Polyhedron Vol. 6, No. 9, pp. 1727–1735, 1987
Printed in Great Britain

0277-5387/87 \$3.00+.00

SYNTHESIS AND CHARACTERIZATION OF NOVEL PLATINUM GROUP METAL COMPLEXES OF BIS[2-(DIPHENYLPHOSPHINO)ETHYL]AMINE

M. M. TAQUI KHAN* and **E. RAMA RAO**

Discipline of Co-ordination Chemistry and Homogeneous Catalysis, Central Salt & Marine Chemicals Research Institute, Bhavnagar 364002, India

(*Received* 9 *December* 1986; *accepted* 6 *March* 1987)

Abstract—A mixed donor tridentate ligand bis [2-(diphenylphosphino)ethyl]amine (DPEA) was synthesized in its hydrochloride form by a modified procedure and characterized by ^{1}H, ^{13}C and ^{31}P NMR spectral data. Reaction of $RhCl(CO)(PPh_3)_2$ with DPEA·HCl and $NaBPh_4$ in methanol gave the cationic Rh(I) complex $[Rh(DPEA)PPh_3]BPh_4$ but the reaction of $IrCl(CO)(PPh_3)_2$ with DPEA·HCl in boiling benzene gave a unique complex, [Ir(H)(Cl)(CO)(DPEA)]Cl, in which five different donor atoms are coordinated to the single Ir(III) ion. A neutral, Rh(III) complex of the composition $[RhCl_3(DPEA)]$ was prepared by the reaction of $RhCl_3 \cdot xH_2O$ with DPEA·HCl in methanol. Reaction of $PdCl_2(COD)$ with DPEA·HCl in benzene or methanol gave the cationic complex [PdCl(DPEA)]Cl the above reaction conducted in benzene-acetone-methanol mixture gave the 1 : 2 complex $[Pd(DPEA)_2]Cl_2$. A novel trinuclear Pt(II) complex of the composition $[Pt_3Cl_3(DPEA)_3]Cl_3$ was prepared by the reaction of K_2PtCl_4 and DPEA·HCl in water-acetone mixture. Reaction of K_2PtCl_4, DPEA·HCl and NH_4PF_6 in water ethanol mixture gave the binuclear, cationic complex, $[Pt_2(DPEA)_3](PF_6)_4$. All the complexes were characterized by elemental analysis, conductivity, ^{1}H and ^{31}P NMR spectral data.

Recently we have been interested in the synthesis and chemistry of transition metal complexes of polydentate ligands containing mixed donor atoms like N, P, As.[1–5] Though considerable research interest has been concentrated on mononuclear complexes of polydentate mixed donor ligands, only recently active interest has been evinced in the use of these polydentate ligands in the synthesis of bi- and polynuclear metal complexes,[6–8] mostly due to their catalytic importance.[9–11]

In this paper we report the synthesis of mononuclear platinum group metal complexes of bis[2-(diphenylphosphino)ethyl]amine (DPEA) which has been synthesized by a modified procedure. Binuclear and trinuclear Pt(II) metal complexes of DPEA in which the two metal ions are held apart at a sufficient distance and incapable of forming metal–metal bonds, have also been synthesized. All the complexes and the ligand DPEA are characterized on the basis of their analytical and spectral data.

RESULTS AND DISCUSSION

The ligand DPEA·HCl is soluble in most of the organic solvents and was characterized by analytical and spectral measurements. The ^{1}H NMR spectrum of the ligand DPEA·HCl, exhibits a complex asymetric phenyl proton resonance at 7.3 δ. The resonance of the protons of the CH_2CH_2 bridge are also observed as multiplets centered at 2.9 δ (-CH_2 protons attached to diphenylphosphino group) and 2.5 δ (-CH_2 protons attached to amine center). The spectrum also exhibits the NH resonance at 1.9 δ, in concurrence with earlier reported values.[12,13] The $^{31}P\{^{1}H\}$ NMR spectrum of the ligand in $CHCl_3$ gave an intense singlet at -20.3 δ. The $^{13}C\{^{1}H\}$ NMR spectrum of DPEA·HCl in $CDCl_3$ gave two well defined doublets centred at 44.4 δ and 24.0 δ in the aliphatic region. The more downfield doublet is assigned to the methylene car-

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* Author to whom correspondence should be addressed.

bon of the CH_2CH_2 bridge attached to phosphorus, with larger $^1J(C–P) = 26.4$ Hz and the other high field doublet with $^2J(C–P) = 17.6$ Hz, can be assigned to the methylene carbon attached to nitrogen. The aromatic carbons of the diphenylphosphino moieties gave doublets centred at 136.3, 132.7 and 128.8 δ with J(C–P) values of 13.2, 19.1 and 5.8 Hz assigned to C-2(6), C-1, C-3(5), respectively, whereas C-4 carbon gave a singlet at 129.7 δ.

