COORDINATION CHEMISTRY OF PHOSPHORUS/NITROGEN CONTAINING ORGANYL BORATES WITH TRANSITION METALS IN LOWER OXIDATION STATES

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IN
CHEMISTRY

BY

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1988
Certified that the work embodied in this dissertation entitled "Coordination Chemistry of Phosphorus/Nitrogen containing Organyl Borates with Transition Metals in lower oxidation states" is the result of original researches carried out under my supervision by Miss Shahla Nusrat Qidwai and is suitable for submission for the award of M.Phil degree of Aligarh Muslim University, Aligarh.

(Zafar Ahmad Siddiqi)
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Shahla Nusrat Qidwai

(Shahla Nusrat Qidwai)
LIST OF PUBLICATIONS

1. Reactions of N-trimethylsilylimidazole and -2-methylimidazole with anhydrous CoCl₂ and [Co(Ph₃P)₂Cl₂]; synthesis and physico-chemical studies on two-coordinate cobalt(II) complexes.


2. Reactivity of N-trimethylsilylimidazole and -2-methylimidazole; synthesis and physico-chemical studies on transition metal imidazolates and mixed ligand imidazolates.

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INTRODUCTION

A new sub area of organometallic chemistry has been opened up with the reported synthesis of a novel class of chelating ligands poly(1-pyrazolyl) borate anions by Trofimenko. A wide variety of transition metal complexes incorporating pyrazolyl and substituted pyrazolyl borate ligands have been synthesized and studied during the last two decades. The resulting moieties have been formulated by the general formula $[\text{BH}_{4-n}L_n]^-$ ($L=$pyrazolyl residue and $n=2, 3$ and 4), each representing a new class of chelating ligands resembling conventional chelating agents such as acetylacetonates anion. It has also been reported that hydrotris(pyrazolyl) borate ligand can act as tridentate ligand with $C_{3v}$ symmetry. These ligands have been used in synthesizing complexes with members of the first transition series and a few organotin derivatives. The coordination compounds of $\text{Mn}^{2+}$, $\text{Fe}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$, $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$ with poly(1-pyrazolyl) borate ligand have been characterized by using optical, electronic and NMR spectral studies. The complex $[\text{Fe(HBPz}_3)_2]$ shows an unusual spin isomerism. A single crystal epr study of $[\text{Co(HBPz}_3)_2]$ have also been reported. Effect of the presence of diverse substituents at carbon or boron on the properties of the transition metal poly(1-pyrazolyl) borates has been studied by Trofimenko to devise synthetic approaches for such compounds. It has been observed that while the complexes $\text{Mn[H}_2\text{B(pz)}_2]_2$, $\text{Fe[H}_2\text{B(pz)}_2]$ are extremely air sensitive the analogous methyl substituted pyrazolyl borate chelates are fairly stable. Such enhanced stability has been ascribed to the steric protection of
the central metal ion by the methyl groups in tetrahedral chelates. It was further indicated that the synthetic routes are available for the synthesis of bidentate and tridentate ligands with a wide variety of substituents on carbon or boron. In most of these compounds the symmetry of the parent ligands has been shown to be maintained. However, in squareplaner and tetrahedral chelates the steric factor seems more pronounced.

In order to expand the feasibility of this synthetic approach different class of analogous heterocycles like imidazole, indazole and their substituted derivatives have also been used to synthesize the corresponding anion \([BH_{4-n}L_n^-]\) (\(L=\text{imidazole or indazole, n}=2, 3, 4\)). The ligating characteristic of the resulting novel ligands towards members of the first row transition series have been studied and reported\(^{19-23}\) from this laboratory. It has, recently, been realized that the reactive nature of N-H bond affording these anionic moieties is depicted not only in the above mentioned heterocycles but also in the compounds like succinic anhydride and phthalic anhydride\(^{24-25}\). The succinimidyl/phthalimidyl borates have been reported to have ample coordinating ability towards transition metals forming stable complexes\(^{24,25}\).

A comparison between the coordination behaviour of the isosteric but neutral poly(1-pyrazolyl) alkanes (Fig.-1) with poly(1-pyrazolyl) borates (Fig.-2) has also been made\(^{26}\). It has been concluded on the basis of the above studies that methane substituent closely resembles the boron substituent \([R_nB(pz)_{4-n}]^-\) in its coordinative behaviour. The two ligand classes therefore
comprise a unique, mutually complementary pair of systems with essentially identical geometry but differing by one charge unit per ligand. Advantage can be taken of this in predicting some properties e.g., a \([R_n B(pz)_{4-n}]^-\) complex having only the \([R_n C(pz)_{4-n}]^-\) ligand (or vice-versa), or else in situations where a BH\(_2\) or BH grouping would cause reduction of the metal (e.g. with Pd(II) systems). The coordination chemistry of geminal polypyrazolyl alkanes, therefore, appears to be a fruitful new era for investigation.

The tris (1-pyrazolyl) borate, a uni-negative tridentate ligand with C\(_{3v}\) (or local C\(_{3v}\)) symmetry has been used to prepare the sandwich like compounds, where the transition metal is surrounded essentially in an octahedral fashion by the terminals of the two tridentate ligands. Furthermore, the half sandwiches\(^{27}\), where the three coordination sites on the metal are taken up by the \([RB(pz)_3]^-\) ligand and the remaining coordination sites by the other groups such as CO, \(\pi\)-allyl, alkyl, hydrogen, \(\pi\)-C\(_5\)H\(_5\) etc. have also been reported\(^{28}\). Since these other ligands may be varied in manifold ways, the scope of half sandwich chemistry based on the \([RB(pz)_3]^-\) ligand ought to considerably exceed that of the corresponding full sandwich compounds. In an approach to chiral polypyrazolylborate ligands, the first example of an
asymmetrically substituted species \([\text{H}_2\text{B}(\text{pz}*)(\text{pz})]^-\) was obtained. This species had \(\text{pz}^* = 3,5 \text{Me}_2\text{pz}\), and was converted to Ni(II), Co(II) and Zn(II) chelates and to the free acid \(\text{H}[\text{H}_2\text{B}(\text{pz}*)(\text{pz})]\). Two isomers of the square planer Ni(II) chelate\(^{29}\) were observed by NMR. The free acid derived from the ligand (Fig-3) was prepared along with similar asymmetric analogous containing different \(\text{pz}^*\) group but was not used in metal chelation\(^{30}\). With \(\text{CH}_2[\text{CH}_2(\text{CH}_2\text{NMe})_2\text{B}(\text{pz})]\), the reaction of substituted pyrazoles

![Diagram](image)

\(\text{Hpz}^*\) led to the equilibrium \([\text{B}(\text{pz})(\text{pz}^*)]\text{H} \rightleftharpoons \text{B}(\text{pz}) + \text{Hpz}^*\), which was 90% toward the free acid with Hpz, but mostly toward unreacted components with sterically hindered Hpz\(^*\)\(^{31,32}\).

In some of the complexes reducing power of the BH\(_2\) group is retained and chelates of Co, Ni, Cu, Zn and Cd have been studied as reducing agents for cyclohexanone and cyclohexa-3-enone. The Ni and Cd derivatives had good selectivity toward the carbonyl group\(^{33}\).
The ligand \([H_2B(pz)_2]^-\) forms square planer \([NiL_2]\) and \([CrL_2]\) and distorted octahedral \(K[Vl_3]\), as established by X-ray crystallography. From \([H_2B(pz*)_2]^- (pz* = pz, 3,5 Me_2pz)\), the complexes \([LM(CO)_2]\) and \([LM(CO)(PPh_3)]\) (\(M = Rh, Ir\)) were prepared, as were \([LRh(COD)]\) and \([H_2B(pz)_2TaMe_3]\).

A new tridentate ligand, \([HB(3,5 Me_2pz)_2SAr]^-\), was prepared from \(ArSH\) and \(K[H_2B(3,5 Me_2pz)_2]\). It was converted to tetrahedral \([LMSR]\) complexes of \(Cu(II)\) and \(Co(II)\), synthetic approximations of the active site in poplar plastocyanin.

