

Synthesis, spectral and catalytic hydrogenation studies of palladium(II) complexes containing substituted tertiary phosphines

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Abstract : Neutral and cationic mononuclear palladium(II) substituted tertiary phosphine complexes containing acetylacetonate, carbonmonoxide and chloride as co-ligands have been synthesized in quantitative yield and characterized on the basis of elemental analysis, conductance measurements, IR, NMR (^1H , ^{13}C and ^{31}P), mass and electronic spectral data. The catalytic hydrogenation activity of some of these complexes has been studied and found that they are efficient catalysts for reduction of organic nitro, olefinic, acetylenic and aldehyde groups under mild reaction conditions.

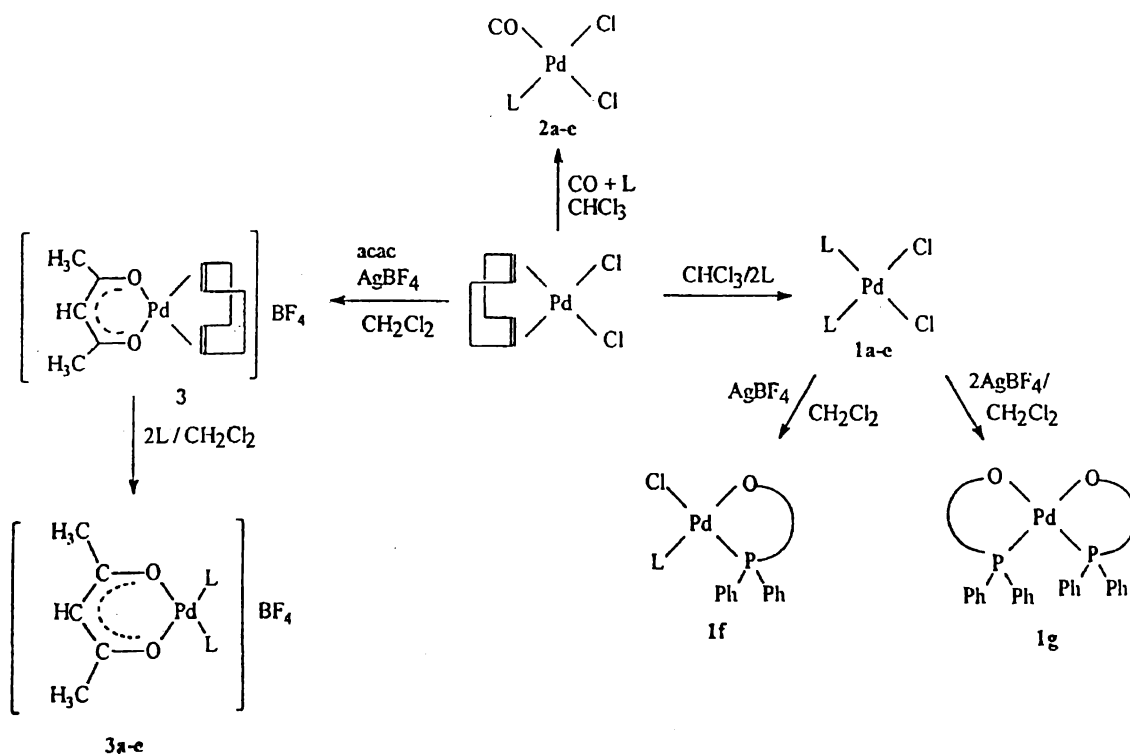
Keywords : Catalytic hydrogenation, tertiary phosphines, palladium(II), carbonmonoxide.

Transition metal complexes with phosphorous donor ligands, in particular platinum and palladium complexes of the type $[\text{MX}_2\text{L}_2]$ ($\text{M} = \text{Pt}$ or Pd , $\text{X} =$ anionic ligand, $\text{L} =$ tertiary phosphine) are found to be useful as starting materials in organometallics and coordination chemistry¹. In this paper, we report the synthesis of new complexes obtained by the reactions of $[\text{Pd}(\text{COD})\text{Cl}_2]$ with carbonmonoxide and carboxylated/formyl/pyridyl tertiary phosphines. The spectral studies and catalytic hydrogenation reactions of these complexes were also reported.

Results and discussion

Treatment of $[\text{Pd}(\text{COD})\text{Cl}_2]$ with substituted tertiary phosphine produced the complexes **1a-e** as shown in Scheme 1. When *cis* complex, **1a** was treated with one equivalent of AgBF_4 yielded the complex **1f**. On the other hand, treatment of **1a** with two equivalents of AgBF_4 gave the chlorine free complex, **1g**. $[\text{Pd}(\text{COD})\text{Cl}_2]$ also reacts with CO and substituted tertiaryphosphines to give complexes **2a-e**. The cationic complexes, **3a-e** are obtained by the reaction of $[\text{Pd}(\text{COD})\text{Cl}_2]$ with 2,4-pentanedione and substituted tertiary phosphines in the presence of AgBF_4 . All the palladium(II) complexes are synthesized in quantitative yield which are air-stable crystalline solids. The compositions of the complexes have been confirmed by elemental analysis.

