Cent. Eur. J. Chem. • 10(1) • 2012 • 165-171
DOI: 10.2478/s11532-011-0120-9

VERSITA

Central European Journal of **Chemistry**

Syntheses and characterisation of chloro(η3-allyl) dicarbonylmolybdenum(II) complexes of chiral and achiral ditertiaryphosphines

Research Article

Joe G. Jesu Raj[1*], Devendra D. Pathak[3], Pramesh N. Kapoor[2]

[1]*Institut National de la Recherche Scientifique (INRS), Centre Energie Matériaux Télécommunications, Bionanotechnology Laboratory, Varennes (Québec) J3X 1S2, Canada*

[2]*Department of Applied Chemistry, Indian School of Mines, Dhanbad 826 004, India*

[3]*Department of Chemistry, University of Delhi, Delhi 110 007, India*

Received 2 June 2011; Accepted 27 September 2011

Abstract: A series of the complexes of the general formula $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P)]$, [where (P-P) = (*m*-$CH_3C_6H_4)_2P(CH_2)_2PPh_2$ (*m*-t-dppe); *cis*-$Ph_2PCH{=}CHPPh_2$ (*cis*-diphos); $Ph_2PCH_2CH_2AsPh_2$ (arsaphos); $Ph_2P(CH_2)_4PPh_2$ (dppb); (±)-1,2-$C_6H_4(PMePh)_2$ (*rac*-diphos); (*2R,3R*)$Ph_2PC^*H(Me)C^*H(Me)PPh_2$ (+)-chiraphos; (*R,R*)-$Me_2C(O)_2\{C^*HCH_2PPh_2\}_2$ (-)-diop] were synthesised by the reaction of the precursor complex $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(CH_3CN)_2]$ with the corresponding ditertiary phosphine in acetone. The complexes were isolated as yellow to orange air-stable solids and characterised by elemental analyses, FTIR and multinuclear NMR [^1H, $^{31}P\{^1H\}$] spectroscopic techniques. The carbonyl force constant values were calculated by Cotton and Kraihanzel approximate secular equations using $\nu_{C\equiv O}$ stretching frequencies observed in the FTIR and these were found to be 14.30 – 14.59 mdyne Å^{-1} and 0.23 – 0.70 mdyne Å^{-1} for K_1 and K_i respectively. Spectroscopic evidences have confirmed *cis*-octahedral structures for the synthesized complexes.

Keywords: *Chelating ligands • phosphines • carbonyl force constants • Cotton and Kraihanzel approximations and allylic moiety*

1. Introduction

The chemistry of ditertiaryphosphines and their derivatives has aroused much interest in the last few decades because of their reactivity, structural novelty and catalytic activity [1-5]. Gilani *et al*. [6] synthesized allyl complexes containing molybdenum and tungsten with monodentate ligands.

Allyl molybdenum complexes of the type $[XMo(CO)_2(\eta^3\text{-}C_3H_5)L_2]$ and $[XMo(CO)_2(\eta^3\text{-}C_3H_5)(L\text{-}L)]$ [where X = halide or pseudohalide and L = monodentate or bidentate ligand] have been known for quite some time [7]. It has been found that complexes of this type can be used as catalysts in polymerization reactions of some dienes [8] (when $X{=}CF_3$ and $L\text{–}L{=}CH_3O(CH_2)_2OCH_3$). The potential of these complexes in allylic alkylation reactions was exploited by Trost *et a.* [9] and Sjögren *et al.* [10]. The catalytic activities of these allyl complexes have been reviewed by Kurosawa *et al.* [11]. In these complexes the allylic group has its terminal carbon atoms eclipsing the carbonyls, which has been demonstrated to be the most energetically favorable arrangement. The stereochemical non-rigidity in molybdenum(II)-allyl complexes was studied [12] and showed that they can adopt, in the solid state, either a symmetric or a non-symmetric structure [13]. Recently, Perez *et al.* [14] investigated the reactions of the precursor complex $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)_2]$ [15] with variable ratios of ditertiaryphosphines, such as dmpm and dppm, to afford different products in which the ditertiaryphosphines as chelating ligands, *e.g.* $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P)]$, $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(NCMe)(P\text{-}P)]$ and $[\{Mo(\eta^3\text{-}C_3H_5)(CO)_2\}_2(\mu\text{-}Cl)_3]$ or as a bridging ligand as in $[\{Mo(\eta^3\text{-}C_3H_5)\text{-}(CO)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}P\text{-}P)]$, (P-P = dmpm, dppm). The precursor complex $[XM(CO)_2(\eta^3\text{-}C_3H_5)(CH_3CN)_2]$ has been used for the synthesis of allylic derivatives, which may be obtained by replacement of the weakly bonded nitriles by nitrogen [16-18] phosphorus [19] or carbocyclic [20] ligands.

