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Research Article**STUDIES ON THE SYNTHESIS AND CHARACTERISATION OF MOLYBDENUM (V)
ORGANOPHOSPHONIUM COMPLEXES**Jyotsna Ratan*¹ and Niraj Saxena²¹Department of Chemistry, Zakir Husain Delhi College, University of Delhi²Department of Chemistry, Bareilly College, BareillyDOI: <http://dx.doi.org/10.24327/ijrsr.2021.1311.0541>**ARTICLE INFO****Article History:**Received 10th October, 2022Received in revised form 20th October, 2022Accepted 15th November, 2022Published online 28th November, 2022**ABSTRACT**

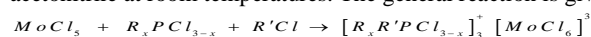
The reaction between Molybdenum (V) chloride and diphenyl chlorophosphine, triphenyl phosphine in presence of t-butylchloride, iso-butylchloride, t-amylalchloride, cyclohexylchloride and triphenyl methylchloride as alkylating agents have been studied. The

molybdenum (V) derivatives of the type $[Bu^iPh_2PCl]^+[MoCl_6]^-$ (I), $[Bu^{iso}Ph_2PCl]^+[MoCl_6]^-$

(II) $[Am^iPh_2PCl]^+[MoCl_6]^-$ (III) $[C_6H_{11}Ph_2PCl]^+[MoCl_6]^-$ (IV) $[Ph_3CPh_2PCl]^+[MoCl_6]^-$ (V),

$[Bu^iPh_3P]^+[MoCl_6]^-$ (VI) $[Bu^{iso}Ph_3P]^+[MoCl_6]^-$ (VII) $[Am^iPh_3P]^+[MoCl_6]^-$ (VIII),

$[C_6H_{11}Ph_3P]^+[MoCl_6]^-$ (IX), $[Ph_3CPh_3P]^+[MoCl_6]^-$ (X) have been isolated 1 : 1 molar reaction. The reactions have been carried out in organic solvents media like CCl_4 or CH_2Cl_2 or acetonitrile at room temperatures. The general reaction is given as:



Where $x = 1, 2, 3$ $R = Ph, Cl$, $R' = Bu^i, Bu^{iso}, Am^i, Cydohexyl, Ph_3C$

The isolated components are coloured solids. The compounds are insoluble in organic solvents. The compounds are highly sensitive to air moisture. They are sticky in nature. The compounds have been characterized by elemental analysis, Infra-red (near and far) spectral studies, electrical conductivity and magnetic susceptibility.

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INTRODUCTION

The reaction between organophosphines, and alkyl/aryl halide gave an ionic product like $[R_xP]^+ X^-$ containing organophosphonium cation and halide anion¹. The formation of adducts between trichlorophosphine and metal halides of metals like Pt², Pd³, Au⁴, Cu⁵, Cr⁶ and Ti⁷ have been reported in literature. The formation of organophosphonium derivatives of Aluminum (III) chloride and trichlorophosphine in presence of several alkyl/aryl chlorides in dichloromethane solvent have been reported⁸⁻¹¹. Puri and Saini¹² have reported the formation of organophosphonium derivatives of FeCl₃, NbCl₅ and TaCl₅¹³ with PCl₃ and MePcl₂ in presence of alkyl/aryl chlorides as alkylating agents, Puri and Saini¹⁴ and Bullock et.al¹⁵ reported the formation of ionic product $[RR'Pcl_2]^+[Wcl_6]^-$ in the reaction of tungsten (V) chloride, trichlorophosphine or methyl/phenyl dichlorophosphine in presence of alkyl/aryl chloride as alkylating agents, Bullock et.al¹⁶ also reported the formation of $[Bu^iPcl_3]^+[Re_3cl_9]^-$ complex having Re-Re bond in anion. The

formation of phosphonium derivatives as chloro Bromo and mixed chloro=Bromo mettalates of metals like Zn, Cd, Hg, Ce, Au, Pd and Pt were reported by Burmiester et.al¹⁷ and Clark, et.al.¹⁸ Keeping view of the fact that chloro metallates of phosphonium cation have wide utility as better catalysis in synthetic and polymers ion reactions of olefins and acetylene as well as of great biological activity, the organophosphonium derivatives of molybdenum (V) were synthesized and characterized by chemical analysis, infrared spectral studies, electrical conductivity and magnetic susceptibility measurements.

MATERIAL AND METHODS**Chemicals**

Molybdenum (V) chloride (Fluka) was used as such after drying and analysis. Diphenyl chlorophosphine, triphenyl phosphine, alkylating agents as t-butyl, iso-butyl, t-amyl, cyclohexyl and triphenyl chlorides, organic solvents like carbon tetra chloride, methelen chloride and acetonitrile were used after making anhydrous by known methods.

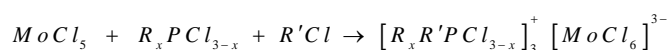
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EXPERIMENT

(i) The reactions between molybdenum (V) chloride and diphenyl chlorophosphine, triphenyl phosphine in presence of alkylating agents like t-butylchloride, iso-butylchloride, t-amylchloride, cyclohexyl chloride and triphenyl methyl chloride were carried out in carbon tetrachloride or methelene chloride or acetonitrile media in 1 : 1 molar ratio at room temperature. The reactants were taken in calculated amount. Anhydrous molybdenum (V) chloride was dissolved in organic solvent. To this solution organophosphine derivative and alkylating agent were added slowly in stepwise in a stoppered flask at room temperature. The reaction mixture was shaken well and kept for completion of the reaction. The reaction was complete in about 8-10 days duration. The coloured solid was deposited in the bottom of the flask. The coloured solid product was separated and washed with methelene dichloride. The product was dried under reduced pressure (2 mm of Hg) at room temperature. The coloured product was kept under anhydrous conditions and was analysed.