The molar conductance values for the complexes **3a-e** in dichloromethane at room temperature which are observed in the range $60\text{--}80 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ confirm their 1 : 1 electrolytic nature. The other complexes **1a-g** and **2a-e** show no appreciable conductance and this fact supports the hypothesis of their neutral nature. The analytical data and melting points of all the complexes are given in the Table 1. The IR spectra of the palladium(II) complexes formed with CO were observed in the range of $1995\text{--}1980 \text{cm}^{-1}$, which suggests that it was coordinated to the metal center. The position of $\nu(\text{COOH})$ of respective tertiary phosphine shows absorption band in the range of $1730\text{--}1720 \text{cm}^{-1}$ and the position of $\nu(\text{CHO})$ of tertiary phosphine exhibit a band around 1680cm^{-1} . These two bands were almost unchanged in the spectra of complexes **1a-d**, **2a-d**, when compared to the free tertiary phosphine ligands confirming the non-involvement of these functional groups in coordination. In complex **1f** and **1g**, both (2-carboxyphenyl)diphenylphosphine ligands are coordinated as chelates by involvement of carboxylated oxygen along with phosphorous atoms. A strong absorption band at 1720cm^{-1} in the free ligands due to $\nu(\text{COOH})$ was absent in the complex **1g** and exhibit two new bands at 1590 and 1380cm^{-1} corresponding to $\nu_{\text{asy}}(\text{COO}^-)$, $\nu_{\text{sym}}(\text{COO}^-)$, respectively, indicating coordination of the carboxylate group to palladium, whereas complex **1f** shows characteristic absorption bands in the IR spectrum for



L = (a) $\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{COOH}$, (b) $\text{Ph}_2\text{P}-3\text{-C}_6\text{H}_4\text{COOH}$, (c) $\text{Ph}_2\text{PCH}_2\text{COOH}$, (d) $\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{CHO}$, (e) $\text{Ph}_2\text{P}-2\text{-C}_5\text{H}_4\text{N}$

Scheme 1

Table I. Analytical data of Pd^{II} tertiary phosphine complexes

Complex	Molecular formula	Analyses (%) : Found (Calcd.)		Decomp. temp. (°C)
		C	H	
1 (a) $[\text{Pd}(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{COOH})_2\text{Cl}_2]$	$\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{O}_4\text{P}_2\text{Pd}$	57.65 (57.76)	3.85 (3.80)	255
(b) $[\text{Pd}(\text{Ph}_2\text{P}-3\text{-C}_6\text{H}_4\text{COOH})_2\text{Cl}_2]$	$\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{O}_4\text{P}_2\text{Pd}$	58.76 (57.76)	3.75 (3.80)	240
(c) $[\text{Pd}(\text{Ph}_2\text{PCH}_2\text{COOH})_2\text{Cl}_2]$	$\text{C}_{28}\text{H}_{26}\text{Cl}_2\text{O}_4\text{P}_2\text{Pd}$	50.52 (50.49)	4.20 (3.90)	228
(d) $[\text{Pd}(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{CHO})_2\text{Cl}_2]$	$\text{C}_{38}\text{H}_{30}\text{Cl}_2\text{O}_2\text{P}_2\text{Pd}$	60.32 (60.20)	3.95 (3.96)	251
(e) $[\text{Pd}(\text{Ph}_2\text{P}-2\text{-C}_5\text{H}_4\text{N})_2\text{Cl}_2]$	$\text{C}_{28}\text{H}_{28}\text{Cl}_2\text{N}_2\text{P}_2\text{Pd}$	53.25 (53.21)	4.45 (4.43)	242
(f) $[\text{Pd}(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{COOH})(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_5\text{COO})\text{Cl}]$	$\text{C}_{38}\text{H}_{29}\text{ClO}_4\text{P}_2\text{Pd}$	60.65 (60.56)	3.95 (3.98)	238
(g) $[\text{Pd}(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{COO})_2]$	$\text{C}_{38}\text{H}_{28}\text{O}_4\text{P}_2\text{Pd}$	63.50 (60.65)	3.95 (3.98)	225
2 (a) $[\text{Pd}(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{COOH})(\text{CO})\text{Cl}_2]$	$\text{C}_{20}\text{H}_{15}\text{Cl}_2\text{O}_3\text{PPd}$	46.80 (46.92)	2.95 (2.93)	236
(b) $[\text{Pd}(\text{Ph}_2\text{P}-3\text{-C}_6\text{H}_4\text{COOH})(\text{CO})\text{Cl}_2]$	$\text{C}_{20}\text{H}_{15}\text{Cl}_2\text{O}_3\text{PPd}$	47.10 (46.92)	2.98 (2.93)	237
(c) $[\text{Pd}(\text{Ph}_2\text{PCH}_2\text{COOH})(\text{CO})\text{Cl}_2]$	$\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{O}_3\text{PPd}$	41.20 (40.05)	3.02 (2.89)	220
(d) $[\text{Pd}(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{CHO})(\text{CO})\text{Cl}_2]$	$\text{C}_{20}\text{H}_{15}\text{Cl}_2\text{O}_2\text{PPd}$	48.94 (48.44)	3.48 (3.02)	257
(e) $[\text{Pd}(\text{Ph}_2\text{P}-2\text{-C}_5\text{H}_4\text{N})(\text{CO})\text{Cl}_2]$	$\text{C}_{18}\text{H}_{14}\text{Cl}_2\text{ONPPd}$	47.52 (46.11)	3.20 (2.98)	241
3 (a) $[\text{Pd}(\text{acac})(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{COOH})_2]\text{BF}_4$	$\text{C}_{43}\text{H}_{37}\text{O}_6\text{BF}_4\text{P}_2\text{Pd}$	57.84 (57.05)	5.20 (4.09)	269
(b) $[\text{Pd}(\text{acac})(\text{Ph}_2\text{P}-3\text{-C}_6\text{H}_4\text{COOH})_2]\text{BF}_4$	$\text{C}_{43}\text{H}_{37}\text{O}_6\text{BF}_4\text{P}_2\text{Pd}$	58.12 (57.05)	5.28 (4.09)	272
(c) $[\text{Pd}(\text{acac})(\text{Ph}_2\text{PCH}_2\text{COOH})_2]\text{BF}_4$	$\text{C}_{33}\text{H}_{33}\text{O}_6\text{BF}_4\text{P}_2\text{Pd}$	51.20 (50.74)	4.31 (4.22)	239
(d) $[\text{Pd}(\text{acac})(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{CHO})_2]\text{BF}_4$	$\text{C}_{43}\text{H}_{37}\text{O}_4\text{BF}_4\text{P}_2\text{Pd}$	62.50 (61.32)	5.20 (4.39)	260
(e) $[\text{Pd}(\text{acac})(\text{Ph}_2\text{P}-2\text{-C}_5\text{H}_4\text{N})_2]\text{BF}_4$	$\text{C}_{39}\text{H}_{35}\text{O}_2\text{N}_2\text{BF}_4\text{P}_2\text{Pd}$	58.34 (57.18)	4.80 (4.27)	269