* *E-mail: raj@emt.inrs.ca*

Allyl substituted organophosphorus compounds find applications in organic synthesis, in which, functionalization chemistry concerns the α-carbanions, which are formed upon abstraction of a proton from the allyl moiety by a strong base. When such anions are generated from triphenylphosphonium salts, reaction with carbonyl compounds leads to the formation of a conjugated alkene through a Wittig reaction, and its reactivity has been widely explored in the synthesis of natural compounds like callystatin-A [21], astaxanthin analogues [22], ratjadone [23], epolactaene [24], viridenomycin [25] or superstolide-A [26]. In such cases, however, the loss of the phosphorus moiety is necessary to complete the synthesis.

In view of its applications in synthetic organic chemistry, metal carbonyl complexes containing allyl and ditertiaryphosphine ligands ligands have gained much importance in recent years. However, a thorough literature review revealed that virtually no work has been done on the synthesis of metal carbonyls containing chiral and achiral phosphines and allylic linkages. Herein, we wish to report syntheses of Mo(II)-allyl complexes of general formula $[XMo(\eta^3\text{-}C_3H_5)(CO)_2(L\text{–}L)]$ with some relatively new chiral and achiral ditertiaryphosphine ligands. The structures of these complexes were established using elemental analyses, FTIR, and multinuclear NMR spectroscopic techniques.

2. Experimental procedure

Ditertiaryphosphines are highly reactive towards oxygen to form ditertiaryphosphine oxides in solution. In order to avoid the possibility of oxide formation, special precautions were taken to exclude oxygen from apparatuses, solvents, and the atmosphere.

All reactions were carried out in an atmosphere of oxygen free, dry nitrogen using standard Schlenk tube technique on a vacuum line. Special type of apparatuses having inlet and outlet passage for nitrogen was used. During removal of solvents and volatile fractions under reduced pressure, traps of conventional design, using liquid nitrogen/dry ice-acetone, and fused calcium chloride towers were used to prevent the back diffusion of moisture from the pump or the passage of solvent vapors into the pump.

Ligands (+)-chiraphos, (-)-diop, dppb, arsaphos were obtained from Aldrich and used as received without further purification.

Acetonitrile (B.D.H) was kept over anhydrous potassium carbonate and then distilled. Acetone was dried over anhydrous sodium sulfate and then distilled.

The Infrared spectra of solid samples were recorded in KBr pellets in the region 4000 - 400 cm^{-1}. Liquid samples were recorded in chloroform in the above region on a Perkin-Elmer 2000 Fourier Transform Infrared (FTIR) spectrometer in the Department of Applied Chemistry, Indian School of Mines, Dhanbad.

The ^{1}HNMR spectra of complexes and starting materials were recorded on a Bruker AV400MHz instrument in $CDCl_3$ using Tetramethylsilane (TMS) as an internal standard. The ^{1}HNMR of complexes were recorded in $CDCl_3$ solvent at the Indian Institute of Chemical Technology, Hyderabad, Indian Institute of Chemical Biology, Kolkata and at the ChemBioTek Research International, Kolkata.

The $^{31}P\{^1H\}$NMR spectra were recorded on a Bruker AV-400 spectrometer with a scanning frequency of 161.9 MHz using 85% Orthophosphoric acid (H_3PO_4) as an external reference, at the University of Texas, El Paso and at the ChemBioTek Research International, Kolkata.

Elemental analyses were done at the ChemBioTek Research International, Kolkata.

Melting points of the complexes were measured at the Indian Institute of Chemical Biology (IICB), Kolkata, in a sealed capillary tube.

2.1. Synthesis of 1-diphenylphosphino-2-*bis*(m-tolyl)phosphinoethanechloro(η³-allyl)dicarbonylmolybdenum(II), $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)\{Ph_2P(CH_2)_2P(m\text{-}CH_3C_6H_4)_2\}]$

The ligand, 1-diphenylphosphino-2-*bis*(*m*-tolyl) phosphinoethane (150 mg, 0.35 mmol) dissolved in 15 mL of dry acetone was added dropwise to the allyl precursor, $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(CH_3CN)_2]$ (108 mg, 0.35 mmol) dissolved in 10 mL of acetone. The solution was heated at 40°C for 6 h under nitrogen atmosphere. During this period the solution had turned bright orange from initial yellow. After removal of the solvent *in vacuo*, the residue was dissolved in chloroform (10 mL). The solution was filtered through a G-3 sintered funnel to get a clear solution. Dropwise addition of petroleum ether (40-60°C) to this solution precipitated a lemon yellow powder, which was recrystallised from a mixture of chloroform-petroleum ether (40-60°C) to give a lemon yellow complex (138 mg, 61%; m.p. 174-176°C (decomp.); Anal. Calcd. for $C_{33}H_{33}O_2ClP_2Mo$: C, 60.52; H, 5.08; Found: C, 60.38; H, 5.22.