Platinum group metal complexes

The ligand DPEA • HCl was utilized for the synthesis of various platinum group metal complexes.

The reaction of DPEA • HCl with $RhCl(CO)(PPh_3)_2$ in 1 : 1 molar ratio gave the cationic complex, $[Rh(DPEA)(PPh_3)]BPh_4$ **1** best isolated as its BPh_4^- salt. Complex **1** gave a conductance value indicative of a 1 : 1 electrolyte[14] (Table 1). The $^{31}P\{^1H\}$ NMR spectrum of complex **1** (Fig. 1, Table 2) exhibits an A_2MX pattern of spectrum with a pair of triplets and doublets. The doublets are centred at 41.5 and 38.2 δ with $J(Rh–P_a) = 134.3$ Hz and are assigned to the two equivalent *trans* phosphorus atoms (P_a) of the ligand (structure I). The triplets are centred at 32.0 and 29.3 δ with $J(Rh–P_b) = 117.2$ Hz, $J(P_a–P_b) = 24.4$ Hz, and assigned to triphenyl phosphine (P_b), which is coordinated to rhodium *trans* to the nitrogen of DPEA. There is a considerable downfield shift of ^{31}P resonance of the phosphorus atoms of the ligand DPEA upon chelation to form a five-membered ring[15] and also the $^1J(Rh–P_a)$ coupling is larger than that of $^1J(Rh–P_b)$, due to the strong bond of the chelated phosphorus atoms rather than the monodentate phosphorus atom. Complex **1** can be assigned a square-planar structure as shown in Structure I.

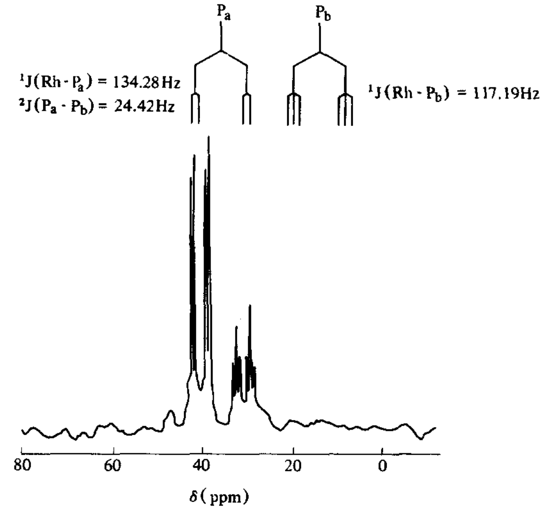


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Rh(DPEA)(PPh_3)]BPh_4$.

Table 1. Analytical and other physical data of metal complexes

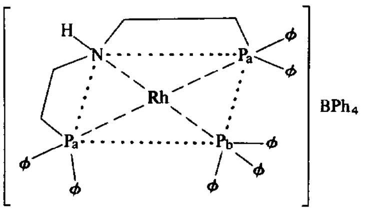
Complex[a]	Colour	Melting/ decomposition point (°C)	Elemental analysis[b] %C	%H	%N	%Cl	Conductivity[c] λ_∞ Ω^{-1} cm^2 mol^{-1}
$[Rh(DPEA)(PPh_3)]BPh_4$ **1**	Pale yellow	178	74.7 (74.4)	5.7 (5.7)	1.2 (1.2)	—	32[d]
$[Rh(DPEA)Cl_3]$ **2**	Pale yellow	248	51.6 (50.8)	4.5 (4.5)	2.1 (2.1)	—	32[e]
[Ir(Cl)(H)(CO)(DPEA)]Cl **3**	White	245–247	49.9 (48.9)	4.3 (4.3)	2.0 (1.9)	10.1 (10.1)	65[e]
[Pd(DPEA)Cl]Cl **4**	Yellowish-green	243–245	54.3 (54.1)	4.7 (4.7)	2.2 (2.1)	11.4 (11.4)	106
$[Pd(DPEA)_2]Cl_2$ **5**	Yellow	> 200	63.4 (63.2)	5.7 (5.7)	2.6 (2.5)	—	130[e]
$[Pt_2(DPEA)_2(\mu^3\text{-}DPEA)(PtCl_3)]Cl_3$ **6**	White	212–216	47.5 (47.0)	4.1 (4.1)	1.9 (1.9)	—	181
$[Pt_2(DPEA)_2(\mu\text{-}DPEA)](PF_6)_4$ **7**	White	228	43.1 (42.8)	3.7 (3.6)	1.7 (1.7)	—	212

[a] DPEA = bis[2-(diphenylphosphino)ethyl]amine.
[b] Found values are in parentheses.
[c] Conductivity measurements were done in methanol at room temperature and values reported for infinite dilution.
[d] Dichloromethane.
[e] DMF.