The curling of the pseudoaxial B-substituent toward the metal results in bonding interactions with the metal even by a typical donors such as alkyl groups. In compounds \(Et_2B(pz)_2Mo(Co)_2(\eta^3-2\text{Phallyl})\), x-ray crystallography showed that one hydrogen of the pseudo-axial methylene group is involved in a C-H-Mo three center, two - electron bond (H-Mo distance \(\approx 2.2\) \(\text{Å}\)), imparting an 18 electron configuration to Mo. In the analogous \(Et_2B(pz)_2Mo(Co)_2(\eta^3-C_7H_7)\) formation of the three - centre C-H-Mo bond was found to take precedence over the alternative way of achieving an 18 electron configuration, namely via \(\eta^5-C_7H_7\) structure. Detailed NMR analysis of \(LMO(CO)_2(\eta^3\text{-allyl})\) and its \(\eta^3-2\text{Phallyl}\) analogue revealed a low temperature process involving exchange of the two pseudoaxial methylene protons (\(E_a = 14\) K cal mol\(^{-1}\)) and a higher temperature process (\(E_a = 17-20\) K cal mol\(^{-1}\), approximating the strength of the C-H-Mo bond) involving inversion of the \(B(pz)_2Mo\) ring. The C-H-Mo bond is broken by stronger donors attacking in a trans fashion and producing a conventional 18 electron configuration on Mo. The structure of such an adduct \(LMO(CO)_2(\eta^3-\)
allyl)(Hpz), was established by X-ray crystallography: Hpz is trans to the (η^3-allyl) group and the B(pz)Mo ring is in an unusual distorted chair conformation. A similar structure was found for Ph_2B(pz)_2(CO)_2(C_7H_7)(Hpz). The structure of [L_2Ni] and of the surprisingly air-stable [L_2Cr], both of which are square planar, were determined by X-ray crystallography.

Additional examples of three center B-H-M bonds were found in H_2B(3,5 Me_2pz)_2Mo(CO)_2(η^3-C_7H_7), in the seven coordinate LTaClMe_3, in [L Pt Me_3] and possibly in [L CuPR_3]. There is no B-H-M bond in L_2Ni, where the distance from the pseudoaxial H to Ni is about 3.05 Å, nor in LRh(COD). The B-H-Pt bridge in L Pt Me_3 is broken by various ligands (phosphites, Hp^* and CO) with the formation of [L Pt Me_3 L].

While axial B-Et and B-H form three center bonds to Mo in, for instance L^*Mo(CO)_2(η^3-allyl), such bonds are absent in the Ph_2B(pz)_2 analogues, because the pseudoaxial Ph group is forced by nonbonding interactions into a conformation precluding the C-H-Mo bond found in L_2^*Ni and in L^*Mo(CO)_2(η^3-allyl).

Rh(I) derivatives of the type L^*RhL_2(L^* = Et_2B(pz)_2; L = CO, RNC) were prepared and converted to Rh(III) compounds by oxidative addition of I_2, MeI or HgCl_2. Stable MePt(II) complexes Et_2B(pz)_2-PtMeL and Ph_2B(pz)_2PtMeL, where L = PR_3, RNC or various acetylenes, were prepared with the acetylenes Ph-C ≡ C-Ph and Ph-C ≡ C-Me; with F_3CC ≡ CCF_3 or ROOCC ≡ COOCR, however, insertion took place and products isolated as PPh_3 adducts were L^*Pt(RC=CRMe)
PPh$_3$$^{54,55}$. The structure of the square planer Et$_2$B(pz)$_2$ PtMe
(PhC \equiv CMe) shows the acetylenic substituent cis-bent away
from Pt by 18-21° and the distance from the pseudoaxial C-H to
Pt is 2.65 Å$^{56}$.

Complexes of the type B(pz)$_4$Mn(CO)$_2$L(L= various phosphines)
and HB(3,5 Me$_2$pz)$_3$ Mn(CO)$_2$P(OPh)$_3$ were prepared and studied by IR
and NMR. Free rotation about the B-Mn axis occurs in the former
at 5°, whereas the later is stereochemically rigid$^{57}$.

Amine-boranes constitute an important class of boron-
nitrogen compounds since they or their derivatives provide a
direct entry to the synthesis of aminoboranes or borazines$^{58,59}$
or to boron cations$^{60-62}$. Simple and convenient methods of syn-
thesis of amineboranes are known. The various versatile synthetic
methods include direct combination of ethereal lithium borohydride
with ammonium salts$^{63}$ or transamination of an already formed amine
borane$^{64,65}$, or less direct methods like reduction of an appro-
priate boron compound using hydrogen or borohydride$^{66-68}$. A new
method incorporating a convenient one step synthesis of borane
adducts using sodium borohydride, appropriate donors and iodine
is reported$^{69}$. This method has been successfully worked out for
the synthesis of ammonia boranes, boranes of different aliphatic
amines which include primary and monoamines and tertiary di- and
triamines, and boranes of substituted phosphine-boranes. The
coordinating behaviour of a few phosphine boranes has recently
been reported. The complexes of bis(trimethyl phosphine)- diborane
B$_2$H$_4$.2P(CH$_3$)$_3$ with Zn(II) and Cu(I) represented the first example
of metal complexes of a neutral borane adduct. Important feature of this complex is that the boron hydride ligand is coordinated to metal via two B-H-M bridges, this kind of bidentate bridging mode of coordination has previously been observed in the complexes of BH₄⁻, B₂H₆²⁻ and B₃H₆⁻ borane anions. It has also been noted that the metal salt did not react with BH₃-P(CH₃)₃ under the same condition which has been interpreted to be due to the unfavourable vicinal H-H distance for the chelation owing to a shorter H-H distance. The coordination chemistry of analogous amine-boranes has not been explored and therefore requires a thorough investigation if it has any reactivity towards substrates with metal centers.
The preparation of a few already known amine boranes which include picoline-borane, 2,2'-(dipyridyl) bis-borane were performed with a view to study their coordinating behaviour towards transition metal ions and their complexes, as a part of the present programme. The heterocycles were chosen for the following two reasons (a) such heterocycles are capable to yield addition product comprising electrophilic BH$_3$ segment, (b) these may also provide favourable vicinal H-H distance suitable for chelation to metal ions. Reactions of these reagents with transition metal ions (ranging from hard (a) to soft (b) types) as well as their derivative complexes were carried out at room temperature. However, all these reactions did not provide any evidence of their interactions, as unreacted starting materials have been isolated, though in some cases some drastic conditions were also applied. This indicates that probably it is not only the vicinal H-H distance which accounts for their chelation but the nature of nucleophilic centre bound to boron is also important.

The second phase of this programme included the study of the reactivity of imidazolyl borate anion i.e. dihydrobis(imidazolyl)borate, hydrotris(imidazolyl)borate and tetrakis(imidazolyl)borate towards transition metal derivative complexes particularly with [CO(Ph$_3$P)$_2$Cl$_2$], [Ni(Ph$_3$P)$_2$Cl$_2$], [Cu(Ph$_3$P)$_3$Cl] and [Zn(Ph$_3$P)$_2$Cl$_2$]. It has been observed that the product of the reactions carried out at room temperature conditions does not contain tri-
phenyl phosphine coordinated to metal ion rather is released as free \( \text{Ph}_3\text{P} \). An equivalent amount of liberated \( \text{Ph}_3\text{P} \) has been recovered from the mother liquor. Furthermore, the results of the elemental analyses and spectroscopic investigations disclosed that the product of these reactions are almost identical to those already reported for reactions using metal salts. This observation is similar to that reported for the reactions of \( \text{Cp}_2\text{TiCl}_2 \) with hydrotris(pyrazolyl)borate anion, in which case too cyclopentadienyl is liberated free from the product. This may be attributed to the strong \( \sigma \)-donor nature of the borate moieties.