2.2. Synthesis of 1,4-*bis*(diphenylphosphino) butanechloro(η^3-allyl) dicarbonylmolybdenum(II), [ClMo(CO)$_2$(η^3-C$_3$H$_5$)- {Ph$_2$P(CH$_2$)$_4$PPh$_2$}]

The ligand, 1,4-*bis*(diphenylphosphino)butane (150 mg, 0.35 mmol) was dissolved in 15 mL of dry acetone and added dropwise to a solution of [ClMo(CO)$_2$(η^3-C$_3$H$_5$)(CH$_3$CN)$_2$] (108 mg, 0.35 mmol) in 10 mL of acetone. The contents were warmed to 40°C for 5 h under nitrogen atmosphere to give a bright yellow solution. The solution was cooled to room temperature and the solvent removed in *vacuo*. The residue was dissolved in CHCl$_3$ (10 mL) and the solution filtered through a G-3 crucible. Petroleum ether (40-60°C) was added dropwise to the clear filtrate to initiate precipitation. The pale yellow solid so obtained was filtered off, dried under reduced pressure and recrystallised from a mixture of CHCl$_3$ and petroleum ether (40-60°C). (170 mg, 75%; m.p. 158-160°C (decomp.); Anal. Calcd. for C$_{33}$H$_{33}$O$_2$ClP$_2$Mo: C, 60.52; H, 5.08; Found: C, 60.24; H, 5.31.

2.3. Synthesis of 1,2-*bis*(methylphenylphosphino)benzenechloro(η^3-allyl) dicarbonylmolybdenum(II), [ClMo(CO)$_2$(η^3-C$_3$H$_5$)-{(Me)(Ph)PC$_6$H$_4$P(Ph)(Me)}]

The ligand, 1,2-*bis*(methylphenylphosphino)benzene (144 mg, 0.45 mmol) dissolved in 15 mL of dry acetone was added dropwise to a solution of [ClMo(CO)$_2$(η^3-C$_3$H$_5$)(CH$_3$CN)$_2$] (140 mg, 0.45 mmol) in 10 mL of acetone, in a Schlenk tube under nitrogen atmosphere. The solution was stirred at 40°C for 5 h to give a bright orange solution. The solution was cooled to room temperature and the solvent removed in high *vacuo*. The residue was dissolved in chloroform (10mL) and filtered through celite. To the clear filtrate, petroleum ether (40-60°C) was added dropwise to initiate precipitation. The product was filtered off from the mother liquor and recrystallised from a mixture of chloroform - petroleum ether (40-60°C) to give a yellow crystalline powder. (126 mg, 51%; m.p. 146-148°C (decomp.); Anal. Calcd. for C$_{25}$H$_{25}$O$_2$ClP$_2$Mo: C, 54.52; H, 4.57; Found: C, 54.39; H, 4.32.

2.4. Synthesis of (2R,3R)-(+)-*bis*(diphenylphosphino)butanechloro(η^3-allyl) dicarbonylmolybdenum(II),[ClMo(CO)$_2$(η^3-C$_3$H$_5$)-{PPh$_2$C*H(Me)C*H(Me)PPh$_2$}]

The ligand, (*2R, 3R*)-(+)-*bis*(diphenylphosphino)butane (200 mg, 0.47 mmol) dissolved in 15 mL of dry acetone was added dropwise to a Schlenk tube containing the allyl precursor, [ClMo(CO)$_2$(η^3-C$_3$H$_5$)(CH$_3$CN)$_2$] (148 mg, 0.47 mmol) in 10 mL of acetone. The solution was warmed to 40°C and stirred for 3 h under nitrogen atmosphere. The solution had turned bright orange yellow. The reaction mixture was cooled to room temperature and solvent removed under reduced pressure. The residue was then dissolved in chloroform (5mL) and the solution filtered through celite. To the clear filtrate, petroleum ether (40-60°C) was added dropwise to initiate precipitation. The crude orange yellow product was then recrystallised from chloroform-petroleum ether (40-60°C) to afford an orange yellow complex. (240 mg, 77%; m.p. 138-140°C (decomp.); Anal. Calcd. for C$_{33}$H$_{33}$O$_2$ClP$_2$Mo: C, 60.52; H, 5.08; Found: C, 60.43; H, 5.22.