Table 2. The $^{31}P\{^1H\}$ NMR spectral data[a] of the metal complexes

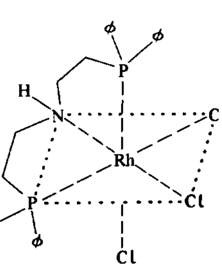
Complex[b]	Solvent	Chemical shifts[c] (δ/ppm) Pa	Pb	Pc	Coupling constant (Hz) J(M–P) J(M–P_a)	J(M–P_b)	J(P–P) J(P_a–P_b)
$[Rh(DPEA)(PPh_3)](BPh_4)$ **1**	$CHCl_3$	41.5(d) 38.2(d)	32.0(t) 29.3(t)	—	134.3	117.2	24.4
$[Rh(DPEA)Cl_3]$ **2**	CH_2Cl_2						
(A) *Mer*		28.4(d)	—	—	84.2	—	—
(B) *Fac*		44.5(d)	—	—	122.1	—	—
[Ir(Cl)(H)(CO)(DPEA)]Cl **3**	$CHCl_3$	27.7(s)	—	—	—	—	—
[Pd(DPEA)Cl]Cl **4**	$CHCl_3$	37.2(s)	—	—	—	—	—
$[Pd(DPEA)_2]Cl_2$ **5**	$CHCl_3$	45.4(d)	15.5(t)	−22.4(s)	—	—	~24
$[Pt_2(DPEA)_2(\mu^3\text{-DPEA})(PtCl_3)]Cl_3$ **6**	$CHCl_3$	42.0(d)	−5.3(t)	—	2578	3123	19.5
$[Pt_2(DPEA)_2(\mu\text{-DPEA})](PF_6)_4$ **7**	CH_2Cl_2	42.0(d)	−7.0(t)	—	2537	3147	19.5

[a] Positive Chemical Shifts Downfield from 85% H_3PO_4.
[b] DPEA = bis(2-(diphenylphosphino)ethyl)amine.
[c] s = singlet, d = doublet, t = triplet.

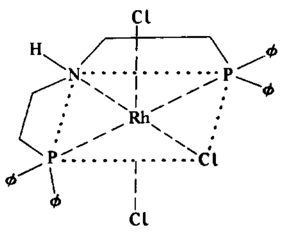


I

Interaction of hydrated rhodium trichloride with DPEA · HCl in 1 : 1 mole ratio gives a neutral, octahedral complex of the composition $[RhCl_3(DPEA)]$ **2** which can exist in two isomeric forms: *facial* and *meridional*. The far-infrared spectrum exhibits a broad band at 335 cm^{-1} and also two more bands at 350 and 386 cm^{-1} indicative of ν(Rh–Cl) and cannot be unambiguously assigned to either isomer. However, $^{31}P\{^1H\}$ NMR spectrum (Table 2) corroborates the presence of both *facial* and *meridional* isomers. The spectrum displays two doublets centred at 44.5 δ (J(Rh–P) = 122.2 Hz) and 28.4 δ (J(Rh–P) = 84.2 Hz) that can be assigned to the *fac* and *mer* isomers (Structure II, IIa), respectively. The above spectral assignment was based on the following considerations in the *fac* isomer (**II**) the two phosphorus atoms *trans* to a more electronegative and a weak ligand would exhibit a more downfield resonance with a large J(Rh–P) in comparison to the *mer* isomer, in accordance with the earlier observed data.[16,17]



II



IIa

Interaction of DPEA · HCl with $IrCl(CO)(PPh_3)_2$ in boiling benzene, however gave a unique and interesting complex of the composition [Ir(H)(Cl)(CO)(DPEA)]Cl **3** wherein the metal ion is coordinated to five different donor atoms. Analytical and conductivity data (Table 1) support the above formulation for complex **3**. Complex **3** is obtained by an oxidative-addition of the HCl, derived from the ligand DPEA · HCl, to the Ir(I) complex $IrCl(CO)(PPh_3)_2$ followed by the coordination of Ir(III) to DPEA. The infrared spectrum of complex **3** (Fig. 2) displays an intense peak at 2020 cm^{-1} indicative of the coordinated carbonyl absorption band. This band is red shifted about 50 cm^{-1} compared to that of the starting material (Vaska's complex) and is in support[18] of the oxidation of Ir(I) to Ir(III). The IR spectrum of the complex also exhibits an intense metal-hydride stretching frequency at 2095 cm^{-1} (Fig. 2). The far-infrared spectrum of **3** shows a ν(Ir–Cl) band at 333 cm^{-1}.