It has been revealed from survey of literature that trimethylsilyl group in the reagents \( \text{N-} \)trimethylsilylimidazole and \( \text{N-} \)trimethylsilyl-2-methylimidazole is quite reactive towards C-Cl bonds (in organo derivatives) resulting in the isolation of a wide variety of \( \text{N-} \)substituted derivatives. However, there is, to our knowledge, no report, so far appeared in literature regarding the reactivity of these reagents towards M-Cl bond of either transition metal, post transition metal or rare-earth metal chlorides as well as of their organometallic derivatives. It has, recently, been reported that trimethylsilyl group in \( \text{(Me}_3\text{SiN})_2\text{S} \) reacts with \( \text{VCl}_4 \), \( \text{VOCl}_3 \) or \( \text{WCl}_6 \) producing an inorganic heterocycles i.e. metalla-cycles(\( \text{Cl}_n\text{M}_2\text{N}_3 \)\( \text{x} \)), with delocalized \( \pi \)-electrons involving additional \( \text{p} \pi\text{- d} \pi \) overlap with d orbital of the metal centre. There are reports showing that the reactions of \( \text{(Me}_3\text{Si})_2\text{X} \) (\( \text{x} = \text{S}, \text{Se or Te} \)), with \( \text{[M(PH}_3\text{P})_2\text{Cl}_2] } \) (\( \text{M} = \text{Co, Ni} \)) yield a chalcogen cluster along with \( \text{PH}_3\text{P} \) in the coordination sphere. Furthermore, transition
metal complexes of imidazole have been the subject of considerable investigations during the last two decades because they are models for histidyl residues of proteins or of bovine erythrocyte superoxide dismutase. Attempts by previous workers to prepare imidazolato-complexes of first row transition metals employing transition metal salts and imidazole in aqueous media in the presence of KOH have yielded polymeric substances which neither melt nor dissolve in any solvent. We have, however, observed that N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole are potential reagents for the synthesis of monomeric imidazolato complexes which melt sharply and are soluble in most non-polar organic solvents. In this dissertation I have described the results of the reactions of the reagents N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole with a few transition metal chloride e.g. CoCl₂, NiCl₂, CuCl₂ and also with their derivative complexes [Co(Ph₃P)₂Cl₂], [Ni(Ph₃P)₂Cl₂], [Cu(Ph₃P)₃Cl]. The products of these reactions have been characterized using physicochemical methods. The physico-chemical data presented here strongly suggest that [CoLCl] and [CoL₂] possess a linear D∞h geometry, an example of uncommon two coordinate Co(II) derivatives. The X-ray crystal structure, if possible, would be done to confirm the present investigation. Another known example of this geometry of Cobalt(II) is [bis{di(trimethyl silyl) amino}Cobalt(II)].

As the present investigations which are mainly focussed towards the study of the reactivity of N-trimethylsilylimidazole/2-methylimidazole towards inorganic substrates possessing M-Cl bonds, and would be further expanded to see the feasibility of
this reagent(vide supra) for the production of monomeric imida- 
zolates as well as mixed ligand imidazolate derivatives incorpo-
rating heavy metal ions. The results are already in hand which 
provide ample information regarding the versatility of the re-
agents. In view of this, I would like to change the topic of 
my Ph.D. thesis emphasizing the study of the reactivity of the 
reagents towards M-Cl bonds, metalloid-chlorine and also towards 
chlorine bonded to non-carbonic non-metal atoms like phosphorus 
and sulphur.
EXPERIMENTAL METHODS

However, molecular geometry of the compound indicating the exact disposition of the various atoms in the molecule are obtained by using single crystal X-ray crystallographic studies. The present complexes have been analysed by using molecular weight and magnetic susceptibility measurements, I.R., electronic and reflectance spectral studies.

The results of the elemental analysis for carbon, hydrogen and nitrogen were obtained by the Micro analytical laboratory of the Indian Institute of Technology, Kanpur. The estimation of halogen was done gravimetrically and the metals were estimated by titrating with standard E.D.T.A., solution. For the metal estimation, a known amount of complex was decomposed with a mixture of nitric, perchloric and sulphuric acids and the halogen was estimated by fusing a known amount of the compound with fusion mixture (KNO₃ and K₂CO₃).

The infrared and far- infrared spectra were recorded as KBr discs on a Perkin Elmer 621(4000-200 cm⁻¹) spectrophotometer in the chemistry department of Guru Nanak Dev University, Amritsar. Reflectance spectra of the solid samples were recorded on a Carl Zeiss VSU-2P spectrophotometer using MgO as calibrant and electronic spectra in CH₂Cl₂, THF or MeOH were recorded on a Pye unicam 8800 spectrophotometer at room temperature. ¹H NMR spectra were recorded in CDCl₃ on a varian A60D spectrometer.
using Me₄Si as an internal indicator. Results of the magnetic susceptibility measurements were obtained by using a Faraday balance at 25°C at the chemistry department of Banaras Hindu University, Varanasi. Molecular weights of the compounds were determined by Rast method using camphor as a solvent.

**Important group frequencies located in the I.R. spectra:**

- \(-\text{Si(CH}_3\text{)}_3\) stretching vibrations:

In the series of open chain compounds examined by Wright and Hunter a strong band is shown at 841 cm\(^{-1}\) which decreases in intensity as the chain length is increased. A second band whose intensity varies with chain length occurs in the same compounds at 756-754 cm\(^{-1}\). They are clearly associated with vibrations involving the \(\text{Si(CH}_3\text{)}_3\) end groups of the open chain materials. These findings were confirmed by Richards and Thompson in their series of compounds, whilst twelve aryl trimethyl silanes examined in solution by Clark et al. show absorption close to 840 cm\(^{-1}\). In trimethyl chlorosilane the first of these bands occurs at 857 cm\(^{-1}\) and has been identified as the \(\text{CH}_3\) rocking mode.

**Imidazole ring vibrations:**

Band assignments were obtained by examining the infra-red spectra of the deuterated derivatives of imidazole and imidazolium ion by previous workers. The in-plane bending and ring stretching modes of imidazole undergo sizable shifts to higher
frequencies upon formation of the imidazolium ion. The spectra of metal complexes are more characteristic of free imidazole than of imidazolium ions. These large frequency shifts indicate that upon protonation (and to a lesser extent, upon complex formation) the imidazole ring undergoes extensive $\pi$-electron redistribution.

In the present complexes, imidazole ring vibrations appear in the region 1500-1300 cm$^{-1}$ and are slightly shifted (10-20 cm$^{-1}$) from the position in the free imidazole.

**P-Ph stretching vibration:**

Dasch and Smith have found P-Ph bands in the regions 1450-1435 cm$^{-1}$ and 1005-995 cm$^{-1}$ which are sharp and of moderate intensity.

**Metal-Nitrogen(M-N) stretching bands:**

The M-N stretching frequency is of particular interest since it provides direct information about the coordinate bond. In present complexes it generally appears in the region 370-390 cm$^{-1}$.

**Metal-Chlorine stretching vibration:**

The M-Cl stretching frequency for Co(II) complexes appears around 320 cm$^{-1}$ while for Cu(II) complexes it appears at lower regions i.e. 270 cm$^{-1}$. 
Metal-Phosphorus stretching vibration:

The M-P stretching frequency generally appears as a weak band at about 320 cm$^{-1}$. 
EXPERIMENTAL

Materials and methods:

Reagents Used:

The reagents, triphenyl phosphate (Sisco), sodium borohydride (BDH), 2-picoline (BDH), iodine (E. Merck), 2,2'-dipyridyl (BDH), potassium borohydride (BDH), imidazole (Loba), 2-methyl-imidazole (Sisco), hexamethyldisilazane (Sisco), CoCl₂.6H₂O (Glaxo-India), NiCl₂.6H₂O (BDH) and CuCl₂.2H₂O (E. Merck) were commercially pure samples. Solvents tetrahydrofuran, dichloromethane, dimethyl formamide, benzene, chloroform, n-hexane, petroleum ether, methanol and ethanol were commercially pure samples, all dried by literature methods.

Preparation of precursors

1. Dehydration of CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O:

(a) Dehydration of CoCl₂.6H₂O:

Fine CoCl₂.6H₂O (6 gm) powder was placed in a flask provided with a ground joint and was covered with SOCl₂. The mixture was refluxed for several hours. The excess of SOCl₂ which clings to the product (which is blue in colour) was removed by repeated evacuation of the flask.

(b) Dehydration of NiCl₂.6H₂O:

NiCl₂.6H₂O (10 gm) was mixed with 60 ml acetic anhydride and heated for 1 hr. Filtered and dried in vacuo giving yellow coloured crystalline solid.
(c) Dehydration of CuCl₂.2H₂O :

CuCl₂.2H₂O (5 gm) was refluxed with 50 ml. SOCl₂.
Removal of the excess SOCl₂ was carried out by distillation
and evaporation of residual solvent in vacuum.

Preparation of chloro tris(triphenyl phosphine)Copper(I):

Triphenyl phosphine (6.55 gm, 25 mmol) was dissolved
in 100 ml CHCl₃, in which CuCl(0.6015 gm, 6.5 mmol) was added in
portions with continuous stirring, and then dry 400 ml C₂H₅OH
was added followed by vigorous stirring Ca.2 hrs. A shining
white microcrystalline solid separates out [m.pt 150-160°C].