2.5. Synthesis of (-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-*bis*(diphenylphosphino) butanechloro(η^3-allyl)dicarbonyl-molybdenum(II), [ClMo(CO)$_2$(η^3-C$_3$H$_5$) (Me$_2$C(O)$_2$ {C*HCH$_2$PPh$_2$}$_2$)]

The ligand, (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-*bis*(diphenylphosphino)butane (208mg, 0.42 mmol) was dissolved in 15 mL of dry acetone and carefully added dropwise to a Schlenk tube containing the precursor [ClMo(CO)$_2$(η^3-C$_3$H$_5$)(CH$_3$CN)$_2$] (130 mg, 0.42 mmol) dissolved in 10mL of acetone. The solution was stirred at 40°C for 4h under nitrogen atmosphere. During this period the solution had turned bright yellow. The solvent was removed in high *vacuo*. The residue was dissolved in chloroform (10 mL). The resultant solution was filtered through a G-3 sintered funnel and petroleum ether (40-60°C) was added to the filtrate to initiate precipitation. The crude product emerged out from the solution was recrystallised from a mixture of chloroform-petroleum ether (40-60°C) to give the desired product as pale yellow solid. (228 mg, 76%; m.p. 150-152°C (decomp.); Anal. Calcd. for C$_{35}$H$_{35}$O$_4$ClP$_2$Mo: C, 58.96; H, 4.95; Found: C, 58.63; H, 4.72.

2.6. Synthesis of 1-diphenylphosphino-2-diphenylarsinoethanechloro(η^3-allyl)dicarbonylmolybdenum(II), [ClMo(CO)$_2$(η^3-C$_3$H$_5$){Ph$_2$P(CH$_2$)$_2$AsPPh$_2$}]

The ligand, 1-diphenylphosphino-2-diphenylarsinoethane (106 mg, 0.24 mmol) dissolved in 10 mL of dry acetone was added dropwise to a Schlenk tube containing the complex [ClMo(CO)$_2$(η^3-C$_3$H$_5$)(CH$_3$CN)$_2$] (75 mg, 0.24 mmol) in 10 mL of acetone under constant stirring. The solution was stirred at 45°C for 5 h under nitrogen atmosphere. During this period, the solution had turned bright orange. The solvent was removed under reduced pressure to give a

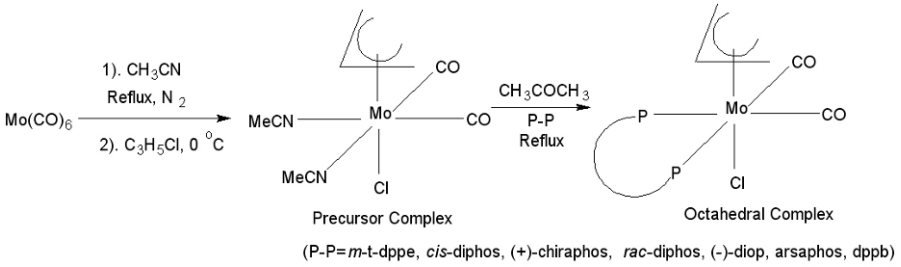


Figure 1. Reaction Scheme.

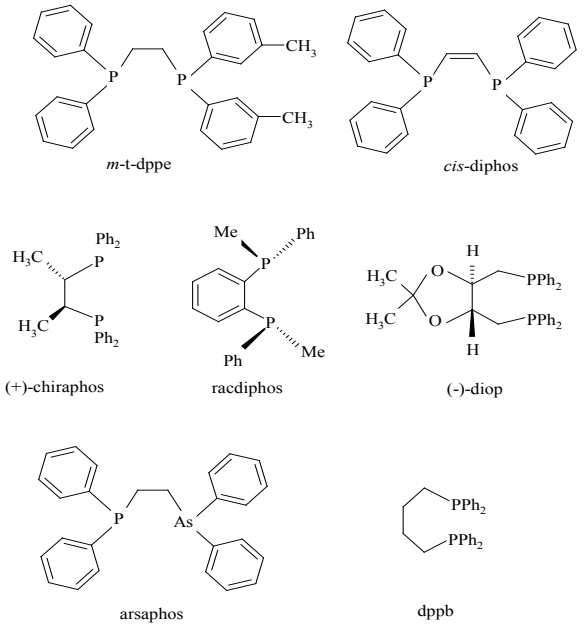


Figure 2. Structures of the chiral and achiral ditertiaryphosphine ligands.

