has been found to be a poorer π-acceptor and better π-donor ligand compared to pyridine. E and C values for 1-methylimidazole suggest that it is a stronger base than pyridine with 'softer' properties. Hence, it is expected that the properties and structural features of complexes of the present ligand would be vary considerably from those of the dppy analogs.

Reaction of stoichiometric amount of the dpim with $[Cu(MeCN)_4]ClO_4$ in acetonitrile leads the binuclear complex $[Cu_2(\mu\text{-dpim})_3(MeCN)](ClO_4)_2 \cdot 2CH_3CN$ (**23**· $2CH_3CN$), whose structure has been determined by the single crystal X-ray analysis. The solid state structure shows that the two copper ions are held by three dpim ligands (Fig. 5). The coordination geometry around each metal atom is different, one being three- and the other four-coordinated. This structural type with higher number of bridging ligand is a rare example, probably due to the extensive crowding around the metal centers. Cu1 forms a distorted tetrahedral array with two P and one N atoms from the dpim ligand and to an additional N atom from an acetonitrile ligand. The other Cu atom, Cu2, is three coordinated being comprised with two N and one P atoms from dpim ligand.



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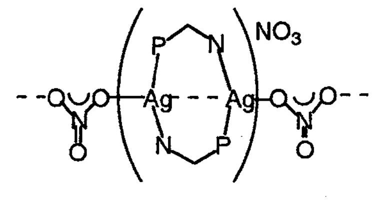

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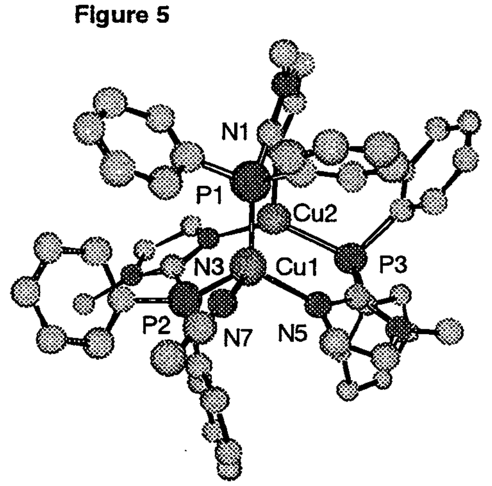
Reaction of dpim with $AgNO_3$ afforded a polymeric silver(I) complex, $\{[Ag_2(\mu\text{-dpim})_2(NO_3)](NO_3)\}_n$ **24**. The X-ray structure of this complex reveals that its structure is a polymeric linear chain consisting of $[Ag_2(\mu\text{-dpim})_2(NO_3)](NO_3)$ units having a crystallographic C_i symmetry (Fig. 6). The two Ag atoms doubly bridged by two ligands in a head-to-tail configuration. Two kinds of nitrate anions are presented in this complex: one makes an infinite polymeric chain by connecting the basic dimeric units in an anti-anti bridge-bonding mode through its two different oxygen atoms,[Ag-O 2.643 Å] while the other is disorderly arranges to the left and right sides of the polymeric chain with a -0.5 charge occupancy. Each silver atom is tricoordinated in a trigonal fashion. This structural feature is completely different from that of the dppy silver complex, $[Ag_2(NO_3)_2(\mu\text{-dppy})_2]$, which is a dinuclear complex. Variable temperature ^{31}P NMR of **24** in acetone indicates a ligand exchange process involving dissociation of Ag-P bonds.

Figure 5



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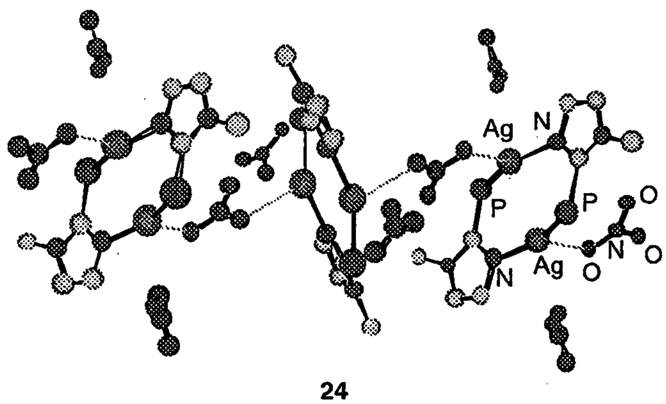
The binuclear palladium(I) complex $[Pd_2Cl_2(dpim)_2]$ **26** has been prepared by a conpropotion reaction between complex $[PdCl_2(dpim)_2]$ **25** and $[Pd(dba)_2]$ (dba = dibenzylideneaceton)

