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Multi-Nuclear NMR Investigation of Nickel(II), Palladium(II), Platinum(II) and Ruthenium(II) Complexes of an Asymmetrical Ditertiary Phosphine

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ABSTRACT. Complexes synthesized by reacting alkyl and aryl phosphines with different transition metals are of great interest due to their catalytic properties. Many of the phosphine complexes are soluble in polar solvents as a result they find applications in homogeneous catalysis. In our present work we report, four transition metal complexes of Ni(II), Pd(II), Pt(II) and Ru(II) with an asymmetrical ditertiaryphosphine ligand. The synthesized ligand bears a less electronegative substituent such as methyl group on the aromatic nucleus hence makes it a strong σ-donor to form stable complexes and thus could effectively used in catalytic reactions. The complexes have been completely characterized by elemental analyses, FTIR, ^{1}HNMR, ^{31}PNMR and FAB Mass Spectrometry methods. Based on the spectroscopic evidences it has been confirmed that Ni(II), Pd(II) and Pt(II) complexes with the ditertiaryphosphine ligand showed *cis* whereas the Ru(II) complex showed *trans* geometry in their molecular structure.

Key words: Ditertiaryphosphines, Catalysis, Configuration, Isomerism, Chirality

INTRODUCTION

Organophosphines are high use in applications such as ligands for homogeneous catalysis, phase transfer catalysis, intermediate syntheses, vulcanizing agents, metal extraction reagents and fire retardants. Metal complexes of phosphines have been widely used in clinical field including the use of a Au(I)PEt$_3$ complex as heart-imaging agents, anti-arthritic and anti-cancer drugs.[1] Metal based drugs have attracted major attention in recent times due their potential use in the anti-cancer activity.[2–4] Data on cytotoxicity and anticancer activity are surveyed in detail with particular emphasis on diphosphines and their copper, silver and gold complexes. Much phosphine chemistry of relevance to biology has yet to be explored. Metal complexes of ditertiary phosphines have also found applications in homogeneous and heterogeneous catalysis. Ditertiary phosphine complexes of nickel, palladium, and platinum exhibit various modes of coordination in square planar configuration. Recently palladium complexes tris(2-methoxyphenyl)phosphine complexes have been successfully used in the telomerization of 1,3-butadiene which is an important step in the 1-octene process.[5] Palladium-phosphine complexes have also found applications in cross-coupling of aryl halides with arylboronic acids and is one of the most valuable synthetic methods for the synthesis of biphenyl derivatives,[6] potential drug candidates,[7] coordinating ligands,[8] and functional materials[9] and also in homogeneous catalysts.[10] Supported palladium-phosphine complex catalyzed Suzuki-Miyaura cross-coupling reactions have also been reported.[11] Phosphine sulfonate complexes of nickel have found potential application in the olefin polymerization reactions.[12] Homogeneous ruthenium-phosphine complex has been successfully employed in the hydrogenation of carbon dioxide to form ethanol.[13] Phosphine complexes of Ni, Pd and Pt have been used in the catalytic hydrogenolysis of biphenylene under H$_2$ at moderate temperature.[14] In view of the immense applications of metal complexes of phosphines R.N. Kapoor[15] et al., synthesized and characterized Ni(II), Pd(II), Pt(II) complexes of a diphos ligand, 1-diphenylphosphino-2-*bis*(m-tolyl)phosphineethane.[15] Their work describes the characterization of these complexes only by methods such as magnetic susceptibilies, electronic, electrical conductance and FTIR. ^{1}N HMR spectroscopy was not discussed in detail. Also they have not reported the Ru(II) complex of the 1-diphenylphosphino-2-*bis*(m-tolyl)phosphine ethane. In our present work, we synthesized and completely characterized Ni(II), Pd(II), Pt(II) and Ru(II) complexes of 1-diphenylphosphino-2-*bis*(m-tolyl)phosphinoethane. This unsymmetrical ligand has the ability to tune the electronic properties of complex and hence can find potential applications in polymerization or homogeneous/heterogeneous catalysis reactions. All these complexes have been successfully synthesized from their metal salt precursors and characterized by the elemental analysis, FTIR, multinuclear magnetic resonance spectroscopy (^{1}H NMR and ^{31}P{^{1}H}NMR) and Mass spectrometric studies. All these complexes have been obtained in good yield.