yellow solid. It was dissolved in chloroform (10mL) and filtered through G-3 fritz. To the filtrate, petroleum ether (40-60°C) was added dropwise to initiate precipitation. The crude product so obtained was recrystallised from chloroform-petroleum ether (40-60°C) to afford a bright orange yellow powder. (126 mg, 78%; m.p. 154-156°C (decomp.); Anal. Calcd. for $C_{31}H_{29}O_2ClPAsMo$: C, 55.50; H, 4.36; Found: C, 55.28; H, 4.16.

2.7. Synthesis of cis-1,2-*bis*(diphenylphosphino)ethenechloro(η^3-allyl)dicarbonylmolybdenum (II), [ClMo(CO)$_2$(η^3-C$_3$H$_5$)-{Ph$_2$P(CH=CH)PPh$_2$}]

The ligand, *cis*-1,2-*bis*(diphenylphosphino)ethene (128 mg, 0.32 mmol) was dissolved in 10 mL of dry acetone and added dropwise to the complex [ClMo(CO)$_2$(η^3-C$_3$H$_5$)(CH$_3$CN)$_2$] (100 mg, 0.32 mmol) dissolved in 15 mL of acetone in a Schlenk tube under nitrogen. The solution was stirred at 40°C for 6 h under nitrogen atmosphere to give an orange yellow colour. The solvent was removed under high vacuum. The residue was dissolved in $CHCl_3$ and filtered through celite. To this filtrate, petroleum ether (40-60°C) was added slowly with constant stirring to initiate precipitation. The product was filtered, dried and recrystallised from a mixture of chloroform - petroleum ether (40-60°C) to afford pure orange solid. (142 mg, 71%; m.p. 170-172°C (decomp.); Anal. Calcd. for $C_{31}H_{27}O_2ClP_2Mo$: C, 59.58; H, 4.36; Found: C, 59.38; H, 4.24.

3. Results and discussion

Various ditertiaryphosphine complexes of the type [XMo(CO)$_2$(η^3-C$_3$H$_5$)(P-P)] were synthesized by reaction of the precursor complex [XMo(CO)$_2$(η^3-C$_3$H$_5$)(CH$_3$CN)$_2$] with the corresponding ditertiaryphosphine in acetone under nitrogen atmosphere and refluxed. The Complete reaction scheme is shown in Fig. 1.

The precursor complex was prepared by the reaction of metal hexacarbonyl with acetonitrile followed by the addition of allylic halides using literature method [15]. The complexes were isolated as orange yellow to brown solids in good yields (43 – 77%). These complexes were characterized by elemental analyses, FTIR, ^{1}HNMR and ^{31}P{^{1}H}NMR studies. All complexes were found to be soluble in common organic solvents such as chloroform and dichloromethane, but insoluble in non-polar solvents such as, *n*-hexane and petroleum ether (40-60°).

3.1. FTIR spectra of complexes [ClMo(CO)$_2$ (η^3-C$_3$H$_5$)(P-P)]

The carbonyl force constants for the allyl complexes, [ClMo(CO)$_2$(η^3-C$_3$H$_5$)(P-P)], were calculated by using the following Cotton and Kraihanzel approximate secular equations [27]. The values of carbonyl force constants are given in Table 1.

All complexes of the type [ClMo(CO)$_2$(η^3-C$_3$H$_5$) (P-P)], (P-P = ditertiaryphosphine), exhibited two bands of equal intensity in the carbonyl region (2100 – 1800 cm^{-1}). These bands were assigned to A_1 and B_1 modes of carbonyl groups, consistent with their symmetries. These two carbonyl frequencies indicated

Table 1. Selected FTIR and force constant data on $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P)]$.

S.No	Complex	$\nu_{C\equiv O}/cm^{-1}$		Carbonyl Force Constants (mdyne Å^{-1})	
		A_1	B_1	K_1	K_i
1	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(m-t-dppe)]	1935	1845	14.43	0.69
2	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(cis-diphos)]	1937	1851	14.49	0.66
3	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(racdiphos)]	1934	1842	14.40	0.70
4	$[ClMo(CO)_2(\eta^3C_3H_5)$\{(+)-chiraphos\}]	1943	1858	14.59	0.65
5	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$\{(-)-diop\}]	1920	1843	14.30	0.58
6	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(arsaphos)]	1938	1848	14.48	0.68
7	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(dppb)]	1915	1885	14.58	0.23

Table 2. ^{1}HNMR and ^{31}PNMR data on $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P)]$.