(Scheme 8). Only one geometric isomer, probably head-to-tail (HT), was formed in this reaction. Complex **25** has been prepared by treating $[PdCl_2(PhCN)_2]$ with two moles of ligand in dichloromethane solution. In this complex the ligand act as a *P*-monodentate. In solution it exists as a mixture of *cis* and *trans* isomers. Complex **26** does not give any ring opening product or A-frame complex with small organic molecules such as CO. However, the dppy-bridged palladium complex gives ring opening products with CO. This observation suggests that imidazolyl nitrogen is more strongly bound with metal ion than pyridine nitrogen.

Figure 6



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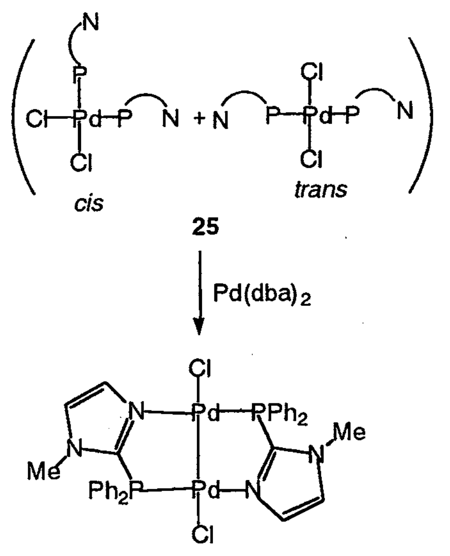
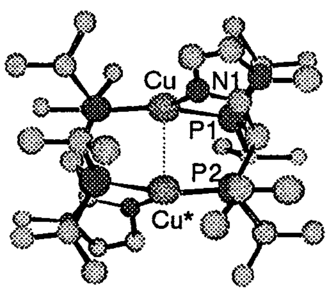
The ligand PPN is interesting because it is able to give bridged binuclear complexes of the well known face to face and A-frame type molecules. The dicationic dinuclear complex $[Cu_2(PPN)_2][ClO_4]_2$ **27** was prepared by reaction of the ligand with $[Cu(MeCN)_4]ClO_4$ in acetonitrile. The reaction of the ligand with $AgNO_3$ in propane-2-ol followed by addition of NH_4PF_6 led to formation of a similar type complex $[Ag_2(PPN)_2][PF_6]_2$ **28**. In these two complexes, the two metal ions are doubly bridged by two ligands and each of the ligand acts as a μ_2–η^1:η^2 tripod, being a P and N atoms chelate to one metal ion and the remaining one P donor binds to another metal ion afforded a face-to-face type molecule. An eight-membered $M_2P_4C_2$ ring and a ten-membered $M_2P_2N_2C_4$ ring may be identified in this unusual structure. The coordination core is approximately trigonal planar. The most striking feature of these two structures is the M···M, 2.671 Å for copper complex and 2.858(3) Å for silver complex, These two values are significantly shorter than those in related complexes of the ligand bis(diphenylphosphino)methane (dppm). To the best of our knowledge that each of these M···M separation, in binuclear copper(I) and silver(I) complexes, is the shortest one compared to those in the related complexes of other bridging phosphine or hybrid phosphine ligands

Scheme 8



Both of these two complexes exhibit dynamic behavior in solution which is established by variable temperature ^{31}P NMR. This dynamic motion is result from the exchange of the labile nitrogen donor of the ligand around the two metal centers.