Preparation of dichloro bis(triphenyl phosphine)Nickel(II):

A solution of NiCl₂.6H₂O (1.19 gm, 5 mmol) in water
was diluted with 25 ml glacial acetic acid and triphenyl phos­
phine(2.62 gm, 10 mmol) in 50 ml glacial acetic acid was added.
The olive green microcrystalline mass precipitates out, when
kept in contact with its mother liquor for 24 hrs. gave dark
blue crystals which were filtered off, washed with glacial
acetic acid and dried in vacuum dessicator [M.pt. 244 °C].

Preparation of dichloro bis(triphenyl phosphine)Cobalt(II):

An excess of triphenyl phosphine (1.5 times the stio-
chiometric amount) was melted in a water bath and CoCl₂.6H₂O
was slowly added to this molten triphenyl phosphine with con­
tinuous magnetic stirring. The reaction mixture was stirred for
5-10 mints. thereafter, cooled and ground in a mortar. The blue product obtained was treated with hot ethanol for recrystallization [M.pt-225 °C].

Synthesis of 2-picoline-Borane:

The apparatus consists of a nitrogen flushed 250 ml two necked flask fitted with a pressure compensated dropping funnel and an outlet tube leading to a bubbler containing a benzene-amine mixture. To a mixture of sodium borohydride (1.390 gm, 36.77 mmol) and 2-picoline (3.00 gm, 32.26 mmol) in 40 ml of dry dichloromethane, iodine (3.855 gm, 5.18 mmol) dissolved in 35 ml of dry dichloromethane was added dropwise over a period of 3 hr. The reaction mixture was kept stirred throughout the experiment, while the hydrogen gas was escaping through the bubbler. About 5 ml of dichloromethane was used to wash down the sides of the funnel at the end of the reaction. The solvent was then removed by pumping and the resulting solids were extracted with 130 ml of benzene to separate the soluble amine-borane from sodium iodide and unreacted sodium borohydride. The insoluble solid (NaI and NaBH₄) was dried.

The filtrate was mixed with 20 ml of hexane and kept at 5°C for crystallization. The crystals appeared in the solution the very next day but started disappearing soon, in this way we could not isolate the crystals. Then it was again dried in vacuum to give light yellow sticky crystalline solid [m.pt 47°C].
Synthesis of 2,2'-Dipyridyl-bis(borane)\(^{69}\):

To sodium borohydride(0.5 gm) and 2,2' dipyridyl(2.05 gm) in stoichiometric ratio, iodine(0.4174 gm) taken in 100 ml of dichloromethane was added and stirred for four hours. Filtered the content of the flask and evaporated the filtrate to 1/3 rd of its original volume, mixed it with hexane and kept at 5°C for crystallization. The crystals appeared after 24 hrs were yellow in colour [m.pt decomposition temperature ranges from 125 °C to 133°C, turns dark brown at high temperature].

Preparation\(^{22}\) of potassium dihydrobis(2-methylimidazolyl)borate anion[KDMIB] :

2-methylimidazole(10 gm, 12.18 mmol) and KBH\(_4\) (3.25 gm, 6.09 mmol) were mixed in 50 ml DMF and refluxed till the calculated amount of hydrogen is evolved. Filtered and washed the white solid with ethanol and dried under vacuum [m.pt >360 °C].

Reaction of potassium dihydrobis(2-methylimidazolyl)borate anion with [Ni(PPh\(_3\))\(_2\)Cl\(_2\)] :

[Ni(PPh\(_3\))\(_2\)Cl\(_2\)](0.3270 gm, 0.5 mmol) in chloroform was stirred for few minutes after mixing with KDMIB(1.9 gm, 1 mmol) taken in CH\(_3\)OH. The colour of the solution changes from blue to light green, stirred it for 3-4 hours and kept at low temperature for crystallization. After few days yellowish green crystals appeared which were filtered and dried under vacuo. Recrystallized from chloroform [m.pt decomposes above 300°C and turns grey at high temperature].
Reaction of KDMIB with $[\text{Co(PPh}_3\text{)}_2\text{Cl}_2]$:

$[\text{Co(PPh}_3\text{)}_2\text{Cl}_2](0.3270 \text{ gm, 0.5 mmol})$ was dissolved in 25 ml chloroform and 20 ml methanol was added to this, colour of the solution changes from blue to royal blue. To this solution KDMIB (1.90 gm, 1.0 mmol) dissolved in methanol was added, the colour of the solution gradually changes from royal blue to purple followed by pink colouration. This was kept at low temperature for crystallization. Filtered and dried in vacuo [m.pt decomposes above 300°C].

Reaction of KDMIB with $[\text{CuCl(PPh}_3\text{)}_3]$:

$[\text{CuCl(PPh}_3\text{)}_3](0.448 \text{ gm, 0.5 mmol})$ was dissolved in methanol, to this solution KDMIB 0.090 gm, 0.5 mmol) dissolved in methanol was added. A greenish blue solid immediately appears in the solution, stirred it further for 1/2 hr, filtered and dried in vacuo [m.pt. decomposes and turns grey at high temperature $> 300°C$].

Preparation of potassium dihydrobis(imidazolyl)borate anion:

Imidazole (1gm, 14.44 mmol) and KBH$_4$ (0.3929 gm, 7.22 mmol) were mixed in DMF (50 ml) and refluxed till the requisite amount of H$_2$ evolved. A small amount of product obtained, it was filtered and dried. The filtrate was added to hot and dry toluene and was stirred for an additional 1/2 hr. Filtered when cool and dried in vacuo [m.pt 247°C].
**Preparation of N-trimethylsilylimidazole:**

Hexamethyldisilazane (12.1 gm, 75 mmol) was taken in a round bottomed flask fitted with a reflux condenser and drying tube. Dry nitrogen was flushed in to expel air, acidified and then imidazole (6.8 gm, 100 mmol) was added. Vigorous reaction took place and it was refluxed, then fractionally distilled under vacuum. The fraction distilling at 92°C and 12 torr were collected. The purity of the reagent was checked by I.R. and $^1$H NMR spectra. Anal calculated for C$_6$H$_{12}$SiN$_2$: C, 51.40; H, 8.62; N, 19.97; obsd. 51.09, 8.15, 19.89 respectively; IR, 3145m, 3125m, 1549m, 1480m, 1480s, 1440m, 1330s, 1260s, 1165s, 1060s, 930m, 850s, 770s, 750s, 670s, 620s cm$^{-1}$; $^1$H NMR 0.856(9H), 6.86(2H) and 7.616 (1H).

**Preparation of N-trimethylsilyl-2-methylimidazole:**

It was prepared in the same manner as described above for parent reagent by taking 2-methylimidazole (7.2 gm, 87 mmol) and hexamethyldisilazane (10.5 gm, 68 mmol). The crude was fractionated and fraction distilling at 180°C and 20 torr were collected. In this case too purity of the reagent has been checked by I.R. and $^1$H NMR. Anal calculated for C$_7$H$_{14}$SiN$_2$: C, 54.50; H, 9.15; N, 18.16; obsd. 54.45, 9.07, 18.07 respectively. I.R. 3200-2900 sb, 1600m, 1570m, 1400s, 1290s, 1255s, 1180s, 1150s, 1050s, 985s, 850sb, 760s, 745s, 650s, 620s cm$^{-1}$; $^1$H NMR, 0.396 (8.7H), 2.386(3H) and 6.86(2H).
Preparation of Chloro(imidazolato)cobalt(II), (1) and chloro(2-methylimidazolato)cobalt(II), (2):

\[ \text{N-trimethylsilylimidazole or N-trimethylsilyl-2-methylimidazole (0.4116 g, 2.94 mmol) diluted with 30 ml benzene was added dropwise from a dropping funnel fitted to a round bottomed flask containing CoCl}_2(0.136 g, 1.05 mmol) suspended in 30 ml benzene with continuous magnetic stirring at room temperature under dry nitrogen atmosphere. The formation of a light blue oily product was immediately indicated and the reaction mixture was stirred for about 1/2 hr. The mother liquor was decanted off leaving behind the oily mass which was washed several times with petroleum-ether and vacuum dried giving a microcrystalline solid [m.pt.125°C for (1) and 98°C for (2)]. The crude was dissolved in 50 ml CH\_2Cl\_2 filtered off to remove impurity mixed with n-hexane and kept at 5°C for about two weeks. This gave light blue coloured hexagonal crystals [m.pt.130°C for (1) and 102°C for (2)].} 

Preparation of bis(imidazolato)cobalt(II) (3) and bis(2-methylimidazolato)cobalt(II) (4):

\[ \text{N-trimethylsilylimidazole (1.28 g, 9.2 mmol) diluted with 30 ml benzene was added dropwise to a solution of [Co(Ph}_3P)_2Cl}_2 (3.00 g, 4.6 mmol) in 200 ml THF with continuous stirring at room temperature under dry nitrogen atmosphere. When whole of the Me}_3Si-imidazole had been dropped (30 min) the reaction mixture was vigorously stirred for an additional 1/2 hr and left standing}
for 1 hr. The colourless mother liquor was decanted off leaving behind the blue oily mass, which was immediately washed with benzene-THF mixture, then with petroleum ether and the washings were mixed to the filtrate mother liquor. The mass was vacuum dried giving light blue coloured amorphous solid [m.pt 135-145 °C]. The mother liquor was vacuum dried giving 2.3 gm of a colourless microcrystalline material [m.pt 79-82°C] which has been identified as Ph₃P (2 mole equivalent) from I.R. and elemental analysis. The main product has been recrystallized from CH₂Cl₂/n-hexane giving a microcrystalline solid melting at 147°C.