uncoordinated and coordinated carboxylic groups of tertiary phosphines. Further, no change in the absorption of ring nitrogen of pyridyl phosphine in its palladium(II) complexes, **1e**, **2e**, **3e** reveals the non-participation of pyridyl nitrogen. The IR spectra of palladium(II) complexes **3a-e** formed with 2,4-pentanedione have shown two strong bands around 1570 and 1550 cm^{-1} which may be ascribed to the combination of $\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{O})$ and $\nu(\text{C}-\text{O}) + \nu(\text{C}-\text{C})$ bands of a chelated O-bounded 2,4-pentanedione, respectively.

The new absorption band is found in all the palladium(II) complexes in the far infrared 500–550 cm^{-1} which ascribed to $\nu(\text{Pd}-\text{P})$ in *cis* position². The far IR spectra of complexes **1a-f**, **2a-e** show $\nu(\text{Pd}-\text{Cl})$ bands at 280–298 and 305–330 cm^{-1} attributed to Cl atoms present in *cis* fashion. In addition to this, the IR spectral study of cationic complexes shows two strong bands at 1067 and 530 cm^{-1} for uncoordinated BF_4^- ion³. Further, evidence for the coordinating mode of the ligands is obtained from the ^1H and ^{13}C NMR spectra.

All these compounds were exhibiting two intense *d-d* bands in the UV-visible range 470–490 and 375–390 nm and were assigned to $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1E_g$ transitions. Further, a strong charge transfer band has been observed around 365 nm for all the compounds. The measured electronic spectral data also suggests squareplanar geometry for all the palladium(II) complexes.

In the ^1H NMR spectra, integral intensities of each signal of the complexes are found to agree with the number of different types of protons present. The ^1H NMR spectra of complexes **1a-c**, **1f**, **2a-c**, **3a-c**, show a signal in the down field region between δ 11.68–12.20, which attributed to the carboxylic group proton of respective tertiary phosphine clearly indicates the non-participation of these carboxylic functional groups in coordination. The ^1H NMR signal displayed by complexes **1d**, **2d**, **3d** in the down field region δ 10.63–10.72 is assigned to formyl protons of tertiary phosphines. The complexes **3a-e** exhibit one signal in the range δ 1.52–1.84, which is ascribed to the methyl protons of the chelated 2,4-pentanedione. Another proton signal is observed in the range δ 4.89–5.58, which ascribed to the methine protons of 2,4-pentanedione reveals that it was bonded to the palladium(II) metal ion in the anionic form. All the complexes possess the multiplet signals in the range δ 6.60–8.52 and are attributed to aromatic protons of phenyl rings of tertiary phosphines. On the other hand, the signals observed in the up field region for complexes **1c**, **2c** and **3c** in the range of δ

3.46–3.78 are assigned to the methylene protons of (carboxymethyl) diphenylphosphine ligand.