EXPERIMENTAL

Synthesis of Ligand

The ligand 1-diphenylphosphino-2-*bis*(m-tolyl)phosphino ethane (m-t-dppe) has been synthesized as described elsewhere.[16] The product was obtained in almost quantitative yield.

Synthesis of *cis*-Dichloro-1-diphenylphosphino-2-*bis* (m-tolyl)phosphinoethanenickel(II), [Ni{$Ph_2P(CH_2)_2P$ (m-$CH_3C_6H_4)_2$}Cl_2] Complex

$NiCl_2.6H_2O$ (120 mg, 0.51 mmol) in 1-butanol (10 mL) was heated at 80 °C under nitrogen for 4 h to give a clear green solution. The solution was then cooled to room temperature. To this solution, the ligand, 1-diphenylphosphino-2-*bis*(m-tolyl)phosphinoethane (216 mg, 0.50 mmol) was added which produced a brick red colour. It was further stirred at 80–90 °C for 2 h. After the completion of the reaction, the mixture was cooled to room temperature. The solid was filtered, washed several times with cold ethanol and dried under vacuum to yield brick0red powder.

Yield: 170 mg, 61%; m.p. 233–235 °C (decomp.) Anal. Calcd. for $C_{28}H_{28}Cl_2P_2Ni$: C, 60.48; H, 5.08; Found: C, 60.23; H, 5.01; FAB Mass Spectrum: (m/z) Calcd. for $C_{28}H_{28}Cl_2P_2Ni$ = 556.08; obsd. = 556 $[M]^+$.

Synthesis of *cis*-Dichloro-1-diphenylphosphino-2-*bis*(m-tolyl)phosphinoethane palladium(II), [Pd{$Ph_2P(CH_2)_2$ P(m-$CH_3C_6H_4)_2$}Cl_2] Complex

$PdCl_2$ (100 mg, 0.56 mmol) and acetonitrile (10 mL) were mixed and heated to reflux at 80 °C for 4 h. To this the ligand 1-diphenylphosphino-2-*bis*(m-tolyl)phosphino ethane (240 mg, 0.56 mmol) was added and the solution heated on an oil bath at 80 °C for 6 h. Removal of the solvent from the reaction mixture under vacuum afforded pale yellow crystals.

Yield: 234 mg, 69%; m.p. 256–258 °C (decomp.) Anal. Calcd. for $C_{28}H_{28}Cl_2P_2Pd$: C, 55.70; H, 4.67; Found: C, 55.52; H, 4.32; FAB Mass Spectrum: (m/z) Calcd. for $C_{28}H_{28}Cl_2P_2Pd$ = 603.78, obsd = 603 $[M]^+$.

Synthesis of Dichloro*bis*(benzonitrile)platinum(II), [Pt ($NCC_6H_5)_2Cl_2$]

$PtCl_2$ (225 mg, 0.85 mmol) and benzonitrile (4 mL) were heated to reflux at 100 °C under nitrogen for 12 h in a Schlenk tube. The hot solution was filtered under nitrogen atmosphere and cooled to 0 °C. To the filtrate n-hexane was added dropwise. Addition of n-hexane precipitated a light yellow compound, which was dried under vacuum. Yield: 322 mg, 80%; m.p. 218–220 °C (decomp.) FTIR: $\nu_{(C\equiv N)}$: 2287 cm^{-1} (obsd.) Anal. Calcd. for $C_{14}H_{10}N_2Cl_2Pt$: C, 35.61; H, 2.13; N, 5.93, Found: C, 35.92; H, 2.22; N, 5.79 FAB Mass Spectrum: (m/z) Calcd. for $C_{14}H_{10}N_2Cl_2Pt$= 472.14, obsd.=472 $[M]^+$.