S.No	Complex	^{1}HNMR	^{31}PNMR (AB Spectrum) $J_{P\text{-}P}$ Coupling Constant (Hz)
1	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(m-t-dppe)]	δ 1.88 (H_a), 3.66 (H_b), 3.70(H_c); δ 2.44, s, *m*-CH_3; δ 7.66-7.10, *m*, Ar-H	13.8
2	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(cis-diphos)]	δ 1.92 (H_a), 3.62 (H_b) 3.76 (H_c); δ 6.92 (s, -CH=CH-); δ 6.51-7.63, *m*,Ar-H	14.2
3	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(racdiphos)]	δ 1.68 (H_a), 3.49 (H_b) 3.68 (H_c); δ 2.44, 2.46 d, -CH_3; δ 6.81-7.92, *m*, Ar-H; δ 6.84-7.96, *m*, Ar-H (P-P)	14.1
4	$[ClMo(CO)_2(\eta^3C_3H_5)$\{(+)-chiraphos\}]	δ 1.65 (H_a), 3.52 (H_b) 3.74 (H_c); δ 7.60-7.21, *m*, Ar-H; δ 0.85, s, CH_3; δ 1.43, s, -CH	13.9
5	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$\{(-)-diop\}]	δ 1.63 (H_a), 3.49 (H_b) 3.66(H_c); δ 1.1, s -CH_2, 1.45, s -CH, 0.86, s CH_3-; δ 7.82-7.34, *m*, Ar-H	14.3
6	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(arsaphos)]	δ 1.65 (H_a), 3.52 (H_b) 3.74 (H_c); δ 7.78-7.31, *m*, Ar-H; 1.45-1.47, d, –CH_2-	-
7	$[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(dppb)]	δ 1.61 (H_a), 3.44 (H_b) 3.62 (H_c); δ 7.62-7.45, *m*, Ar-H; δ 1.6 – 2.0, *m* –CH_2-	13.5

the presence of two *cis* carbonyl groups in the complex. The IR spectra of all complexes confirmed the absence of coordinated acetonitrile peaks, which were present in the precursor complex $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(CH_3CN)_2]$ at 2285 and 2236 cm^{-1}. This clearly indicated the displacement of acetonitrile ligands by the incoming ditertiaryphosphine ligand.

3.2. Proton and phosphorus-31 nuclear magnetic resonance spectroscopy

The ^{1}HNMR spectrum of the complex, $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$(*m*-t-dppe)] gave a complicated pattern for allyl as well as ligand protons. Since a number of $J_{H\text{-}H}$, $J_{P\text{-}H}$ and $J_{P\text{-}P}$ are involved in the spectrum, resonances of allyl and the ligands were assigned based on the published results [19]. The methyl protons of the uncoordinated ligand, *m*-t-dppe appeared as singlet at δ 2.28. In the

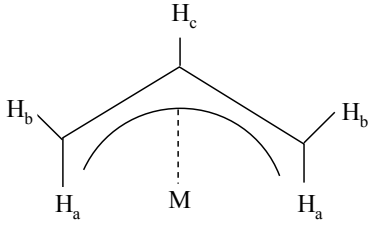


Figure 3. Classification of allyl protons.

complexes, these protons were observed at δ 2.44, slightly downfield. The five protons of coordinated allylic group have been divided in to three types, *i.e.*, H(a), H(b) and H(c), respectively. The allylic resonances were observed at δ 1.88, 3.66 and 3.70 due to H(a), H(b) and H(c) protons, respectively as shown below.

The latter two resonances appeared to be merging and the complex exhibited an aromatic region

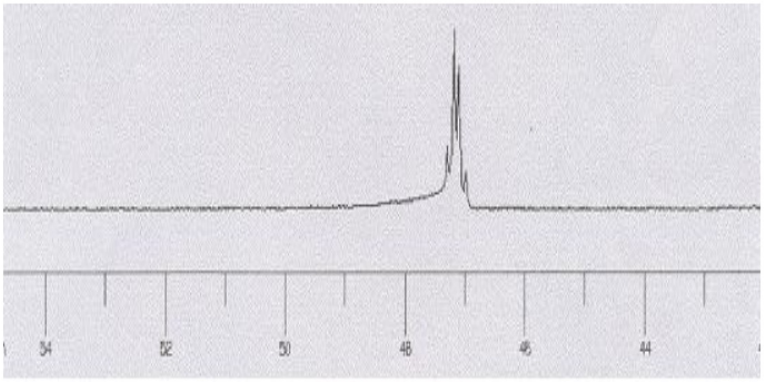


Figure 4. $^{31}P\{^{1}H\}$ spectrum of $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(m\text{-t-dppe})]$.