The ^{13}C signals observed in the down field region for the complexes **1a-c**, **2a-c**, **3a-c** in the range δ 167.11–172.24 are assigned to the uncoordinated carboxylic groups of respective tertiary phosphines⁴, whereas the complexes **1f** and **1g** exhibit a down filed signal around δ 180 which supports the involvement of carboxylate oxygen in coordination. The ^{13}C signals for the complexes **1d**, **2d** and **3d** in the range of δ 180.15–180.58 are assigned to the uncoordinated formyl carbon of tertiary phosphine. Further, complexes **3a-e** exhibit the signals in the range δ 22.80–26.24 and δ 107.51–109.24 and are attributed to methyl carbons and methine carbons of 2,4-pentanedione, respectively, whereas the carbonyl carbon of O-bounded 2,4-pentanedione exhibits the signals in the respective complexes at δ 192.42–195.21. The aryl carbons are resonated in the range of δ 128.00–136.88, respectively. In addition to the resonance of the aryl carbons, the methylene carbon of (carboxymethyl)diphenyl phosphine exhibit a signal in the range of δ 42.35–42.48 in the complexes of **1c**, **2c** and **3c**. The IR and NMR spectra of the studied complexes support the *cis* configuration of the phosphine ligands.

^{31}P NMR spectra of all the complexes except **1f** exhibit only one signal in the down field region in the range of δ 22.92–26.82, indicating *cis* coordinated phosphines, which is consistent with the presence of single isomers⁶. ^{31}P NMR spectrum of complex **1f** shows two signals (Fig. 1), which reveals the *cis* coordination of phosphine ligand wherein one ligand coordinated to palladium exclusively with phosphorous and the other ligand acts as a bidentate chelate with the phosphorous and the carboxylate oxygen atoms.

The phosphine Pd^{II} complexes exhibit molecular ion peaks at m/z (M^+) 789.4 (**1a**), 789.0 (**1b**), 665.1 (**1c**), 757.3 (**1d**), 630.6 (**1e**), 752.3 (**1f**), 716.8 (**1g**), 511.0 (**2a**), 510.4 (**2b**), 448.2 (**2c**), 496.2 (**2d**), 468.8 (**2e**), 904.2 (**3a**), 904.8 (**3b**), 779.8 (**3c**), 872.0 (**3d**) and 818.2 (**3e**) and these values are in good agreement with the proposed molecular formulae (Figs. 2a and b).

Catalytic hydrogenations : The catalytic hydrogenation of nitro aromatics leads to the formation of the corresponding amines in almost all cases except *m*-dinitrobenzene, where the final product was only the corresponding hydroxylamine⁷. New palladium(II) complexes reduced the non-substituted or *p*-substituted