Synthesis of *cis*-Dichloro-1-diphenylphosphino-2-*bis*(m-tolyl)phosphinoethane platinum(II), [Pt{$Ph_2P(CH_2)_2$ P(m-$CH_3C_6H_4)_2$}Cl_2] Complex

The complex [$Pt(C_6H_5CN)_2Cl_2$] (150 mg, 0.32 mmol) and the ligand, 1-diphenylphosphino-2-*bis*(m-tolyl)phosphino ethane (135 mg, 0.32 mmol) were dissolved in chloroform (10 mL) and then heated to reflux at 60 °C under nitrogen for 4 h. The reaction mixture was cooled to room temperature and the solvent removed under vacuum that resulted yellow product, which was then redissolved in chloroform (10 mL). Addition of petroleum ether (5 mL) gave pale yellow product. Yield: 172 mg, 78%; m.p. 267–269 °C (decomp.) Anal. Calcd. for $C_{28}H_{28}Cl_2P_2Pt$: C, 48.57; H, 4.08; Found: C, 48.39; H, 4.02; FAB Mass Spectrum: (m/z) Calcd. for $C_{28}H_{28}Cl_2P_2Pt$=692.19, obsd.=692 $[M]^+$.

Synthesis of Dichlorotetrakis (dimethyl sulphoxide) ruthenium(II)[$RuCl_2\{(CH_3)_2SO\}_4$]

Ruthenium trichloride trihydrate (2 g, 0.01 mol) dissolved in dimethylsulphoxide (10 mL) was boiled under reflux for 4 h to give an orange solution under nitrogen atmosphere. The solution was then cooled to room temperature and dry acetone (25 mL) was added to give a yellow powder. The yellow powder was filtered off, washed several times with cold acetone and petroleum ether (40–60 °C) then dried under vacuum. On standing, slow evaporation of the solvent yielded lemon yellow needles. Yield: 2.8 g, 75%; m.p. 203–205 °C (decomp.) FTIR: $\nu_{(Ru-S)}$: 1085, 1114 cm^{-1} (obsd.); $\nu_{(Ru-O)}$: 936 cm^{-1} (obsd.)

Synthesis of *trans*-Dichloro-*bis*-[1-diphenyl phosphino-2-bis(m-tolyl)phosphine ethane] ruthenium(II), [Ru {$Ph_2P(CH_2)_2P$(m-$CH_3C_6H_4)_2\}_2Cl_2$]

The complex [$RuCl_2(DMSO)_4$] (100 mg, 0.21 mmol) [DMSO=dimethyl sulphoxide] and the ligand, 1-diphenylphosphino-2-bis(m-tolyl)phosphinoethane (176 mg, 0.41 mmol) were dissolved in 20 mL of deoxygenated ethanol and the mixture was heated to reflux at 80 °C for 30 h. During this period the solution had turned from initial light yellow to orange and then finally lemon yellow in colour. After completion of the reaction, the solution was cooled to room temperature and the solvent removed under reduced pressure to give a brownish yellow powder. It was recrystallized from a mixture of chloroform and ethanol to afford the lemon yellow crystals of the desired complex.

Yield: 158 mg, 75%; m.p. 246–248 °C (decomp.) Anal. Calcd. for $C_{56}H_{56}Cl_2P_4Ru$: C, 65.63; H, 5.51; Found: C, 65.42; H, 5.31; FAB Mass Spectrum: (m/z) Calcd. for $C_{56}H_{56}Cl_2P_4Ru$ = 1024.94, obsd. = 1025 $[M]^+$.

RESULTS AND DISCUSSION

FTIR Spectroscopy

The infrared spectrum of the ligand, 1-diphenylphosphino-2-*bis*(m-tolyl)phosphinoethane was obtained in KBr pellet between 4000 to 400 cm^{-1}. A comparison of the spectrum of 1,2-*bis*(diphenylphosphino)ethane (dppe) and 1-diphenyl phosphino-2-*bis*(m-tolyl)phosphinoethane (m-t-dppe) shows the presence of many additional C–H stretching vibrations at 2929 and 2898 cm^{-1}, due to the presence of methyl groups in the spectrum of m-t-dppe. The IR spectra of the complexes are similar to that of the ligand but the most notable change being an increase in frequency and intensity of the ν_{P-C} (aromatic) at 1106–1109 cm^{-1}, which indicates the coordination of phosphorus to the metal atom.[21] The presence of a sharp band at ~880 cm^{-1} in all the complexes of nickel(II), palladium(II), platinum(II) and ruthenium(II) confirms the chelating behaviour of the ligand.[22]