δ 7.66-7.10 and aliphatic region (δ 4.24 to 0.87). The integration values of aromatic to aliphatic suggested that there were total of fifteen aliphatic protons (5*H* of allyl + 6*H* of two methyl groups + 4*H* of two methylene groups). The aliphatic protons show a complicated pattern. The representative example of $^{31}P\{^{1}H\}$NMR spectrum of the complex, $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(m\text{-t-dppe})]$, in $CDCl_3$ (Fig. 4) showed an AB spectrum with the phosphorus-phosphorus coupling constant of 13.8 Hz. The values of chemical shifts of both the phosphorus nuclei confirmed that both phosphorus atoms are coordinated to the metal centre.

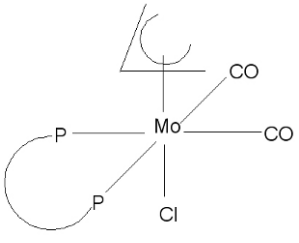
The ^{1}HNMR spectrum of the complex $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(cis\text{-diphos})]$ in $CDCl_3$ clearly indicate three resonances at δ 1.92 (*d*, J = 7 Hz), 3.66 (*qt*) and 3.76 (*m*) in the ratio 2:2:1, confirming the presence of allylic moiety. These resonances have been assigned to H(a), H(b) and H(c) protons of the allylic group, respectively. Further the ligand olefinic protons (-C*H*=C*H*-) were observed at δ 6.92 and 7.10 as multiplets. The P-P coupling constant was found to be 14.2 Hz. All the synthesised complexes have shown four distinct peaks that correspond to AB spectrum since these contain two phosphorus nuclei. The $^{31}P\{^{1}H\}$ NMR spectrum of the complex $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)$ (arsaphos)] contained a sharp singlet, as the complex contained only one phosphorus, at δ 37.02, which confirmed the coordination of phosphorus to the metal centre.

4. Conclusions

These complexes were isolated as bright yellow to light brown crystalline solids and found to be soluble in common organic solvents such as chloroform or dichloromethane, but insoluble in *n*-pentane, *n*-hexane and petroleum ether (60-80°C). These complexes have been characterized by elemental analyses, FTIR, ^{1}HNMR, and $^{31}P\{^{1}H\}$NMR spectroscopy.

The FTIR spectra of all these complexes depicted two prominent peaks in the range 2100-1800 cm^{-1}, corresponding to the presence of two *cis* carbonyl groups and consistent with the numer of carbonyl groups in the complexes. The two peaks were assigned to A_1 and B_1 modes of carbonyl stretching. The ^{1}HNMR spectra of all these complexes showed slight downfield shift of both aromatic as well as aliphatic protons. Complexes of the type $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P)]$ showed three allylic signals with intensity ratio 1:2:2. All these complexes exhibited a doublet for H(a) protons, a quartet for H(b) protons and a multiplet for H(c) protons of the allylic group. The *meso* proton signals were partially resolved from ligand -CH_2- absorptions. The $^{31}P\{^{1}H\}$NMR spectra of the complexes exhibited peaks corresponding to the presence of two non-equivalent phosphorus nuclei. The arsaphos complex contained only one phosphorus atom whose chemical shift was observed at δ 37.02. All these chemical shift values confirmed the coordination of phosphorus nuclei to the metal centre.

Elemental analyses, FTIR, ^{1}HNMR, $^{31}P\{^{1}H\}$NMR spectroscopic techniques have confirmed octahedral structure for the synthesized complexes $[ClMo(CO)_2(\eta^3\text{-}C_3H_5)(P\text{-}P)]$.



In the above octahedral structure, the allylic moiety is *trans* to the unidentate anion. The phosphorus donor ligand and the two *cis* carbonyl groups are coplanar.

Acknowledgements

One of the authors, Joe Gerald Jesu Raj, is grateful to the Director, Indian School of Mines, Dhanbad for the award of research fellowship.