The ^1H and ^{31}P NMR are of great help in corroborating the above formulation for complex **3**. The ^1H NMR spectrum (Fig. 3) exhibits the proton resonance centred at 7.5 δ and two types of the methylene protons at 3.4 and 3.3 δ as broad intense peaks. The proton of the secondary amine gave the resonance at 10.1 δ (Fig. 3) indicating the coor-

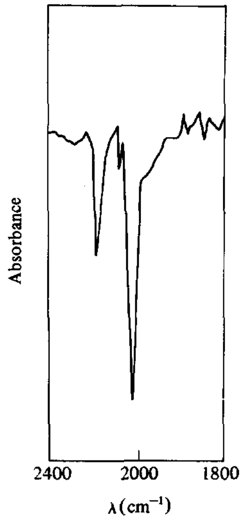


Fig. 2. IR spectrum of [Ir(H)(Cl)(CO)(DPEA)]Cl.

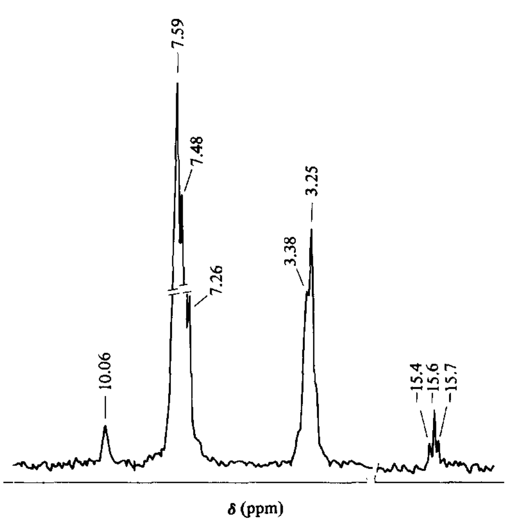
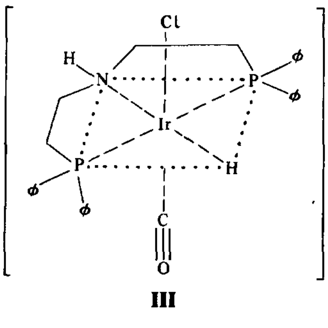


Fig. 3. ^{1}H NMR spectrum of [Ir(H)(Cl)(CO)(DPEA)]Cl.

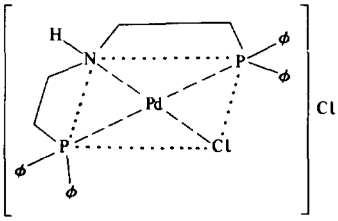
dination of nitrogen of the secondary amine to the metal ion.[19] The ^{1}H NMR spectrum in the high field region displays a well defined triplet (Fig. 3) centred at -15.6 δ indicating the presence of hydride species in the coordination sphere of the metal ion. The triplet is due to coupling of the hydride with two equivalent *trans* disposed phosphorus atoms of the ligand DPEA (Structure III). The J(P–H) of 12.8 Hz is also in agreement with the *cis* disposition of the hydride to the two phosphorus atoms of the ligand.[20]



III

The ^{31}P{^{1}H} NMR spectrum exhibits an intense singlet at 27.7 δ in support of structure III for complex **3**.

The reaction of $PdCl_2(COD)$ with DPEA·HCl in refluxing methanol or benzene, resulted in the formation of the square planar complex [PdCl(DPEA)]Cl **4**, by the complete displacement of 1,5-COD. The conductance value is consistent with a 1 : 1 electrolyte[14] (Table 1). The far-infrared spectrum of the complex displays a ν(Pd–Cl) absorption band at 337 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum of complex **4** exhibits a singlet at 37.2 δ indicating the magnetic equivalence of the two *trans* disposed phosphorus atoms of the ligand DPEA, as shown in Structure IV.



IV

When the reaction of $PdCl_2$ with DPEA·HCl was conducted in a methanol/acetone/benzene mixture a five-coordinated 1 : 2 complex of the composition $[Pd(DPEA)_2]Cl_2$ **5** resulted. The formulation of complex **5** is corroborated by the elemental analysis, conductance values (Table 1) and the ^{31}P{^{1}H} NMR. The ^{31}P{^{1}H} NMR spectrum of complex **5** displays an interesting spectrum (Fig. 4). The spectrum has a downfield doublet centred at 45.4 δ, a triplet centred at 15.5 δ and a higher field singlet at -22.4 δ. The spectrum suggests that one of the two coordinated DPEA ligands which is potentially terdentate is coordinated to the metal ion through only one of two phosphorus atoms and the other phosphorus donor end (P_c) is free as