Figure 7



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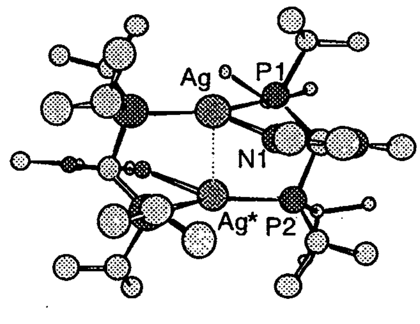

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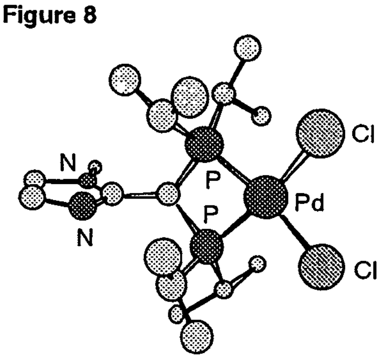
Beside these dinuclear complexes the ligand PPN was also gave a mononuclear palladium complex, [$PdCl_2$(PPN)] **29**, when it was treated with equimolar amount of [$PdCl_2(PhCN)_2$] in benzene. In **3** the ligand acts as a bidentate chelate through its two phosphorus atoms leaving the imidazole donor dangling. We also prepared a P,P-bridged dinuclear palladium(I) complex, [$Pd_2Cl_2(PPN)_2$]$\cdot$ 0.5$CHCl_3$ **30** by reacting two equivalent of PPN with one equivalent [$PdCl_2(PhCN)_2$] in tetrahydrofuran followed by addition of one equivalent palladium(0) complex, $Pd(dba)_2$.

Figure 8



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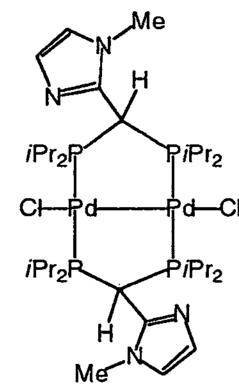

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Conclusion

We developed several new chelating and bridging P,N ligands containing an imidazole N-donor. A variety of mono- and binuclear metal complexes has been prepared by using these ligands. This new P-N ligand system is well suited to stabilizing all octahedral, tetrahedral and square-planar complexes with a variety of metal oxidation states and their sizes. In many cases, the properties and the structures of these complexes are significantly different from those of the complexes of other P-N ligands. We also developed a very convenient method for modifying the chalating imidazolylphosphine P-N ligands. The two bridging ligands are very effective to hold two metal ions into very close proximity and afford, in some cases, very unusual complexes.

学位論文審査結果の要旨

本論文に関し，平成13年1月15日に第1回学位審査委員会を開催し，口頭発表と面接審査を行った。さらに，2月5日に第2回審査会を開催し，口頭発表の後に協議した結果，以下のように判定した。

本論文は，イミダゾール(NIM)を含む種々のPR-NIM(Rはリン原子上の置換基)配位子を新規合成し，また触媒的な応用(カルボニル挿入反応，不斉触媒反応など)の面から重要視されている型の金属錯体も合成し，それらの構造や反応を調べたものである。研究成果は以下の通りである。

1) ニッケル(II)錯体の合成においては，$NiCl_2$ (PR－NIM (R＝C_6H_5または-C_3H_7)は，R＝C_6H_5のとき紫色，常磁性，5配位の二量体となるが，R＝i-C_3H_7のときは，赤色，反磁性，平面四配位錯体となる。上記二錯体の特徴は，水やメタノール等の溶媒に溶けて黄色の反磁性溶液となることである。特にR＝C_6H_5のときは，固体状態で5配位常磁性のものが溶液中で反磁性に変化する新奇なものであった。また$[Ni(PR-NIM)_2]^{2+}$型の平面四配位錯体では，X線結晶解析によりR＝C_6H_5でcis，R＝i-C_3H_7でtrans型で前者のNi-N結合距離は，他のP-Nのそれらより短いことが分かった。
2) コバルト(III)錯体の合成においては，他のP-N配位子よりも金属イオンに強い配位子場を与えていることが分かった。
3) Mo(O)錯体$[Mo(CO)_4(PR-NIM)]$が空気中で安定な結晶として単離でき，その配位子反応により種々の新規配位子の錯体を合成した。
4) 二つの金属に橋かけする型の配位子を合成し，種々の二核錯体を合成したところ，Ag(I)及びCu(I)の錯体はこれまで知られたP－N配位子二核錯体よりも金属－金属距離が短いものが合成されることが判明した。
5) PR－NIM及び橋かけ型の配位子で，Pd(0, I, II)錯体を合成し，酸化的付加反応，カルボニル挿入反応などの反応性を検討した。

以上のように，本論文は，イミダゾールを含む全く新しい型のP－N配位子を種々合成し，それらの遷移金属錯体の構造と新しい反応性を種々報告しており，博士論文に値すると判定した。