Bis(2-methylimidazolato)cobalt(II) was synthesized in the same manner by taking (0.45 gm, 2.9 mmol) trimethylsilyl-2-methylimidazole in 20 ml benzene and (0.685 gm, 1.05 mmol) [CoCl₂(Ph₃P)₂] in 60 ml THF at room temperature. The crude was recrystallized from CH₂Cl₂/n-hexane giving a blue microcrystalline solid (m.pt. 130°C). In this case too the mother liquor and washings have afforded 0.55 gm Ph₃P.

Preparation of bis(imidazolato)nickel(II) (5) and bis(2-methylimidazolato)nickel(II), (6):

N-trimethylsilylimidazole (0.7 gm, 5.0 mmol) diluted in 50 ml THF was added dropwise to NiCl₂ (0.324 gm, 2.5 mmol) dissolved in 150 ml THF, with continuous stirring at room temperature under dry nitrogen atmosphere. When all of the reagent had been dropped, the reaction mixture was vigorously stirred for 1 hr. It was filtered off to remove the unreacted NiCl₂ impurity
and then vacuum dried, washed several times with pet-ether to give amorphous solid. The crude was recrystallized from CH$_2$Cl$_2$-n-hexane [m.pt.190°C].

Bis(2-methylimidazolato)nickel(II) was synthesized in the same manner by taking (0.77 gm, 5.0 mmol) trimethylsilyl-2-methylimidazole diluted in 50 ml THF and NiCl$_2$ (0.324 gm, 2.5 mmol) suspended in 150 ml THF at room temperature. The crude was recrystallized from CH$_2$Cl$_2$-n-hexane[m.pt.200°C].

Reactions of [Ni(Ph$_3$P)$_2$Cl$_2$] with N-trimethylsilylimidazole/2-methylimidazole affording bis(imidazolato)nickel(II)(5) and bis(2-methylimidazolato)nickel(II) (6):

The diluted reagent (N-trimethylsilyl-imidazole/2-methylimidazole(0.56 gm, 4.0 mmol)/(0.616 gm, 4.0 mmol) in 40 ml THF was dropped to solution of [Ni(Ph$_3$P)$_2$Cl$_2$] (1.308 gm, 2.0 mmol) in 100 ml THF with continuous stirring. An immediate change in colour was observed from dark green to light pea green. It was vacuum dried giving a green oily mass which after several washings with pet-ether converted to pea green solid. The crude was recrystallized in CH$_2$Cl$_2$-n-hexane [m.pt.190°C for (5) and 200°C for (6)]. The pet-ether washings in either case, on evaporation left colourless microcrystalline solid (Ca. 2.0 mole equivalent) which has been identified as Ph$_3$P from m.pt.,I.R. and microanalysis.
Reactions of N-trimethylsilylimidazole or N-trimethylsilyl-2-methylimidazole with CuCl$_2$ yielding bis(imidazolato)Copper(II) (7) and bis(2-methylimidazolato)copper(II) (8):

The reagents N-trimethylsilylimidazole/N-trimethylsilyl-2-methylimidazole (0.7 gm, 5.0 mmol)/(0.77 gm, 5.0 mmol) were dropped to the suspension of the CuCl$_2$ (0.336 gm, 2.5 mmol) in 150 ml THF with continuous stirring in the manner as above. The reaction mixture was further stirred for ca. 1 hr. after the reagent has been completely added. It was filtered off to remove the unreacted metal salt impurity and vacuum dried, washed several times with pet-ether to give amorphous solid. The crude was recrystallized from CH$_2$Cl$_2$-n-hexane [m.pt 180°C for (7) and 210°C (8)].

Reactions of [CuCl(PPh$_3$)$_2$] with N-trimethylsilylimidazole/or N-trimethylsilyl-2-methylimidazole giving imidazolato bis(triphenylphosphine)(Copper(I))(9) or (2-methylimidazolato) bis(triphenylphosphine)copper(I)(10):

The reagent was treated with equimolar solution of [Cu(Ph$_3$P)$_3$Cl] in THF as above. Immediate curdy white solid formed which slowly redissolved with magnetic stirring at room temperature. The reaction mixture was vacuum dried, washed with pet-ether and dried in vacuo. The crude was recrystallized from CH$_2$Cl$_2$-n-hexane, giving colourless microcrystalline solid [m.pt 185°C for (9) and 195°C for (10)]. Here also the washings have yielded equivalent amount of liberated Ph$_3$P.
Preparation of Chloro(imidazolato)bis(triphenyl phosphine)-Copper(II)(11) and chloro(2-methylimidazolato)bis(triphenyl phosphine)copper(II) (12):

To a suspension of CuCl₂(0.336 gm, 2.5 mmol) in 80 ml THF, solution of Ph₃P(1.31 gm, 5.0 mmol) and of the reagent N-trimethylsilyl-imidazole/-2-methylimidazole(0.7 gm, 5.0 mmol)/0.77 gm, 5.0 mmol) both in 50 ml THF taken in separate dropping funnels were simultaneously dropped with a slow rate with continuous stirring at room temperature. The reaction mixture was stirred for an additional 2 hr. after the whole of the reactants have been added, filtered off to remove the impurity of unreacted CuCl₂. The mother liquor was vacuum dried and washed with ether. The crude was recrystallized from CH₂Cl₂-n-hexane [m.pt 215°C for (11) and 185°C for (12)].
RESULTS AND DISCUSSION

The observed reactivity of N-trimethylsilylimidazole and N-trimethylsilyl-2-methylimidazole towards transition metal chlorides and their complexes is reasonably the consequence of the affinity of Me3Si group in the reagents for the chlorine atom in the substrates, effecting the release of Me3SiCl. The results of the elemental analyses, stoichiometries and the experimentally determined molecular weight of the final products of the various reactions have been shown in Table-I and -II.

Formation of chloro(imidazolato)cobalt(II), (1)
chloro(2-methylimidazolato)cobalt(II), (2), bis(imidazolato)
cobalt(II)/Nickel(II), (3)/(5) and bis (2-methylimidazolato)
cobalt(II)/Nickel(II) (4)/(6):

For the reactions of CoCl2 with trimethylsilylimidazole, and trimethylsilyl-2-methylimidazole, the final product in each case has been characterized as [CoLCl] (L=imidazolate or 2-methylimidazolate) even though, the silyl reagents were taken in excess to that required for the total removal of chlorine as Me3SiCl.

\[
\text{CoCl}_2 + (\text{CH}_3)_3\text{Si}-\text{N} \rightarrow \text{ClCoN} + (\text{CH}_3)_3\text{SiCl}
\]

\[
\text{R} = \text{H}, \ (1) \quad \text{R} = \text{CH}_3, \ (2)
\]
There is no indication of even traces of metallic cobalt in either reaction, as has been reported\(^{88}\) for the reaction of \(\text{LiN(C}_2\text{H}_5)_2\) with \(\text{CoCl}_2\).