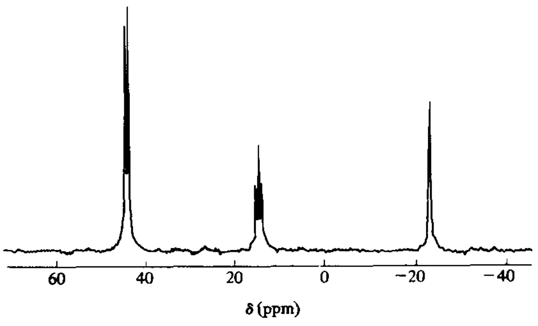
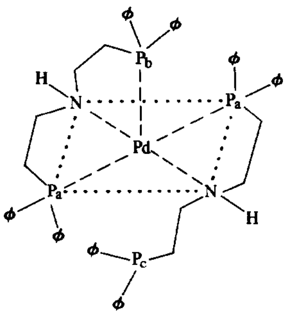


Fig. 4. ^{31}P{^{1}H} NMR spectrum of $[Pd(DPEA)_2]Cl_2$.

evidenced by the high field singlet. Thus the ligand DPEA acts as a bidentate ligand in the complex (Structure V). The doublet is assigned to the two equivalent phosphorus donor atoms (P_a) and the triplet to the phosphorus (P_b). The J(P_a–P_b) value of ~ 24 Hz also confirms the *cis* coordination of the phosphorus atoms P_a and P_b as shown in Structure V. The complex is shown with a five coordinated square pyramidal Pd(II) ion. Such a five coordination of Pd(II) was also suggested in other complexes.[21] Five coordination is more common in Pd(II) complexes as compared to those of Pt(II) complexes.



V

The reaction of $PdCl_2$ with DPEA • HCl in methanol however gave a mixture of complexes **4** and **5** as evidenced by the $^{31}P\{^1H\}$ NMR spectrum in $CHCl_3$ with complex **4** being the predominant species.

The reaction of K_2PtCl_4 with DPEA • HCl in 1 : 1 molar ratio in water–acetone medium gave a trinuclear ligand bridged complex of the composition $[Pt_2DPEA)(\mu^3\text{-DPEA})(PtCl_3)]Cl_3$ **6**. The above reaction when conducted in water–methanol medium in the presence of NH_4PF_6 resulted in the formation of a binuclear, ligand bridged complex of the composition, $[Pt_2(DPEA)_2(\mu\text{-DPEA})](PF_6)_4$ **7**. The elemental analysis and conductance data obtained is in confirmation of the above formulations for the complexes **6** and **7**. The far-infrared spectrum of complex **6** displays a broad band at 325 cm^{-1} due to ν(Pt–Cl).

The infrared spectrum of **7** exhibits a strong absorption at 840 cm^{-1} characteristic of ν(P–F) stretching frequency.[22]

The $^{31}P\{^1H\}$ NMR spectrum of complex **6** supports its formulation as a trinuclear ligand bridged species. The $^{31}P\{^1H\}$ NMR spectrum of **6** (Fig. 5) exhibits a doublet centred at 42.0 δ and a triplet centred at −5.3 δ with ^{195}Pt satellites in 2 : 1 ratio, respectively. This also indicates the presence of two different types of phosphorus atoms in accordance with the geometry shown in Structure VI. The doublet is assigned to the two equivalent *trans* disposed phosphorus atoms (P_a) of the ligand DPEA and the triplet to the phosphorus atom (P_b) which is *trans* to a nitrogen donor and *cis* to the two equivalent P_a nuclei. The platinum–phosphorus coupling constants J(Pt–P_a) and J(Pt–P_b) calculated from the platinum satellites are found to be 2578 Hz and 3123 Hz, respectively, in accordance with the earlier observed values.[17,19,23] The J(Pt–P_b) value is larger as compared to that of J(Pt–P_a) due to the fact that the phosphorus atom (P_b) *trans* to a σ-donor nitrogen group is bound strongly to the metal ion with a greater *s* character of the Pt–P