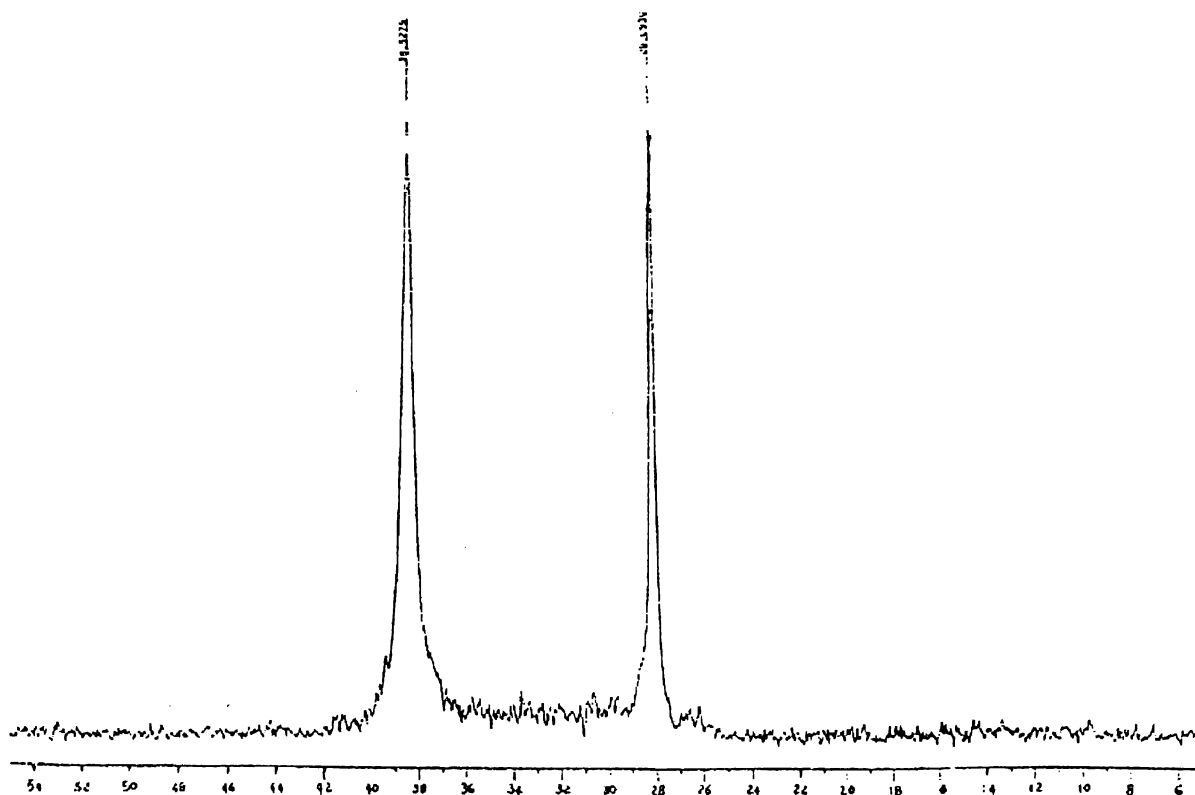


Fig. 1. ^{31}P NMR spectrum of $[\text{Pd}(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{COO})(\text{Ph}_2\text{P}-2\text{-C}_6\text{H}_4\text{COOH})\text{Cl}]\text{CDCl}_3$ (ppm).

nitro aromatics at much faster rates than the corresponding *o*-substituted ones. Nitrobenzene is preferentially reduced almost to 100%, when admitted with any *ortho*-substituted derivatives such as *o*-nitrotoluene and *o*-chloronitrobenzene (Table 2). Alkenes underwent simultaneous reduction and isomerization to produce alkanes and alk-2-ens. The rates of reduction hex-1-ene and hept-1-ene were extremely slow. Styrene, isopropene or cycloocta-1,5-diene, in which the $>\text{C}=\text{C}<$ group is a part of the delocalized system were reduced more rapidly than the isolated double bonds in cycloocta-1,5-diene. On hydrogenation of phenylethylene and phenylacetylene with the corresponding complexes resulted only ethylbenzene. It is observed that in case of phenylethylene the rate of hydrogenation reaction is very high than the rate of phenylacetylene, which may be due to the free rotation of π -electrons in the former one. Diphenylacetylene was reduced first to *cis*-stilbene and then to 1,2-diphenylethane. Diphenylacetylene was reduced at a faster rate than *cis*-stilbene and this may be due to superior coordinating capacity of the former to the metal centre⁸. **3a** appear to be efficient catalyst as

compared to **1a** and **1f** for the reduction of various substrates according to their activities. The catalysts may be arranged in the order **3a** > **1f** > **1a**. The efficiency of a catalyst seems to depend on the extent of metal-ligand π -electron delocalization in the chelate⁹. Very good yield of products under very simple reaction conditions suggests that these complexes can function as catalysts in ambient condition of various substrates showing a very high catalyst turnover number at room temperature.

Conclusion :

$[\text{Pd}(\text{COD})\text{Cl}_2]$ reacts with substituted tertiary phosphines to give neutral complexes of the type $[\text{PdL}_2\text{Cl}_2]$. On the other hand, reaction of $[\text{Pd}(\text{COD})\text{Cl}_2]$ with carbonmonoxide in the presence of respective phosphine produces $[\text{Pd}(\text{CO})\text{LCl}_2]$. Chloride abstraction from $[\text{PdCl}_2\text{L}_2]$ yielding the complexes $[\text{Pd}(\text{L})(\text{LH})\text{Cl}]$ and $[\text{Pd}(\text{L})_2]$, in which the substituted tertiary phosphine acts as a chelate coordinating through the 2-carboxyl oxygen and phosphorous atoms of (2-carboxyphenyl) diphenylphosphine. Cationic complexes of the type