Reactions of \([\text{Co(Ph}_3\text{P})_2\text{Cl}_2]\) with the reagents release all the \(\text{Ph}_3\text{P}\) (experimental section). It is surprising that \(\text{Ph}_3\text{P}\), a strong \(\pi\)-acid is liberated. This has been further substantiated by the observation that the attempt to obtain \([\text{Co(Ph}_3\text{P})_n\text{L}_2]\) \((n=1\ or\ 2)\) by reacting (3) and (4) with \(\text{Ph}_3\text{P}\) in tetrahydrofuran leads to the isolation of unreacted starting materials. The analogous compound \([\text{Co}\{\text{N(SiMe}_3)_2\}_2]\), prepared by Bürger et al.\(^{89}\) also did not form complex with even a strong donor. However, the reaction of \(\text{LiN(Me}_3\text{Si})_2\) with \([\text{Co(Ph}_3\text{P})_2\text{Cl}_2]\) is reported\(^{90}\) to yield the complex \([\text{Co(Ph}_3\text{P})\{\text{N(Me}_3\text{Si})_2\}\_2]\) in which one mole of \(\text{Ph}_3\text{P}\) is retained and the \(\pi\)-accepter properties of \(\text{Ph}_3\text{P}\) is supposed to play an important role. These complexes are sensitive to air, turning to dark blue sticky liquids and are readily solvolysed by water and alcohol forming pink solutions.

For the reactions of anhydrous \(\text{NiCl}_2\) with trimethylsilylimidazole or 2-methylimidazole, the product in each case has been identified as \([\text{NiL}_2]\), suggesting the replacement of both the chlorines by imidazolate moieties as shown below:

\[
\text{NiCl}_2 + 2(\text{CH}_3)_3\text{Si-N} \rightarrow \text{Ni}\left(\begin{array}{c}
\text{N} \\
\text{N}
\end{array}\right)_{2} + 2(\text{CH}_3)_3\text{SiCl}
\]

\(R = \text{H}, (5).\)
\(R = \text{CH}_3, (6).\)
The product \([\text{NiL}_2]\) has also been obtained in quantitative amount when the complex \([\text{Ni(Ph}_3\text{P})_2\text{Cl}_2]\) is reacted with the reagent. This indicates that removal of chlorines is accompanied with the liberation of both the triphenyl phosphines (experimental section) from the precursor as shown by the following equation

\[
[\text{Ni(Ph}_3\text{P})_2\text{Cl}_2] + 2(\text{CH}_3)_3\text{Si-N}\begin{array}{c}
\text{N} \\
\text{R} \\
\text{N}
\end{array} \quad \text{Ni} \quad \left(\begin{array}{c}
\text{N} \\
\text{R} \\
\text{N}
\end{array}\right)^2 + 2\text{Ph}_3\text{P}
\]

\[+ 2(\text{CH}_3)_3\text{SiCl} \quad \ldots \ldots (3)\]

The \(\pi\)-acceptor properties of \(\text{Ph}_3\text{P}\) in the precursor usually plays an important role and is assumed to be generally operative in most of its reactions. However, in the present reactions no such generalization seems to follow. The electron counts in \([\text{NiL}_2]\), considering the imidazolate moeity as four electron donor, suggest that \(\text{Ni(II)}\) would get a share of sixteen electrons, an electron deficient compound, and could have accommodated at least one \(\text{Ph}_3\text{P}\) in the product.

Formation of bis(imidazolato)copper(II), (7), bis(2-methylimidazolato) copper(II)(8), imidazolato bis(triphenylphosphine) copper(I)(9), (2-methylimidazolato) bis(triphenylphosphine) copper(I)(10), chloro(imidazolato) bis(triphenylphosphine) copper(II)(11) and chloro(2-methylimidazolato) bis(triphenylphosphine)copper(II)(12):

The reaction of \(\text{CuCl}_2\) with trimethylsilylimidazole and 2-methylimidazole also follows the same mode as described above.
for NiCl₂ giving the product [CuL₂] in each case. The reaction may be typified as below:

\[
\text{CuCl}_2 + 2(\text{CH}_3)_3\text{Si} - \text{N} \quad \rightarrow \quad \text{Cu} \quad \left( \begin{array}{c} \text{N} \\ \text{R} \end{array} \right) \quad + \quad 2(\text{CH}_3)_3\text{SiCl}
\]

\( R = \text{H}, (7) \)

\( R = \text{CH}_3, (8) \)

The reaction with the precursor \([\text{Cu(Ph}_3\text{P})_3\text{Cl}]\) proceeds with the liberation of one mole equivalent of \(\text{Ph}_3\text{P}\) resulting in \([\text{Cu(Ph}_3\text{P})_2\text{L}]\) as an ultimate product. Assuming the electron counts as indicated above, the central metal ion Cu(I) (in the complex \([\text{Cu(Ph}_3\text{P})_2\text{L}]\)) gains a share of eighteen electrons in its shell (a stable configuration). The reaction in this case may be typified as below:

\[
[\text{Cu(Ph}_3\text{P})_3\text{Cl}] + (\text{CH}_3)_3\text{Si} - \text{N} \quad \rightarrow \quad (\text{Ph}_3\text{P})_2\text{Cu} - \text{N} \quad + \text{Ph}_3\text{P} + (\text{CH}_3)_3\text{SiCl}
\]

\( R = \text{H}, (9) \)

\( R = \text{CH}_3, (10) \)

The reaction of CuCl₂ with \(\text{Ph}_3\text{P}\) is known to yield a Cu(I) complex. However, in the present reaction condition, it has been performed in the presence of the reagent trimethyl silylimidazole or 2-methylimidazole. The final product in either case has the stoichiometry \([\text{Cu(Ph}_3\text{P})_2\text{LCl}]\) (11) or (12). The physico-chemical investigations vide infra agree with a d⁹ configuration of copper having a tetrahedral array of ligands around it.
All of these complexes are soluble in most of the organic solvents, moisture sensitive and get solvolysed with water. The experimentally determined molecular weight agrees with their monomeric nature. The important characteristic imidazolate and Ph$_3$P ring vibrations as well as $\nu$(M-N), $\nu$(M-P) and $\nu$(M-Cl) stretching vibrations manifested in the I.R. spectra of the various complexes have been summarized in Table-III and -IV. The characteristic imidazole ring vibrations are slightly shifted (10-20 cm$^{-1}$) from their positions in the free imidazole, similar to that observed in the spectra of transition metal imidazolato-complexes$^{93,21-23}$ and of [BH$_{4-n}$L$_n$]$^{-}$ (n=2, 3 or 4; and L= imidazolate or 2-methylimidazolate). It can be seen from Table -IV that some of the characteristic bands of the imidazolate ring vibrations overlap with that characteristic of the Ph$_3$P, nevertheless, bands which are diagnostic for the presence of imidazolate and/or Ph$_3$P in the compounds are clearly indicated$^{93,94}$. The absence of a strong band at Ca.500 cm$^{-1}$ (characteristic of Ph$_3$P) in (5) and (6) confirms the mode of reaction shown by equation (3). A band at about 390 cm$^{-1}$ is attributed to $\nu$(M-N) [cf. (M-N) in imidazole complexes appears$^{93}$ at Ca.250 cm$^{-1}$]. In \[\text{[M\{N(SiMe$_3$)$_2$\}$_2$]} (M=Co, Zn, Cd, or Hg) too $\nu$(M-N) occurs at Ca.390 cm$^{-1}$, which has been attributed$^{77,89,95}$ to the $\pi$-donor nature of the ligand. The same may be true in the present complexes. The imidazolate moiety in the present complexes, therefore, acts as a four electron donor($\sigma$ and $\pi$). The band of medium intensity at about 320 cm$^{-1}$ arising in (1) and (2) is assigned$^{96}$ to $\nu$(M-Cl) stretching vibration. The $\nu$(M-Cl) and $\nu$(M-P) stretching vibrations for (2)-(12) are indicated at the appropriate positions$^{94,96}$. 
The results of the electronic spectra and magnetic susceptibility measurements are summarized in Table -V and -VI. The electronic spectra recorded in non polar solvents are nearly identical to the reflectance spectra of the solids, indicating the existence of similar species in solution as well as in solids. The bands observed in CH$_2$Cl$_2$ in (1) - (4) are reasonably assigned to the transitions characteristic of a linear arrangement$^{97}$ of ligand around cobalt(II) in D$_{\infty h}$ symmetry, similar to that reported$^{98}$ for gaseous CoCl$_2$. The electronic spectra in THF are, however, different containing a band at 15000 cm$^{-1}$ with a shoulder Ca. 17000 cm$^{-1}$, attributable to a tetrahedral geometry$^{99}$ around Cobalt(II). This change from linear in the solid and in CH$_2$Cl$_2$ solution to tetrahedral in THF solution may be due to coordination of THF in solution, which does not seem uncommon in view of a strong donor capacity of THF$^{91}$.

Solutions in methanol and ethanol have a pink colour and visible spectra are consistent with an octahedral geometry$^{100}$ for the solvolysed product.