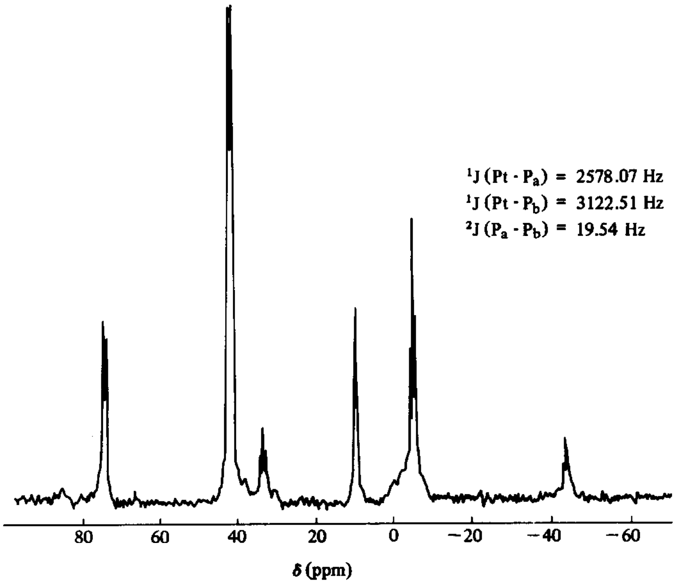
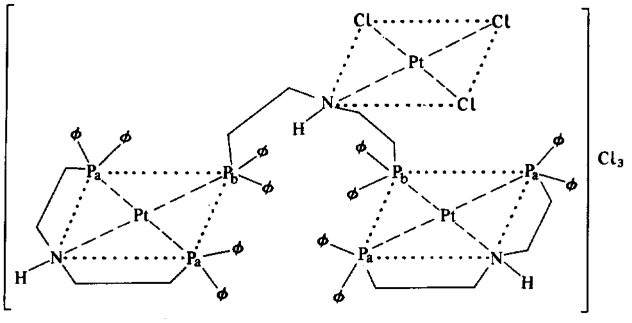


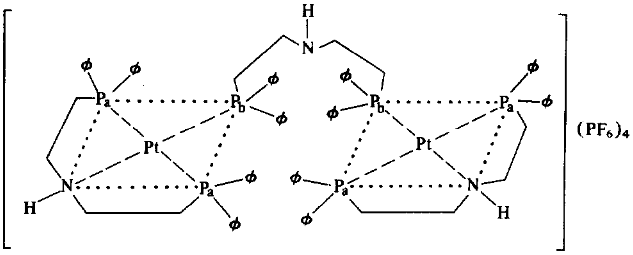
Fig. 5. $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2(DPEA)(\mu^3\text{-DPEA})(PtCl_3)]Cl_3$.



VI

bond as compared to the mutually *trans* phosphorus atom (P_a).[17,23]

The $^{31}P\{^1H\}$ NMR spectrum of complex **7** (Fig. 5) shows a doublet centred at 42.0 δ and a triplet centred at -7.0 δ with ^{195}Pt satellites. The doublet is assigned to *trans* disposed phosphorus aroms (P_a) and the triplet is assigned to the phosphorus atom (P_b) which is *trans* disposed to a σ-donor nitrogen group and *cis* to two P_a atoms as shown in Structure VII. The $^1J(Pt–P_a) = 2537$ Hz, $^1J(Pt–P_b) = 3147$ Hz and $^2J(P_a–P_b) = 19.5$ Hz, values are in accordance with earlier observed data.[17,19,23] The $^{31}P\{^1H\}$ spectrum of complex **7** also displays seven sharp lines ($J = 713$ Hz) in the high-field region centred at -143.3 δ due to the PF_6^- ion.[24,25] The geometry of complex **7** is shown in Structure VII.



VII

The far-infrared spectra of complexes **1**–**7** gave bands around 520 cm^{-1} due to ν(M–P).

The electronic spectral data of all the complexes **1**–**7** agree with the proposed geometries of the complexes. All the square-planar complexes in this work have nd,[8] whereas octahedral complexes have nd^6 valence orbital electronic configurations, respectively. Complex **1** gave bands at 340 nm (4160) and 335 nm (3200) assignable to *d–d* transitions and the bands at 272 nm (25120) and 268 nm (25440) are attributed to π–π^* transitions. Similarly, complex **4** displays a band at 353 nm (31840) assigned to *d–d* transition with LMCT character and bands at 288 nm (35360) and 262 nm (24000) are due to LMCT transitions between the metal ion and the ligand. The polynuclear Pt(II) complexes **6** and **7** gave bands at 274 nm (12900) with LMCT character and 360 nm (3360), respectively, assigned to *d–d* transitions. The bands observed at 256 nm (17000), 226 nm (25000) and 266 nm (25600), 250 nm (24000) for **6** and **7**, respectively, are assigned to charge-transfer transitions between metal ion and the ligand. The results obtained are in agreement with the earlier reported work with nd^8 metal ions.[26,27]

The octahedral Rh(III) complex **2** gave bands at 425 nm (11207), 353 nm (64000), 330 nm (11360) and 257 nm (29046) whereas Ir(III) complex **3** gave bands at 355 nm (2160), 290 nm (11360), 272 nm (15040) and 265 nm (16640). The bands around 425 and 350 nm are assigned to the transitions from $^1A_{1g}$ ground state to the $^1T_{1g}$ excited state. Whereas the other high energy bands are assigned to charge-transfer transitions between metal ion and the ligand.