The infrared spectrum of the complex $[Pt(C_6H_5CN)_2Cl_2]$[21] showed a sharp peak at 2287 cm^{-1} due to coordinated –C≡N. In the complex $[Pt(m\text{-}t\text{-}dppe)Cl_2]$ the coordinated benzonitrile peak was absent. This clearly indicated the displacement of benzonitrile by the ligand, m-t-dppe.

The IR spectrum of the precursor complex $[Ru(DMSO)_4Cl_2]$[22] exhibited peaks at 1085 and 1114 cm^{-1} for sulphur coordinated dimethyl sulphoxide and a peak at 936 cm^{-1} for oxygen coordinated dimethyl sulphoxide to the ruthenium metal centre. The IR spectrum of the complex $[Ru(m\text{-}t\text{-}dppe)_2Cl_2]$, did not show any of these peaks, confirming that all the coordinated DMSO ligands have been replaced by the incoming ligand, m-t-dppe.

^{1}H NMR Spectroscopy

The ^{1}H NMR spectra of the synthesized ligand and the Ni(II), Pd(II), Pt(II) and Ru(II) complexes have been given in the supporting information. The chemical shift values have been calculated and given the following *Table* 1.

***Table* 1.** The ^{1}HNMR chemical shift values of the complexes $[M(m\text{-}t\text{-}dppe)Cl_2]$, (M=Ni, Pd and Pt) and $[Ru(m\text{-}t\text{-}dppe)_2Cl_2]$

Complex	^{1}HNMR, (δ)
$[Ni(m\text{-}t\text{-}dppe)Cl_2]$	7.97–7.71 (m, 8H, Ar*H*) 7.52–7.25 (m, 10H, Ar*H*) 2.38 (s, 6H, $2XCH_3$–) 2.09 (m, 4H, 2X–CH_2–)
$[Pd(m\text{-}t\text{-}dppe)Cl_2]$	7.89–7.62 (m, 8H, Ar*H*) 7.62–7.32 (m, 10H, Ar*H*) 2.35 (s, 6H, $2XCH_3$–) 2.47 (m, 2H, 1X–CH_2–) 2.44 (m, 2H, 1X–CH_2–)
$[Pt(m\text{-}t\text{-}dppe)Cl_2]$	7.87–7.65 (m, 8H, Ar*H*) 7.61–7.29 (m, 10H, Ar*H*) 2.35 (s, 6H, $2XCH_3$–) 2.33 (m, 2H, 1X–CH_2–) 2.24 (m, 2H, 1X–CH_2–)
$[Ru(m\text{-}t\text{-}dppe)_2Cl_2]$	7.61–7.66 (m, 16H, Ar*H*) 7.01–7.34 (m, 20H, Ar*H*) 1.15–1.91 (m, 12H, $4XCH_3$–) 2.02–5.18 (m, 8H, 4X–CH_2–)

The ^{1}H NMR spectrum of the ligand (supporting information) in $CDCl_3$ exhibited a complex multiplet at δ 7.10–7.35 due to to aromatic protons and an overlapping triplet at δ 2.09–2.11 due to two methylene groups of the ligand backbone. The methyl resonances were observed at δ 2.28 as a sharp singlet. The chemical shift between δ 7.10–7.21 and 2.09–2.11 confirm the presence of aromatic protons and aliphatic protons of $Ph_2PCH_2CH_2$- respectively. However the chemical shift between δ 7.25–7.35 $\{P(m\text{-}CH_3C_6H_4)_2\}$ confirms the presence of aromatic protons where as a sharp singlet at δ 2.28 confirms the methyl substituents since both methyl groups are equivalent.