The general reaction is given below



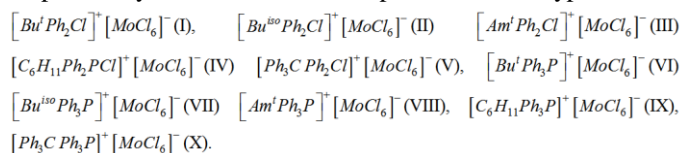
Where $x = 1, 2, 3$ $R = Ph, Cl$, $R' = Bu^t, Bu^{iso}, Am^t, Cydohexyl, Ph_3C$

(ii) Estimation of phosphorus was done by precipitating phosphorus as magnesium ammonium phosphate after oxidizing the sample with nitric acid and potassium permagnates Chlorine was estimated gravimetrically¹⁹ as silver chloride.

Infrared spectra (near and far) were recorded on a Bechman spectrophotometer model IR-20 in nujol null or in neat from taking care to avoid atmospheric moisture. Molar conductivity of the sample in dimethyl sulfoxide (DMSO) solvent were measured using electro-conductivity bridge of typ CM-82-T. The magnetic susceptibility of the samples were determined by Gouy method. The analytical results have been summarized in Table-1 and Table-2.

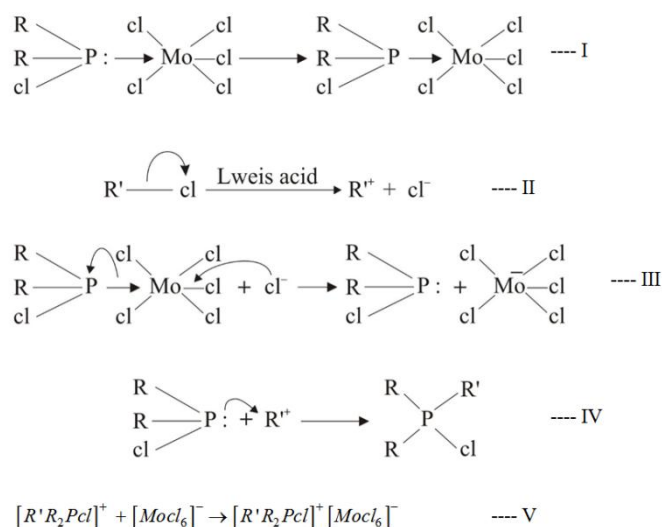
RESULT AND DISCUSSION

The reactions between anhydrous molybdenum (V) chloride, diphenyl chlorophosphine, triphenyl phosphine and alkylating agents like t-butyl chloride, iso-butyl chloride, t-amylchloride, cyclohexyl chloride and triphenyl methyl chloride in carbon tetrachloride solvent media in 1 : 1 molar ratio at room temperature yielded coloured solid products of the type,



The products are dark blue-green coloured solids and highly hygrscopic in nature. These change in colour when placed in moistair.

The products have been characterized on the basis of elemental analysis, electrical conductivity measurements, magnetic susceptibility measurements and infrared (near and far) spectral studies. Analytical results are given in table-1 and table-2. Plausible mechanism of the formation of 1: 1 molar ratio products may be shown as below:



where $R' = Bu^t, Bu^{iso}, Am^t, C_6H_{11}, Ph_3CR = Ph$

The molar magnetic susceptibility of hexachlorometallate of molybdenum were found to be in the range of 0.55 – 0.58 B.M. These results confirm the presence of $[MoCl_6]^-$ type anion as also reported earlier²⁰.

The molar conductance of some compounds was determined in solution ($10^{-3}M$) in DMSO solvent. The molar conductance values suggest the compounds are of ionic in nature. This confirms the presence of complex phosphonium cation $[R'R_xPCl_{3-x}]^+$ and anion $[MoCl_6]^-$ in 1 : 1 adduct. The presence of cation and anion have been confirmed by infrared (near and far) spectral studies.

Study of Cationic Spectra

The infrared spectra (near and far) of molybdenum (V) organophosphonium cation were obtained and interpreted for linkages in cation. Weak IR absorption in the range 785-775 cm^{-1} could be assigned to ν_{P-C} (alkyl) vibration and the medium weak band in the range 485-480 cm^{-1} , strong band at 635 cm^{-1} may be due to ν_{P-Cl} vibrations observation of strong bands in the region 1440-1000 cm^{-1} may be due to ν_{P-Ph} vibrations and strong bands in the range 615-490 cm^{-1} may be due ν_{P-Cl} vibrations.

Study of Anionic Spectra

IR spectra of anion $[MoCl_6]^-$ were in agreement with the octahedral species. The IR-bands observed in the range of 305-300 cm^{-1} may be assigned to ν_3 mode and are in agreement with observed by Bullock *et al.*¹⁶

Conclusion

The organophosphonium complexes of molybdenum (V) chloride with organophosphine derivatives and alkyl/aryl chlorides as alkylating agents are coloured solids insoluble in organic solvents. The products are highly sensitive to moisture. The molar magnetic susceptibility values confirm the presence of $[MoCl_6]^-$ type anion as also reported earlier²⁰. The molar conductance values suggest that the products are ionic in nature. This confirms the presence of complex phosphonium cation $[R'R_xPCl_{3-x}]^+$ and anion $[MoCl_6]^-$ in 1 : 1 adduct. The

presences of cation and anion have been confirmed by infrared (near and far) spectral studies. IR spectra of anion $[MoCl_6]^-$ were in good agreement with octahedral species.

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