EXPERIMENTAL

The hydrated trichlorides of rhodium and iridium, $PdCl_2$ and K_2PtCl_4 were purchased from Alfa Inorganics (USA) and Johnson Matthey (England). Triphenyl phosphine was purchased from Strem Chemicals Inc. (U.S.A.). $NaBPh_4$ and NH_4PF_6 were obtained from SISCO (India). 1,5-cyclooctadiene obtained from Fluka was used as such. The complexes $RhCl(CO)(PPh_3)_2$,[28]

$IrCl(CO)(PPh_3)_2$,[28] were prepared by published procedures. Diethanolamine, thionyl chloride were of Analar grade and were used without further purification. Bis(2-chloroethyl)amine hydrochloride was prepared by published procedure.[29] All the preparations were carried out in a dry nitrogen atmosphere.

Microanalysis, melting points, infrared spectra, conductivity measurements were done as reported.[30] Proton NMR spectra were recorded on a Jeol FX100 spectrometer operating at 100 MHz using TMS as an internal standard. The carbon-13 NMR spectrum of the ligand was also recorded on the same instrument operating at 24.9 MHz in $CDCl_3$ using TMS as an internal standard. The proton noise decoupled phosphorus-31 NMR spectra of the ligand and complexes were taken in the indicated solvents (Table 2) using the same instrument operating at 40.3 MHz in the FT mode with a deuterium lock. 85% H_3PO_4 was used as an external reference. The electronic spectra of complexes were measured on a Shimadzu UV 240 spectrophotometer.

Synthesis of the ligand

The terdentate mixed donor (N and P) ligand bis[2-(diphenylphosphino)ethyl]amine hydrochloride (DPEA · HCl) was synthesized by modified published procedures,[31,32] as shown in scheme.

$$HN(CH_2CH_2OH)_2+2SOCl_2$$

$$\xrightarrow{CHCl_3} \underset{\mathbf{a}}{Cl^-H_2N^+(CH_2CH_2Cl)_2}+2SO_2+2HCl$$

$$\mathbf{a}+10\%NaOH$$

$$\longrightarrow \underset{\mathbf{b}}{HN(CH_2CH_2Cl)_2}+2NaCl+2H_2O$$

$$PPh_3+2K \xrightarrow{1,4,\text{dioxan}} KPPh_2+KPh$$

$$\mathbf{b}+2KPPh_2 \xrightarrow[THF]{1,4,\text{dioxan}} \underset{\mathbf{c}}{HN(CH_2CH_2PPh_2)_2}+2KCl$$

$$\mathbf{c}+2NHCl \xrightarrow{n\text{-hexane}} Cl^-H_2N^+(CH_2CH_2PPh_2)_2$$

Bis(2-chloroethyl)amine hydrochloride **a** was prepared by the published procedure[28] and its free amine **b** was liberated by the treatment of a stoichiometric amount of 10% NaOH. The free amine was liberated as an insoluble oil and was dried over sodium sulfate prior to its use. Free amine **b** (6.42 g, 0.045 mol) was dissolved in 40 cm^3 of THF and added dropwise with stirring to an orange-red solution of $KPPh_2$, which was obtained previously through the reaction of metallic potassium (7.04 g, 0.18 mol) with PPh_3 (25.66 g, 0.09 mol) in dioxane. Prior to the addition of the organic halide **b**, KPh was destroyed carefully by the addition of NH_4Cl to the reaction mixture containing both KPh and $KPPh_2$. This *in situ* method of reaction is found to be more convenient to us. After the addition of **b** the reaction mixture was refluxed for an hour and poured into a beaker containing ice-cold water before which the unreacted potassium was destroyed by methanol. The ligand DPEA was separated as an insoluble oil **c**, which on treatment with 2N HCl, in *n*-hexane with vigorous stirring gave a solid white crystalline ligand **d** in its hydrochloride form. The ligand DPEA · HCl was purified by recrystallizing from hot acetonitrile. Yield: 90%. M.p. 175°C; mol wt. 477.5 (calculated), 470 (experimental, osmometric in chloroform). Found: C, 70.1; H, 6.3; N, 2.9. Calc. for $C_{28}H_{30}NClP_2$: C, 70.4; H, 6.3; N, 2.9%.

Preparation of metal complexes

(1) *Triphenylphosphinebis*[2-(*diphenylphosphino*) *ethyl*]*aminerhodium*(I) *tetraphenylborate*, [Rh (DPEA)(PPh_3)]BPh_4. To a refluxing methanolic solution of DPEA · HCl (0.11 g, 0.22 mmol) was added $RhCl(CO)(PPh_3)_2$ (0.15 g, 0.22 mmol) and further refluxed for 3 h to get a dark yellowish orange solution. An excess of $NaBPh_4$ was then added to the above solution, which on concentration gave a crystalline yellow compound. The compound was filtered, washed with benzene, methanol and recrystallized from dichloromethane-*n*-hexane mixture. Yield: 0.2 g (82%).

