Synthesis and characterization of
dinuclear niobium(IV) complexes with
symmetrical and unsymmetrical
ditertiary phosphines

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A series of dinuclear diamagnetic niobium(IV) complexes of the types Nb2Cl8[~2- p- (CH2)n - p-
(2) (where n = 1 to 6), Nb2Cl8[~2- p- CH = CH - p-
(2) and Nb2Cl8[~2- p- P-CH=CH-P-~2h (p-
FC6H4)2P- (CH2)2 - P-~2h have been
synthesized by the reaction of niobium(IV) chloride
tetrahydrofuran adduct in THF with symmetrical and
unsymmetrical ditertiary phosphines viz., 1,2-
bis(diphenylphosphino)methane (dppm), 1,2-
bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenyl-
phosphino)propane (dppp), 1,4-bis(diphenylphosphino)
butane (dppb), 1,5-bis(diphenylphosphino)pentane
(dpdpent), 1,6-bis(diphenylphosphino)hexane (dpph),
cis-1,2-bis(diphenylphosphino)ethylene (dpen) and
1-diphenylphosphino-2-bis[(p-fluoro)phosphino]ethane
dp[pt/pe).

All these complexes have been characterized by ele-
mental analyses, IR, 1H NMR, 31P NMR, 13C NMR
spectroscopy and magnetic susceptibility measure-
ments.

Phosphorus complexes are of considerable inter-
est as precursors in the synthesis of highly reactive
lowervalent metal derivatives whose role in homogene-
ous catalysis and activation of chem-
ically inert molecules is widely known. The redu-
cing ability of phosphines for early transition
metal compounds in their highest oxidation states
has often been observed, especially for PPh3 and
has been used sometimes for synthetic purposes.
Such behaviour was also found towards niobi-
ium(V) halides. When the reaction was conduct-
ed in the presence of reductants which limit the
role of the phosphines to that of a ligand, molecular
derivatives of lower oxidation states were ob-
tained.

In this note, we have investigated the reactions
of niobium tetrachloride with some symmetrical
and unsymmetrical ditertiary phosphines of the formula
\[ \phi_1 P - (CH_2)_n - P - \phi_2 \] (where n = 1 to 6),
\[ \phi_1 P - CH = CH - P - \phi_2 \]
and (p-
FC6H4)2P- (CH2)2 - P-~2h. These ditertiary phos-
phines were selected to observe the effect of in-
crease in the length of carbon chain present in-
between two phosphorus atoms on the bonding
behaviour of the complexes and also in the hope
that they would stabilize unusual geometries and
stoichiometries of the adducts and induce inter-
esting reactivity and chelating to metal in trans
position or may bridge to give oligomeric sys-
tems.

Experimental
All the manipulations were carried out under
oxygen-free dry nitrogen using Schlenk equilib-
rium and vacuum line techniques. The solvents
were purified by standard methods. THF was dis-
tilled over Na-benzophenone immediately before
use. The complex NbCl4(THF)2 was prepared by
the reduction of NbCl5 with Al powder as de-
scribed in the literature. The compound 1-di-
phenylphosphino-2-bis[(p-fluoro)phosphino]ethane
was prepared by the literature method. All other
reactants were purchased from Aldrich and were
used as such.

The 1H NMR spectra were recorded on Perkin-
Elmer R-32 90 MHz spectrometer. The 31P and
13C NMR spectra were recorded on Bruker 300
MHz spectrometer at RSIC, Chandigarh using
H2PO4 and TMS as standards respectively. The infrared spectra of the compounds were recorded
in the range 4,000-200 cm⁻¹ using Perkin-Elmer
model 842 and 631 grating spectrophotometer and
magnetic susceptibility data was determined
by Faraday method at RSIC, Roorkee. Chloride
was estimated as AgCl and niobium as Nb2O5.
Carbon and hydrogen analyses were done at
RSIC, Chandigarh.