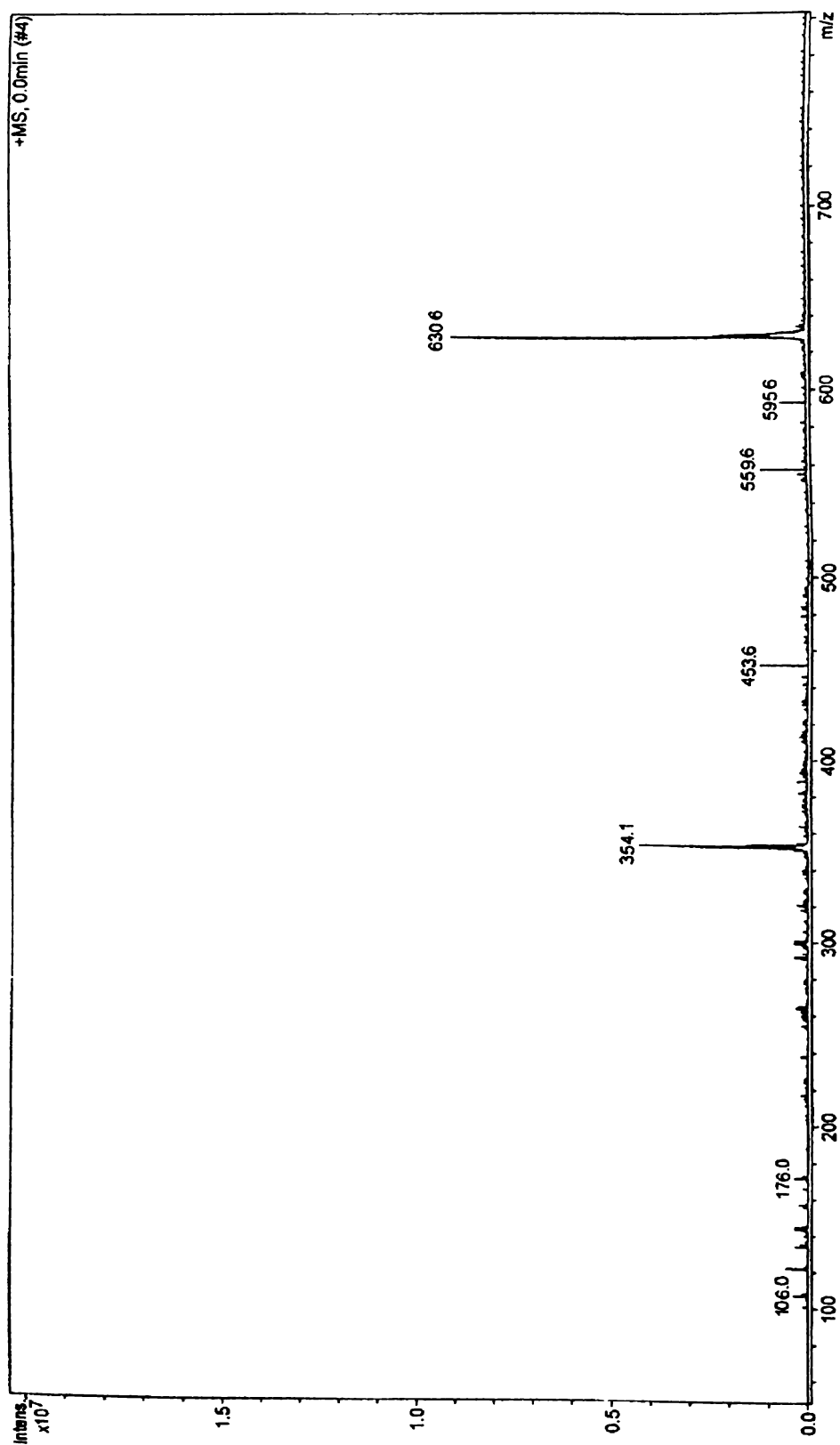


Fig. 2a. Mass spectrum of [Pd(Ph₂P-2-C₆H₅N)Cl₂].