The observed magnetic moment values Table-V are consistent with a high spin d$^7$ system$^{101}$. As has been suggested earlier$^{89,97,98}$, the ligand field by two nitrogens in a linear arrangement would not be large enough to allow the mixing of non-degenerate excited states, resulting in a higher $\mu_{eff}$ from that of the theoretical spin-only value. The observed band positions in (5) and (6) are characteristic of a diamagnetic square-
planer Ni(II) complex \(^{102}\). However, the observed Table-VI abnormal magnitude of \(\mu_{\text{eff}}(\text{Ca} 1.0 \text{ S.M.})\) favours some paramagnetism in the complex. The ground electronic state of Ni(II) complexes (Singlet diamagnetic or triplet paramagnetic) is exceptionally sensitive to geometry and/or the strength of the ligand field \(^{94,103a}\). The square-planer Ni(II) complexes are generally considered to be diamagnetic(singlet ground state \(^{1}A_{1g}\)). However, the ligand field treatment by Ballhausen and Liehr \(^{103b}\) suggests that square planer configuration may be retained even in triplet ground state. It is, quite possible that \([\text{NiL}_{2}]\) is basically square planer with \(^{1}A_{1g}\) ground state but mixed with or in equilibrium with paramagnetic species with \(^{3}A_{1g}\) ground state. Precedence for such behaviour is known \(^{104,105}\). A spin state isomerism \(^{106}\) may also be visualized. In other words the energy levels of different multiplicities are positioned with \(kT\) of each other making the complexes near the magnetic cross-over point whereby population of both states become equally probable.

The broad band appearing at \(\text{Ca} 14000 \text{ cm}^{-1}\) in the ligand field spectrum of bis(imidazolato)copper(II)(7) and bis(2-methyl-imidazolato) copper(II)(8) is assignable to the envelope of transitions \(^{2}A_{1g},^{2}B_{2g},^{2}E_{g} \leftarrow ^{2}B_{1g}\) characteristic of square-planer geometry \(^{107}\). The observed \(\mu_{\text{eff}}\) value is consistent with a \(d^{9}\) configuration of copper.

The \(\mu_{\text{eff}}\) values for (11) and (12) are somewhat higher from the calculated spin-only value \((S=\frac{3}{2})\), as expected owing to the spin-orbit coupling contribution, however, lie in the range
normally observed for various copper(II) complexes. The electronic spectra show a weak broad band at \( \text{Ca. } 22000 \, \text{cm}^{-1} \). The former weak band may be assigned to the blank of the tetrahedrally coordinated copper(II) ion which is generally in 10000-20000 cm\(^{-1}\) region. The main d-d band expected in the near I.R. region could not be recorded as it occurs beyond the range of our instrument. A regular tetrahedral geometry, in view of well known reasons, is unjustified, rather a flattening from regular tetrahedral geometry do occur in some cases. In the present complexes (11) and (12) presumably the steric factor is predominanting for adopting preferentially a tetrahedral structure.

The present data rule out any possibility for the formation of a reduced i.e. Cu(I) species (cf. reaction of CuCl\(_2\) with Ph\(_3\)P invariably yields a copper(I) complex). Furthermore, the products do contain one chlorine vide supra, even though, the reagents were sufficient to cause the replacement of both the chlorines. Steric factor is presumably operative in restricting the further substitution. The same argument seems valid to account for the release of one mole of Ph\(_3\)P from the reaction of [Cu(Ph\(_3\)P)\(_3\)Cl] with the reagents corroborating the reaction given by equation(5). In the absence of any spectral and magnetic data it can however, be assumed, in view of the analogy for the Cu(II) complex, that (9) and (10) also attain a tetrahedral structure.
### TABLE - I

Analytical data of [CoLCl] and [ML₂] [M = Co or Ni; L = imidazolate(Iz) or 2-methyl imidazolate (MeIz)].

<table>
<thead>
<tr>
<th>Complexes</th>
<th>% C Found (Calcd.)</th>
<th>% H Found (Calcd.)</th>
<th>% N Found (Calcd.)</th>
<th>% M Found (Calcd.)</th>
<th>% Cl Found (Calcd.)</th>
<th>Mol. wt. Found (Calcd.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(Iz)Cl]</td>
<td>(1) 22.2 (22.3)</td>
<td>1.6 (1.9)</td>
<td>17.3 (17.4)</td>
<td>36.0 (36.5)</td>
<td>20.8 (22.0)</td>
<td>172 (161)</td>
</tr>
<tr>
<td>[Co(MeIz)Cl]</td>
<td>(2) 27.8 (27.4)</td>
<td>2.5 (2.9)</td>
<td>15.4 (16.0)</td>
<td>32.7 (33.6)</td>
<td>20.0 (20.2)</td>
<td>191 (175)</td>
</tr>
<tr>
<td>[Co(Iz)₂]</td>
<td>(3) 28.5 (28.6)</td>
<td>2.4 (2.4)</td>
<td>22.1 (22.2)</td>
<td>45.4</td>
<td>-</td>
<td>208 (193)</td>
</tr>
<tr>
<td>[Co(MeIz)₂]</td>
<td>(4) 34.2 (34.3)</td>
<td>3.3 (3.6)</td>
<td>19.9 (20.0)</td>
<td>41.8</td>
<td>-</td>
<td>233 (220)</td>
</tr>
<tr>
<td>[Ni(Iz)₂]</td>
<td>(5) 37.0 (37.4)</td>
<td>3.0 (3.1)</td>
<td>28.8 (29.1)</td>
<td>29.5</td>
<td>-</td>
<td>182 (193)</td>
</tr>
<tr>
<td>[Ni(MeIz)₂]</td>
<td>(6) 43.1 (43.5)</td>
<td>4.3 (4.5)</td>
<td>24.9 (25.4)</td>
<td>25.2</td>
<td>-</td>
<td>208 (221)</td>
</tr>
<tr>
<td>[Ni(Iz)₂]</td>
<td>(5) 37.1 (37.4)</td>
<td>3.0 (3.1)</td>
<td>28.9 (29.1)</td>
<td>29.4</td>
<td>-</td>
<td>180 (193)</td>
</tr>
<tr>
<td>[Ni(MeIz)₂]</td>
<td>(6) 43.3 (43.5)</td>
<td>4.2 (4.5)</td>
<td>25.1 (25.4)</td>
<td>25.8</td>
<td>-</td>
<td>230 (221)</td>
</tr>
</tbody>
</table>

* obtained after following the reaction shown by eqn.(3) (See text).
### TABLE - II

Analytical data of [CuL₂], [Cu(Ph₃P)₂L] and [Cu(Ph₃P)₂LCl]

<table>
<thead>
<tr>
<th>Complexes</th>
<th>% C Found (Calcd.)</th>
<th>% H Found (Calcd.)</th>
<th>% N Found (Calcd.)</th>
<th>% M Found (Calcd.)</th>
<th>% Cl Found (Calcd.)</th>
<th>Mol. wt. Found (Calcd.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(Iz)₂]</td>
<td>(7) 36.1</td>
<td>3.0</td>
<td>27.8</td>
<td>30.9</td>
<td>-</td>
<td>205</td>
</tr>
<tr>
<td></td>
<td>(36.5)</td>
<td>(3.0)</td>
<td>(28.3)</td>
<td>(32.2)</td>
<td></td>
<td>(198)</td>
</tr>
<tr>
<td>[Cu(Ph₃P)₂(Iz)]</td>
<td>(9) 70.9</td>
<td>4.9</td>
<td>4.0</td>
<td>8.4</td>
<td>-</td>
<td>635</td>
</tr>
<tr>
<td></td>
<td>(71.5)</td>
<td>(5.0)</td>
<td>(4.3)</td>
<td>(9.7)</td>
<td></td>
<td>(655)</td>
</tr>
<tr>
<td>[Cu(Ph₃P)₂(MeIz)]</td>
<td>(10) 70.8</td>
<td>5.0</td>
<td>4.1</td>
<td>8.5</td>
<td>-</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>(71.8)</td>
<td>(5.2)</td>
<td>(4.2)</td>
<td>(9.5)</td>
<td></td>
<td>(669)</td>
</tr>
<tr>
<td>[Cu(Ph₃P)₂(Iz)Cl]</td>
<td>(11) 67.3</td>
<td>4.7</td>
<td>3.9</td>
<td>7.8</td>
<td>4.7</td>
<td>678</td>
</tr>
<tr>
<td></td>
<td>(67.8)</td>
<td>(4.8)</td>
<td>(4.1)</td>
<td>(9.2)</td>
<td>(5.2)</td>
<td>(690)</td>
</tr>
<tr>
<td>[Cu(Ph₃P)₂(MeIz)Cl]</td>
<td>(12) 68.0</td>
<td>4.9</td>
<td>3.7</td>
<td>8.1</td>
<td>4.2</td>
<td>715</td>
</tr>
<tr>
<td></td>
<td>(68.2)</td>
<td>(5.0)</td>
<td>(4.0)</td>
<td>(9.0)</td>
<td>(5.0)</td>
<td>(704)</td>
</tr>
<tr>
<td>[CuMe(Iz)₂]</td>
<td>(8) 42.0</td>
<td>3.9</td>
<td>24.2</td>
<td>27.0</td>
<td>-</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>(42.6)</td>
<td>(4.4)</td>
<td>(24.8)</td>
<td>(28.2)</td>
<td></td>
<td>(226)</td>
</tr>
</tbody>
</table>
TABLE - III

Imidazole-ring, M-N and M-Cl frequencies (cm⁻¹) observed in the I.R. spectra of [MLCl] and [ML₂].