Preparation of complexes

\[ \text{NbCl4(THF)}_2 \] was prepared by the reduction
of NbCl5 with Al powder (3:1) in acetonitrile
followed by the addition of THF and then isolated
as a yellow product. A general procedure for the
preparation of the complexes of NbCl4(THF)2
with ditertiary phosphines involved the mixing of
contents in THF at room temperature in the molar ratio 1:2. In each case, the stirring period ranged from 2-5 h. It was then filtered and to the filtrate was added pentane slowly and the mixture cooled over liquid nitrogen vapours. The solid product so obtained was filtered, washed with pentane and dried *in vacuo*. The excess of ligand was recovered by drying the mother liquor. The exact melting points could not be determined since all the complexes decomposed in the range 101-152°C. The analytical data of the products are presented in Table 1.

**Results and discussion**

The reactions of NbCl₄(THF)₂ with ditertiary phosphines, \( \phi_2 - P - (CH_2)_n - P - \phi_2 \) (where \( n = 1 \) to 6), \( \phi_2 - P - \text{CH} = \text{CH} - P - \phi_2 \) and \( (p\text{-FC}_6\text{H}_4)\phi_2 - P - (CH_2)_2 - P - \phi_2 \) in the ratio 1:2 in dry THF are represented by the following general equations (where \( \phi P \) represents the corresponding phosphine viz. dppm, dppe, dppp, dppy, dppent, dppb, dpppent, dpph, dppen, dp(pf)pe).

\[
2\text{NbCl}_4(\text{THF})_2 + 4\phi P \xrightarrow{\text{room temp.}} \text{Nb}_2\text{Cl}_8(\phi P)_2
\]

stirring for 2-5 h + 2\( \phi P \)

All the complexes are crystalline solids and extremely sensitive to hydrolysis. These complexes are found to be unstable in solids as well as in solution. They are soluble in THF, ethanol, DMSO, partially soluble in chloroform but insoluble in hexane, pentane, etc.

In the process to replace 2 moles of THF with 2 moles of phosphine, the reaction between NbCl₄(THF)₂ and ditertiary phosphine was carried out in 1:2 molar ratio. The analysis of the product, however, indicated the replacement of both the THF with only one phosphine. On the other hand, when the reaction was carried out in 1:1 molar ratio, the replacement of THF was incomplete even after stirring for longer duration and only 0.6-0.8 moles of phosphine got attached to NbCl₄. This indicates that the excess of phosphine must be playing some role in the replacement of THF. Further, it has been found that as the length of the backbone of the ligands increases, the reaction time increases showing steric involvement in the formation of complexes.

The magnetic susceptibility data reveal very little paramagnetism which can only be explained if the complexes exist as dimers having metal-metal interaction.

The IR spectra of the ligands show characteristic bands for \( \nu(C - H) \) aliphatic, \( \nu(P - C) \) aromatic, \( \nu(C - C) \) and \( \nu(P - C) \) stretching and skeleton modes at \( \sim 3050 \text{ cm}^{-1} \), \( \sim 1085 \), \( \sim 1025 \) and \( \sim 690 \text{ cm}^{-1} \), respectively. The bands due to \( \nu(P - C) \) aromatic and \( \nu(P - C) \) stretching and skeleton show an increase in frequency by 10-20 \( \text{cm}^{-1} \) in the spectra of the complexes indicating that the phosphorus atoms are co-ordinated to the metal atom. Further, the absence of a band at 1155 \( \text{cm}^{-1} \) due to \( \text{R:C(O)H} \)
stretching in the IR spectra of complexes rules out the possibility of oxidation of phosphorus(III) to (V) state by oxygen absorption. The Far-infrared spectra of complexes show medium bands in the region 340-320 cm\(^{-1}\) and 310-290 cm\(^{-1}\) which have been assigned to terminal and bridging chlorines respectively\(^9\).