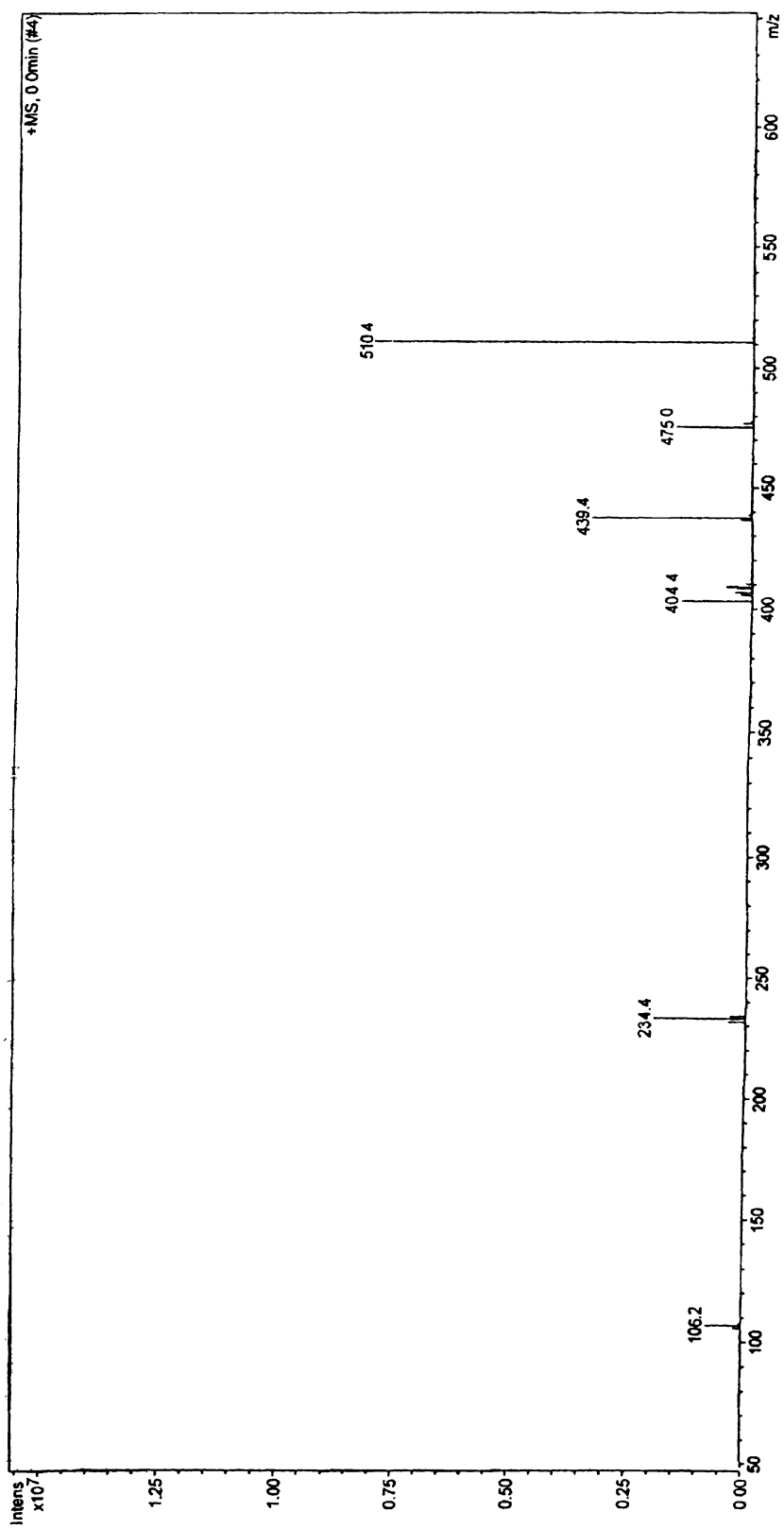


Fig. 2b. Mass spectrum of $[\text{Pd}(\text{Ph}_2\text{P}-3\text{-C}_6\text{H}_4\text{COOH})(\text{CO})\text{Cl}_2]$.

Table 2. Catalytic hydrogenation of Pd^{II} phosphine complexes and yields of main products at 1.5 atm pressure of H₂ and 25 °C in DMF

Substrate	Catalyst (mol L ⁻¹ × 10 ⁻⁴)	Products	Yields (%) with		
			1a	1f	3a
Nitrobenzene	1a, 1f, 3a	Aniline	88	92	98
<i>o</i> -Nitrotoluene	1a, 1f, 3a	<i>o</i> -Toluidine	86	89	96
<i>o</i> -Chloronitrobenzene	1a, 1f, 3a	<i>o</i> -Chloroaniline	82	83	94
<i>p</i> -Nitrotoluene	1a, 1f, 3a	<i>p</i> -Toluidine	88	90	97
<i>m</i> -Dinitrobenzene	1a, 1f, 3a	<i>m</i> -Phenylenediamine	76	85	94
<i>m</i> -Chloronitrobenzene	1a, 1f, 3a	<i>m</i> -Chloroaniline	70	84	98
Styrene	1a, 1f, 3a	Ethyl benzene	84	86	97
Hex-1-ene	1a, 1f, 3a	Hexane	60	64	69
		Hex-2-ene	31	30	28
Maleic acid	1a, 1f, 3a	Succinic acid	91	93	96
Isoprene	1a, 1f, 3a	2-Methylbutane	84	90	93
Cyclo octa 1,5-diene	1a, 1f, 3a	Cyclooctane	89	92	94
Phenyl acetylene	1a, 1f, 3a	Ethyl benzene	90	96	98
Diphenyl acetylene	1a, 1f, 3a	1,2-Diphenyl ethane	88	94	97
Benzaldehyde	1a, 1f, 3a	Benzyl alcohol	90	93	96

[Pd(acac)L₂][BF₄] are synthesized from [Pd(COD)(acac)] precursor. IR and NMR spectral data of all the complexes reveal that the substituted tertiary phosphines are present in *cis* configuration around the metal centre. Catalytic hydrogenation of some aromatic nitro compounds, alkenes, alkynes and aldehydes is carried out by using **1a**, **1f** and **3a** complexes and their catalytic activity is in the order of **3a** > **1f** > **1a** under mild conditions.

Experimental

Reagents and techniques : AnalaR grade reagents, freshly distilled solvents and pure and dry hydrogen gas were used throughout the investigations. All the substrates were purified before use. The starting materials viz. [Pd(COD)Cl₂] and substituted tertiary phosphines were prepared according to the literature procedure¹⁰. The catalytic hydrogenations were carried out in DMF in a stainless steel glass-lined autoclave. After separation the products were purified and testified and their structural information was obtained by IR and NMR techniques.