<table>
<thead>
<tr>
<th>Complexes</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
<th>M-N</th>
<th>M-Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(Iz)Cl]</td>
<td>(1)</td>
<td>1545s</td>
<td>1480m</td>
<td>1420s</td>
<td>1345m</td>
<td>385s</td>
</tr>
<tr>
<td>[Co(MeIz)Cl]</td>
<td>(2)</td>
<td>1565s</td>
<td>1480m</td>
<td>1420s</td>
<td>1330m</td>
<td>390s</td>
</tr>
<tr>
<td>[Co(Iz)₂]</td>
<td>(3)</td>
<td>1555s</td>
<td>1475m</td>
<td>1425s</td>
<td>1350m</td>
<td>385s</td>
</tr>
<tr>
<td>[Co(MeIz)₂]</td>
<td>(4)</td>
<td>1540s</td>
<td>1490m</td>
<td>1420s</td>
<td>1335s</td>
<td>375s</td>
</tr>
<tr>
<td>[Ni(Iz)₂]</td>
<td>(5)</td>
<td>1550s</td>
<td>1480m</td>
<td>1420s</td>
<td>1340m</td>
<td>390s</td>
</tr>
<tr>
<td>[Ni(MeIz)₂]</td>
<td>(6)</td>
<td>1570s</td>
<td>1470m</td>
<td>1420m</td>
<td>1320m</td>
<td>390s</td>
</tr>
<tr>
<td>Complexes</td>
<td>Imidazole</td>
<td>Ph$_3$P</td>
<td>M-N</td>
<td>M-Cl</td>
<td>M-P</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------------------</td>
<td>----------------</td>
<td>-----</td>
<td>------</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>[Cu(Iz)$_2$]</td>
<td>(7) 1555s, 1475m, 1430s, 1320s;</td>
<td>-</td>
<td>375s</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Cu(MeIz)$_2$]</td>
<td>(8) 1550s, 1480m, 1420s, 1340m;</td>
<td>-</td>
<td>375s</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>[Cu(Ph$_3$P)$_2$(Iz)]</td>
<td>(9) 1550s, 1480s, 1430s, 1320m;</td>
<td>1480s, 740s, 1430s, 720s, 1090s, 510s, 490s</td>
<td>370m</td>
<td>-</td>
<td>320w</td>
<td></td>
</tr>
<tr>
<td>[Cu(Ph$_3$P)$_2$(MeIz)]</td>
<td>(10) 1555s, 1475s, 1430s, 1345m;</td>
<td>1475s, 1430s, 750s, 1100s, 720s, 510s, 490s</td>
<td>380m</td>
<td>-</td>
<td>310w</td>
<td></td>
</tr>
<tr>
<td>[Cu(Ph$_3$P)$_2$(Iz)Cl]</td>
<td>(11) 1530s, 1480s, 1420s, 1320m;</td>
<td>1480s, 740s, 1420s, 700s, 1090s, 510s, 490s</td>
<td>370m</td>
<td>270m</td>
<td>330w</td>
<td></td>
</tr>
<tr>
<td>[Cu(Ph$_3$P)$_2$(MeIz)Cl]</td>
<td>(12) 1550s, 1475s, 1430s, 1350m;</td>
<td>1475s, 1430s, 740s, 1090s, 700s, 510s, 490s</td>
<td>375m</td>
<td>270m</td>
<td>310w</td>
<td></td>
</tr>
</tbody>
</table>
TABLE - V

$\mu_{\text{eff}}$ (B.M.) and ligand field bands (cm$^{-1}$) observed in the electronic spectra of [CoLCl], [CoL$_2$] and their assignments.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>[Co(Iz)Cl] (1)</th>
<th>[Co(MeIz)Cl] (2)</th>
<th>[Co(Iz)$_2$] (3)</th>
<th>[Co(MeIz)$_2$] (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.T.</td>
<td>40800, 30300</td>
<td>40520, 30780</td>
<td>40550, 30280</td>
<td>40500, 30800</td>
</tr>
<tr>
<td></td>
<td>(40200, 31260)</td>
<td>(41120, 32260)</td>
<td>(41270, 31260)</td>
<td></td>
</tr>
<tr>
<td>$^4\Pi_g (P) \leftrightarrow ^4\Sigma_g^+ (F)$</td>
<td>23220</td>
<td>23300</td>
<td>23200</td>
<td>23480</td>
</tr>
<tr>
<td></td>
<td>(22410)</td>
<td>(22500)</td>
<td>(22500)</td>
<td></td>
</tr>
<tr>
<td>$^4\Delta_g (P) \leftrightarrow ^4\Delta_g (F)$</td>
<td>16600</td>
<td>16670</td>
<td>16550</td>
<td>16800</td>
</tr>
<tr>
<td></td>
<td>(16000)</td>
<td>(16130)</td>
<td>(16250)</td>
<td>(15750)</td>
</tr>
<tr>
<td>$^4\Delta_g (F) \leftrightarrow ^4\Delta_g (F)$</td>
<td>11500</td>
<td>11360</td>
<td>11360</td>
<td>11560</td>
</tr>
<tr>
<td></td>
<td>(11980)</td>
<td>(12310)</td>
<td>(11790)</td>
<td>(11790)</td>
</tr>
<tr>
<td>$\mu_{\text{eff}}$</td>
<td>4.72</td>
<td>4.68</td>
<td>4.52</td>
<td>4.60</td>
</tr>
</tbody>
</table>

Positions in CH$_2$Cl$_2$ solution given in parentheses
<table>
<thead>
<tr>
<th>Complexes</th>
<th>( \mu_{\text{eff}} )</th>
<th>Band Position</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ni(Iz)_2]</td>
<td>(5) 0.9</td>
<td>30300(29500)</td>
<td>( {1}B_{1g} ) ( \leftarrow {1}A_{1g} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23800(23300)</td>
<td>( {1}A_{2g} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14280(14500)</td>
<td>( {3}A_{2g} )</td>
</tr>
<tr>
<td>[Ni(MeIz)_2]</td>
<td>(6) 1.1</td>
<td>30350(30300)</td>
<td>( {1}B_{1g} ) ( \leftarrow {1}A_{1g} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23620(23500)</td>
<td>( {1}A_{2g} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14140(14000)</td>
<td>( {3}A_{2g} )</td>
</tr>
<tr>
<td>[Cu(Iz)_2]</td>
<td>(7) 1.86</td>
<td>14500(14300)</td>
<td>( {2}A_{1g} ) ( , {2}A_{2g} ) ( , {2}E_g ) ( \leftarrow {2}B_{1g} )</td>
</tr>
<tr>
<td>[Cu(MeIz)_2]</td>
<td>(8) 1.91</td>
<td>14260(14100)</td>
<td>-------------------</td>
</tr>
<tr>
<td>[Cu(Ph_3P)_2Iz]Cl</td>
<td>(11) 1.93</td>
<td>22700(22200)</td>
<td>Blank</td>
</tr>
<tr>
<td>[Cu(Ph_3P)_2(MeIz)Cl]</td>
<td>(12) 1.91</td>
<td>22000(21700)</td>
<td>----do---</td>
</tr>
</tbody>
</table>

Positions in CH_2Cl_2 solution given in parentheses, \(^\dagger\)Non SI unit employed B.M. = 0.9274x10^{-23}\,\text{JT}^{-1}
REFERENCES


64. H.C. Brown, H.I. Schlesinger and S.Z. Cardon, ibid., 64, 325 (1942).