The \(^1\)H NMR spectra of symmetrical ditertiary phosphines in CDCl\(_3\) show a singlet at \(\delta\) 7.2-7.3 due to phenyl groups attached with the two phosphorus atoms. The signals due to \(-\text{CH}_2-\) protons attached directly with the phosphorus atoms are observed at \(\delta\) 2.8 in case of diphenylphosphino methane and at \(\delta\) 2.1-2.0 in case of dppe, dppp, dppe, dppe, and dphp. A signal due to vinyl protons \(-\text{CH=CH-}\) directly attached with phosphorus atoms is observed at \(\delta\) 7.4 to \(\delta\) 7.0 as a triplet in diphenylphosphino ethylene. However, in the case of unsymmetrical ditertiary phosphine, when the spectrum is taken on Bruker 300 MHz spectrometer, two unresolved triplets were observed. The chemical shift difference between the two triplets (\(\sim 0.05\) ppm) is a clear indication of slight non-equivalence of two methylene groups.

The \(^1\)H NMR spectra of Nb(IV) phosphine complexes in DMSO-\(d_6\) shows an ill-resolved multiplet in the region \(\delta\) 7.8-7.2 due to phenyl groups attached with phosphorus atoms. This slight downfield shift in the position of aromatic protons clearly shows the coordination of phosphorus atoms with niobium. This is also indicated by the downfield shift of \(\delta\) 0.4-0.5 in the signals due to methylene and vinyl groups attached to phosphorus.

The \(^{13}\)C NMR spectra of symmetrical phosphines show signals in two distinct region. In the aliphatic region, there is a triplet in the proton-decoupled spectrum of dppm at \(\delta\) 24.94 (\(\text{J}_{p-c}=22.86\) Hz) obviously arising from the methylene carbon equally coupled to two phosphorus. In the aromatic region, there are four signals at \(\delta\) 138.64, \(\delta\) 132.8, \(\delta\) 128.68 and \(\delta\) 128.35, the last three corresponding to protonated carbons (coupled spectra). The singlet observed at \(\delta\) 138.64 fits for the quaternary carbon 1 of the phenyl ring. The triplet observed at \(\delta\) 132.8 (\(\text{J}_{p-c}=10.65\) Hz) can be assigned to the carbons 2 and 6. The signal at \(\delta\) 128.68 being a singlet agrees for carbon-4 of the phenyl ring and the triplet at \(\delta\) 128.35 is due to the carbons 3 and 5 (\(\text{J}_{p-c}=3.82\) Hz).

In the spectra of dppe, dppp and dppe, a multiplet is observed at \(\delta\) \(\sim\) 28.01 arising from overlap of a triplet (\(\text{J}_{p-c}=15\) Hz) and a doublet (\(\text{J}_{p-c}=10\) Hz) at \(\delta\) \(\sim\) 28.06 and \(\delta\) \(\sim\) 27.89 which are expected for terminal methylene and middle methylene groups respectively. In the aromatic region, there is a triplet at \(\delta\) \(\sim\) 128.7 (\(\text{J}_{p-c}=6.88\) Hz) which can be assigned to carbons 3 and 5 and a singlet at \(\delta\) \(\sim\) 128.8 for C-4 of the phenyl ring. A doublet observed at \(\delta\) \(\sim\) 132.95 agrees for carbons 2 and 6 (\(\text{J}_{p-c}=19.9\) Hz). There is a doublet at \(\delta\) \(\sim\) 139.05 which fits for quaternary carbon 1 of the phenyl ring (\(\text{J}_{p-c}=13.7\) Hz).