The ^{1}H NMR spectrum of the complex, $[Ni(m\text{-}t\text{-}dppe)Cl_2]$ exhibited aromatic protons in the range δ 7.97–7.25.

The methyl protons of tolyl group were observed at δ 2.38 as singlet and the methylene protons of the ligand backbone were observed at δ 2.09 as a complex multiplet. A comparison of the ^{1}H NMR spectrum of the free ligand and the complex, indicated a downfield shift of aromatic as well as methyl protons, however, no significant change in methylene protons were observed. The ^{1}H NMR spectrum of the complex, $[Pd(m\text{-}t\text{-}dppe)Cl_2]$ showed a complex multiplet at δ 7.32–7.89 due to aromatic protons. The methyl protons of the tolyl group were observed at δ 2.35. Two resonances centered at δ 2.44 and 2.47 were assigned to methylene protons. A comparison of the free ligand spectrum with the spectrum of the Pd(II) complex confirmed a downfield shift of aromatic protons in the complex. This supports the coordination of the ligand to the metal centre. The ^{1}H NMR spectrum of the Pt(II) complex dichloro-1-diphenylphosphino-2-*bis*(m-tolyl)phosphinoethane platinum(II), gave a complex multiplet at δ 7.29–7.87 indicating the presence of aromatic protons. The methyl protons were observed at δ 2.35 as singlet and methylene protons were observed at δ 2.38 and 2.24 as multiplets. A comparison of the free ligand spectrum with the Pt(II) complex spectrum confirmed a downfield of aromatic as well as aliphatic protons. This downfield shift may be attributed to the coordination of the phosphorus nuclei to the platinum metal centre. The ^{1}H NMR of ruthenium(II) complex, [Ru(m-t-dppe)$_2$Cl$_2$] in CDCl$_3$ exhibited resonances at δ 7.01–7.66, 1.15–1.91 and 2.02–5.18 due to aromatic, methyl and methylene protons, respectively. In free ligand the methyl protons of the tolyl group were observed at δ 2.28. Therefore, it is concluded that upon coordination the methyl protons of the tolyl group experience a slight upfield shift. The methylene protons of the free ligand exhibited resonances at δ 2.1, whereas in the ruthenium complex these were observed at δ 2.7–2.2. It is obvious from the comparison that, on coordination the methylene protons experienced a downfield shift. The absence of DMSO (dimethylsulphoxide) protons of the starting material, [RuCl$_2$(DMSO)$_4$] (which were observed at δ 3.5–2.6) and the appearance of new peak at δ 2.7–2.2 assignable to methylene protons further substantiate the view that all DMSO protons were replaced by the ditertiary phosphine ligand. It has been reported that cis isomer of the type [Ru(P-P)$_2$X$_2$] upon reduction with lithium aluminium hydride (LiAlH$_4$), yield hydrido complex [RuH(P-P)$_2$X], whereas the trans isomer do not react at all.[22] The reduction of [Ru(m-t-dppe)$_2$Cl$_2$] with LiAlH$_4$ did not yield any hydrido complex, thus confirming the trans nature of the complex.