Abbreviations

m-t-dppe: 1-diphenylphosphino-2-*bis*(m-tolyl)phosphinoethane;
dppb: 1,4-*bis*(diphenylphosphino)butane;
rac-diphos: 1,2-*bis*(methylphenylphosphino)benzene;
(+) chiraphos: (*2R,3R*)-(+)-*bis*(diphenylphosphino)butane;
(-) diop: (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-*bis*(diphenylphosphino)butane;
arsaphos: 1-diphenylphosphino-2-diphenylarsinoethane;
cis-diphos: c*is*-1,2-*bis*(diphenylphosphino)ethene.

References

[1] Z. Freixa, P.W.N.M. van Leeuwen, Dalton Trans, 1890 (2003)
[2] L. Gonsalvi, H. Adams, G.J. Sunley, E. Ditzel, A. Haynes, J. Am. Chem. Soc. 124, 13597 (2002)
[3] A. Jakob, P. Ecorchard, M. Linseis, R.F. Winter, H. Lang, J. Organomet. Chem. 694, 655 (2009)
[4] S.H. Chikkali, D. Gudat, F. Lissner, M. Niemeyer, T. Schleid, M. Nieger, Chem. A: Eur. J. 15, 482 (2009)
[5] D.K. Dutta, J.D. Woollins, A.M.Z. Slawin, D. Konwar, P. Das, M. Sharma, P. Bhattacharyya, S.M. Aucott, Dalton Trans. 2674 (2003)
[6] Z. Mehmood, S.R. Gilani, J. Chem. Soc. Pak. 27(1), 95 (2005)
[7] P.K. Baker, Adv. Organomet. Chem. 40, 45 (1996)
[8] F. Dewans, J. Dewailly, J. Meunier-Piret, P. Piret, J. Organomet. Chem. 76, 53 (1974)
[9] B.M. Trost, M.J. Lautens, Organometallics. 2, 1687 (1983)
[10] M.P.T. Sjögren, H. Frisell, B. Åkermark, P.-O. Norrby, L. Eriksson, A. Vitagliano, Organometallics 16, 942 (1997)
[11] H. Kurosawa, J. Organomet. Chem. 334, 243 (1987)
[12] P. Espinet, R. Hernando, G. Iturbe, F. Villafañe, A.G. Orpen, I. Pascual, Eur. J. Inorg. Chem. 1031 (2000)
[13] J.R. Ascenso, C.G. de Azevedo, M.J. Calhorda, M.A.A.F. de C.T. Carrondo, P. Costa, A.R. Dias, M.G.B. Drew, V. Félix, A.M. Galvão, C.C. Romão, J. Organomet. Chem. 632, 197 (2001)
[14] J. Perez, D. Morales, V. Riera, A. Rodriguez, S.G. Granda, J. Chem. Soc., Dalton Trans. 1461 (2003)
[15] R.G. Hayter, J. Organomet. Chem. 13, 1 (1968)
[16] H. Tom Dieck, H. Friedel, J. Organomet. Chem. 14, 375 (1968)
[17] S. Trofimenko, Inorg. Chem. 9, 2493 (1970)
[18] A.T.T. Hsieh, B.O. West, J. Organomet. Chem.112, 285 (1976)
[19] B.J. Brisdon, J. Organomet. Chem. 125, 225 (1977)
[20] J.W. Faller, C. Chen, M.J. Mattine, A. Jakubowski, J. Organomet. Chem. 52, 361 (1973)
[21] (a) M.T. Crimmins, B.W. King, J. Am. Chem. Soc. 120, 9084 (1998); (b) N. Murakami, M. Sugimoto, T. Nakajima, M. Kawanishi, Y. Tsutsui, M. Kobayashi, Bioorg. Med. Chem. 8, 2651 (2000)
[22] Y. Yamano, Y. Sato, Y. Watanabe, K. Namikawa, W. Miki, M. Ito, J. Chem. Soc., Perkin Trans. 1862 (2001)
[23] (a) U. Bhatt, M. Christmann, M. Quitschalle, E. Claus, M. Kalesse, J. Org. Chem. 66, 1885 (2001); (b) D.R. Williams, D.C. Ihle, S.V. Plummer, Org. Lett. 3, 1383 (2001)
[24] S. Marumoto, H. Kogen, S. Naruto, J. Org. Chem. 63, 2068 (1998)
[25] A.G. Waterson, A.W. Kruger, A.I. Meyers, Tetrahedron Lett. 42, 4305 (2001)
[26] M. Tortosa, N.A. Yakelis, W.A. Roush, J. Org. Chem. 73, 9657 (2008)
[27] F.A. Cotton, C.S. Kraihanzel, J. Am. Chem. Soc. 84, 4432 (1962)