(2) *Trichlorobis*[2-(*diphenylphosphino*)*ethyl*]-*aminerhodium*(III), $RhCl_3$(DPEA). $RhCl_3 \cdot 3H_2O$ (0.11 g, 0.42 mmol) in methanol was reacted with the ligand DPEA · HCl (0.2 g, 0.42 mmol) to give a yellow solution. After refluxing the solution for 6–7 h, the solution was concentrated to a small volume by a vacuum rotary evaporator and diethyl-ether added to get a yellow precipitate. The complex was filtered, washed with benzene, diethyl ether and recrystallized from dichloromethane-*n*-hexane mixture. Yield: 0.17 g (63%).

(3) *Chlorohydridocarbonylbis* [2-(*diphenylphosphino*)*ethyl*]*amineiridium*(III) *chloride*, [Ir(Cl) (H)(CO)(DPEA)]Cl. The ligand DPEA · HCl (0.1 g, 0.21 mmol) and $IrCl(CO)(PPh_3)_2$ (0.11 g, 0.21 mmol) in benzene were refluxed for 6 h, to get a pale yellow crystalline complex. The complex was filtered, washed with benzene and dried *in vacuo*. Yield: 0.11 g (73%).

(4) *Chlorobis*[2-(*diphenylphosphino*)*ethyl*] *amine-palladium* (II) *chloride*, [PdCl(DPEA)]Cl. To the refluxing benzene solution of DPEA·HCl (0.2 g, 0.42 mmol) was added $PdCl_2(COD)$ (0.12 g, 0.42 mmol), when a clear solution was obtained. The refluxing was continued till a yellowish green crystalline compound separated. The complex was filtered, washed with benzene and recrystallized from dichloromethane-*n*-hexane mixture. Yield: 0.21 g (72%).

The above reaction when conducted in refluxing methanol also gave the same product.

(5) *Bis* (*bis* [2-(*diphenylphosphino*) *ethyl*] *amine-palladium* (II) *chloride*, $[Pd(DPEA)_2]Cl_2$. The reaction of $PdCl_2$ (0.10 g, 0.56 mmol) with DPEA·HCl (0.27 g, 0.56 mmol) was conducted in a mixture of 25 cm^3 of benzene, 5 cm^3 of acetone and 5 cm^3 of methanol. The above reaction mixture was refluxed for 2 h, and the solution concentrated to a small volume by a vacuum rotary evaporator. The addition of diethyl ether gave a yellow complex which was filtered, washed with diethyl ether and recrystallized from dichloromethane-*n*-hexane mixture. Yield: 0.48 g (80%).

(6) *Bis*(*bis*[2-(*diphenylphosphino*)*ethyl*] *amine*-μ^3-*bis*[2-(*diphenylphosphino*)*ethyl*]*aminediplatinum* (II)*trichloroplatinum*(II)*trichloride*, $[(DPEA)Pt(Ph_2PCH_2CH_2\ N(H)CH_2CH_2PPh_2](PtCl_3)\ Pt(DPEA)]\ Cl_3$. To a 1:1 water acetone mixture of K_2PtCl_4 (0.13 g, 0.42 mmol) was added DPEA·HCl (0.2 g, 0.42 mmol) in hot acetone. On addition of the ligand the solution is decolourized and the reaction mixture was refluxed for 6 h. After removing the acetone by rotary vacuum evaporator, the compound was extracted by dichloromethane. The extracted solution was dried over Na_2SO_4, concentrated to a small volume and the complex precipitated by the addition of *n*-hexane. The complex was filtered, washed with benzene and *n*-hexane and recrystallized from dichloromethane-*n*-hexane mixture. Yield 0.23 (76%).

(7) *Bis* (*bis*[2-(*diphenylphosphino*) *ethyl*] *amine*-μ-*bis*[2-(*diphenylphosphino*)*ethyl*]*aminediplatinum*(II) *hexafluorophosphate*, $[Pt_2(DPEA)_2(\mu\text{-}DPEA)](PF_6)_4$. To an aqueous solution of K_2PtCl_4 (0.13 g, 0.42 mmol) was added an ethanolic solution of the ligand DPEA·HCl (0.2 g, 0.42 mmol) to get a colourless solution. The reaction mixture was stirred for about 2 h at room temperature and then refluxed for 5 h. To the refluxing solution NH_4PF_6 (0.1 g, 0.62 mmol) was added and the refluxing continued for a further period of 2 h. Ethanol was completely removed by a vacuum rotary evaporator and an addition quantity of 10 cm^3 of water was added to the solution. On keeping the solution overnight crystalline flakes were obtained. The complex was filtered, washed with water, benzene and recrystallized from dichloromethane-*n*-hexane mixture. Yield: 0.29 g (78%).

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