^{31}P{^{1}H}NMR Spectroscopy

In the ^{31}P{^{1}H}NMR spectrum of the ligand (supporting information), 1-diphenylphosphino-2-*bis*(*m*-tolyl) phosphineethane (m-t-dppe), gave an AB quartet confirming the non-equivalence of both the phosphorus nuclei. The value of phosphorus–phosphorus coupling constant ($^J{}_{P-P'}$) was found to be 39 Hz. The simple ^{31}P{^{1}H}NMR spectrum featuring both chemical shift and a spin–spin coupling constant arises from a molecule containing two non-equivalent magnetic nuclei. The ligand used in this work possesses two non-equivalent phosphorus nuclei. In principle, two phosphorus nuclei are non-equivalent because one of the phosphorus bears phenyl rings while the other phosphorus bears *m*-tolyl groups. Substituents on chelate ring may be classified as either substituent on phosphorus, substituent on the ligand backbone or substituents on the metal. The phosphorus- phosphorus coupling constant ($^J{}_{P-P'}$) is affected by variation of these substituents and the origin of this effect is attributed to the electronic or steric effects of the substituents. If the two nuclei are separated in their spectrum by a small chemical shift of the same order of the magnitude as the coupling constant then they are said to constitute an AB system. The ^{31}P{^{1}H}NMR spectrum of such a system consists of a pair of doublets. However, the shape of the spectrum is determined by the ratio of Δν to J, i.e., the ratio of chemical shift difference between the nuclei and the coupling constant. When Δν/J is more than 6 then a fairly unperturbed spectrum is anticipated. However, as the Δν/J ratio gets lower, distortion of signals arises. In the case of m-t-dppe, the chemical shift difference between the two phosphorus nuclei is very small. The chemical shift values of both phosphorus nuclei are close to analogues dppe ligand, i.e., –12 ppm. Tolyl group is better electron donor than the phenyl group. Therefore, phosphorus bearing this group is expected to be more shielded compared to the phenyl group. Accordingly, PPh$_2$ is assigned at δ –11.2 and P(m-CH$_3$C$_6$H$_4$) is assigned at δ –11.5. The values of phosphorus-phosphorus coupling constant $J_{P-P'}$ was found to be 39 Hz well within the reported values for other ditertiary phosphine ligands.

The ^{31}P{^{1}H}NMR spectrum of the complex [Ni(*m*-t-dppe)Cl$_2$] contained an unresolved resonance at δ +57.5. In theory we should have expected an AB quartet due to non-equivalence of two phosphorus nuclei, however, it appeared from the spectrum that, the chemical shift separation between the two phosphorus nuclei is very less upon coordination, therefore, both phosphorus nuclei behave almost equivalent. But the value of the chemical shift i.e., δ +57.5 confirmed the coordination of phosphorus nuclei to the metal centre.

The ^{31}P{^{1}H}NMR spectrum of the complex [Pd(*m*-t-dppe)Cl$_2$] showed peaks at δ 64.36 and 63.95 corresponding to the presence of two non-equivalent phosphorus nuclei. The higher d value, i.e., 64.36 may be assigned to the phosphorus atom bearing two phenyl groups and the lower δ value i.e., 63.95 to the phosphorus atom bearing two *meta*-tolyl groups. This may be attributed to the fact that, the phosphorus attached to the *meta*-tolyl groups, experienced a shielding effect because of the presence of methyl groups (+I effect) at the *meta* position in the benzene nucleus whereas no such shielding effect was observed for the phosphorus attached to the phenyl rings. Hence, it gave higher value of chemical shift.

The $^{31}P\{^1H\}$NMR spectrum of the complex [Pt(*m*-t-dppe)Cl_2] showed a central resonance at δ 41.33 accompanied by platinum satellites on both sides because of the coupling to ^{195}Pt (I = ½, natural abundance = 33.7%). The value of platinum-phosphorus coupling constant (J_{Pt-P}) was found to be 3621 Hz. This value is in accordance with the reported value for the analogues complex.[21]

CONCLUSION

The FTIR, ^{1}H NMR, $^{31}P\{^1H\}$NMR spectroscopic studies reveal that all the complexes of nickel (II), palladium (II), platinum (II) with the chelating ligand support *cis* geometry. In ruthenium complex the two phosphine ligands are *trans* to each other as evident from the fact that reaction of the ruthenium complex with the reducing agent lithium aluminium hydride did not yield any hydrido complex. It is anticipated that the complex [Ru(*m*-t-dppe)$_2$$Cl_2$] would prefer *trans* structure rather than *cis* structure on steric ground. A *cis* structure is expected to be sterically more hindered and has been confirmed by the ^{1}H NMR and $^{31}P\{^1H\}$NMR techniques.

Based on the elemental analyses, FTIR, ^{1}H NMR, $^{31}P\{^1H\}$NMR and FAB mass spectrometric data the following *cis*-square planar geometry has been assigned to complexes of the type [M(*m*-t-dppe)Cl_2], (M = Ni, Pd and Pt) and *trans*-octahedral geometry has been assigned to the complex [Ru(*m*-t-dppe)$_2$$Cl_2$].

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