Microanalytical (C, H) data was obtained from Technical University of Berlin, Berlin, Germany by using a Perkin-Elmer 240C CHN elemental analyzer. Molar conductances of the complexes were measured in dichloromethane using a Systronic conductivity bridge of the type 305. Analyses of the product mixture were done as a gas chromatography Varian 3700. UV-Vis spectra were recorded on a Shimadzu MPS-5000 spectrophoto-

meter, IR spectra in KBr pellets on Nicolet 740 spectrophotometer, ¹H NMR spectra on Bruker WP 80 (80 MHz) and Bruker WH 270 (270 MHz), ¹³C NMR on Bruker WH 270 (67.93 MHz), ³¹P NMR on WH 270 (109.29 MHz). CEC-21-110B, Finningan Mat 1210 spectrometer operating at 70 eV using a direct inlet system was used for recording mass spectra at ICT, Hyderabad.

Synthetic procedures :

Dichloro bis(2-carboxyphenyl) diphenylphosphine palladium(II) (1a) : To a stirred solution of (2-carboxyphenyl)diphenyl phosphine (490 mg, 1.6 mmol) in 20 ml chloroform, [Pd(COD)Cl₂] (228 mg, 0.8 mmol) in 20 ml also in chloroform was added over a period of 45 min. The resulting solution was stirred for 1 h and concentrated to half of the volume, under reduced pressure. Diethylether was added slowly to initiate crystallization of the product (**1a**). It was filtered and washed with ether to give white crystals, and dried *in vacuo*. Yield : 645 mg (83%). A similar synthetic procedure was applied to prepare complexes, **1b** to **1e** in a quantitative yield (81–86%).

Chloro[(2-carboxylatophenyl)diphenylphosphine][(2-carboxyphenyl)diphenylphosphine]palladium(II) (1f) : AgBF₄ (41 mg, 0.2 mmol) was added to a solution of dichlorobis(2-carboxyphenyl)diphenylphosphine palladium(II) (173 mg, 0.21 mmol) (**1a**) in 20 ml of dichloromethane. The reaction mixture was stirred for 1 h in the dark. The white precipitate of AgCl was filtered

off. Diethyl ether was added after concentrating the solution. Filtration, followed by washing with ether gave colourless crystals (**1f**). Yield : 140 mg (82%).

Bis [(2-carboxylatophenyl)diphenylphosphine]palladium(II) (1g) : A solution of dichloro bis (2-carboxyphenyl)-diphenylphosphine palladium(II) (**1a**) (189 mg, 0.24 mmol) in 20 ml of dichloromethane was treated with AgBF₄ (97 mg, 0.5 mmol). The resultant mixture was stirred for 2 h in the dark and the precipitated AgCl was removed by filtration. After reduction of the solvent, ether was added and white crystalline compound (**1g**) was isolated. Yield : 153 mg (81%).

Dichloro[(carbonyl)(2-carboxyphenyl)diphenyl phosphine]palladium(II) (2a) : Carbon monoxide was passed through a solution of [Pd(COD)Cl₂] (174 mg, 0.6 mmol) in 15 ml of chloroform. After 1 h, a solution of (2-carboxyphenyl)diphenyl phosphine (180 mg, 0.6 mmol) in 20 ml of chloroform was added for over 30 min and a steam of carbonmonoxide was continued for a further 30 min. The white crystalline compound (**2a**) was precipitated on a high yield. The product was filtered and washed with ether and dried *in vacuo*. Yield : 295 mg (85%). Using the same procedure, complexes **2b** to **2e** were prepared. Yield : 81–85%.

(1,5-Cyclooctadiene)(2,4-pentanedionato) palladium(II) tetrafluoroborate (3) : Dichloro (1,5-cyclooctadiene) palladium(II) (1300 mg, 4.52 mmol) was added to a reaction flask containing suspension of silver tetrafluoroborate (1950 mg, 20 mmol) in 50 ml dichloromethane. This reaction mixture was stirred for 30 min and 2,4-pentanedione (0.75 ml) was added. The stirring was continued for further 20 min and then filtered for the separation of AgCl. Upon addition of diethylether to the filtrate, a white crystalline compound was formed which was filtered and washed with ether. Drying *in vacuo* afforded the product as shiny white crystals. Yield : 1700 mg (83%).

(2,4-Pentanedionato)bis(2-carboxyphenyl)diphenyl phosphinepalladium(II)tetrafluoroborate (3a) : The precursor (1,5-cyclooctadiene)(2,4-pentanedionato) palladium(II)tetrafluoroborate (**3**) (240 mg, 0.6 mmol) dissolved in dichloromethane which was added to a solution of (2-carboxyphenyl) diphenylphosphine (360 mg, 1.2 mol)

was taken in the same solvent. The resultant solution was stirred for 1 h and then its volume was reduced to one third and small amounts of diethyl ether were added for crystallization of the product. The white crystalline compound was filtered and washed with ether and dried *in vacuo*. Yield : 490 mg (82%). The complexes **3b** to **3e** were prepared by following the same method. Yield : 80–84%.

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