The spectrum of dppen shows a triplet due to ethylenic carbons at \(\delta\) \(\sim\) 146.5 (\(\text{J}_{p-c}=7.62\) Hz). The spectra of dpppent and dphp show three doublets at \(\delta\) \(\sim\) 26.05, \(\delta\) \(\sim\) 28.2 and \(\delta\) \(\sim\) 31.1 in the aliphatic region which can be assigned to carbons \(\text{J}_{p-c}=15.27\) Hz, \(\text{J}_{p-c}=10.65\) Hz, \(\text{J}_{p-c}=12.26\) Hz, respectively. In case of dp(pf)pe, the signal due to aliphatic carbons is observed as a triplet at \(\delta\) \(\sim\) 23.5 (\(\text{J}_{p-c}=13.7\) Hz). The nature of the triplet suggests that \(\text{J}_{p-c}\) and \(\text{J}_{p-c}\) are nearly equivalent. In all the cases, the aromatic region shows the usual patterns for carbon 1, 2, 3, 5, 4 and 6 of the phenyl rings.

The \(^{13}\)C NMR spectra of the complexes show signals for aliphatic and aromatic carbons without any significant change. However, each signal due to aromatic carbons further splits into two signals except in dppm (where there is no further splitting) thereby indicating non-equivalence of the phenyl rings and hence suggesting unsymmetrical structures.

The \(^{31}\)P \(^{1}\)H NMR spectra of the symmetrical phosphines consist of a singlet (at \(\delta\) \(\sim\) 12 to \(\delta\) \(\sim\) 23) due to the chemically equivalent phosphorus atoms. However, in case of unsymmetrical phosphines, two doublets are observed at \(\delta\) \(\sim\) 14.6 and \(\delta\) \(\sim\) 12.40 with an identical separation between component of each doublet (\(\text{J}_{p-c}=34.5\) Hz), thus confirming the non-equivalence of two phosphorus nuclei.

The proton decoupled \(^{31}\)P NMR spectra of the complexes with symmetrical and unsymmetrical phosphines show a positive shift of the signals in the region \(\delta\) \(\sim\) 31 - \(\delta\) + 42. This positive shift clearly indicates that both the phosphorus are coordinating to the metal. The presence of two signals in the spectra of symmetrical phosphine complexes except the dppm (where only one signal is observed) in this region shows the magnetic non-equivalence of the two phosphorus atoms and hence the two phosphines are coordinating in such a way that the phenyl groups attached with the two phosphorus atoms lie in different environments. However, unsymmetrical phosphine
complexes show expected AB spin system consisting of a pair of doublets ($J_{P-P'} \approx 41$ Hz) in $^{31}P$ NMR spectra. The appearance of two doublets also indicates the non-equivalence of two phosphorus atoms.

The analysis of AB spectra observed for the ligand-" and complex indicates that the appearance of spectra is markedly dependent upon the relative values of spin-spin couplings ($J_{P-P'}$) and the chemical shift difference between the two non-equivalent phosphorus nuclei. Many factors are known to strongly influence the magnitude of ($J_{P-P'}$)$^2$ including the nature of transition metals, the ligands other than phosphorus in the complex and substituents bonded to phosphorus.

On the basis of the spectral data of Nb(IV) chloride complexes of symmetrical and unsymmetrical ditertiary phosphines, it is tentatively proposed that binuclear complexes of the type Nb$_2$Cl$_6$(PP)$_2$ are formed (I, II) having metal-metal bond interaction. In structure I, the phosphines are present in the same environment having equatorial position while in the binuclear structure II, the two phosphines are present in different atmospheres wherein one PP adopts axial (having an edge sharing biocahedral structure) position on one niobium and the other phosphine group occupy terminal equatorial position on the second niobium. By analogy with the structure of Ta$\_3$Cl$_6$(PMc$_3$)$_4$, the signal at lower $\delta$ value in $^{31}P$ NMR spectra is assigned to equatorial phosphine and resonance at higher $\delta$ value may be due to axial phosphine.

The fact that this dinuclear molecule adopts a more congested configuration indicates a balance between steric and electronic effects. It is the electronic effect which overweighs the steric effect and thereby decides the stereochemistry of these complexes.

References