

0277-5387(95)00300-2

# SYNTHESIS AND CHARACTERIZATION OF DINUCLEAR PLATINUM GROUP METAL COMPLEXES OF A HEXADENTATE LIGAND $\alpha, \alpha'$ -BIS(BIS-(2-(DIPHENYLPHOSPHINO)ETHYL)AMINO)-*m*-XYLENE

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(Received 3 March 1995; accepted 13 June 1995)

Abstract—A number of dinuclear complexes of platinum group metal ions with a hexadentate ligand,  $\alpha, \alpha'$ -bis(bis-(2-(diphenylphosphino)ethyl)amino)-*m*-xylene (L), were synthesized. The reaction of  $[MCl_n(COD)]_x$  (n = 1, x = 2 when M = Rh<sup>1</sup> and Ir<sup>1</sup> and n = 2, x = 1 when M = Pd<sup>II</sup> and Pt<sup>II</sup>) with the ligand L resulted in the formation of square planar dinuclear complexes of the composition  $[M_2LCl_2]^{n+}$  (n = 0 for Rh<sup>I</sup> and Ir<sup>I</sup> and n = 2 for Pd<sup>II</sup> and Pt<sup>II</sup>). The reaction of [Pt Cl<sub>2</sub>(COD)] with L under different experimental conditions yielded a tetranuclear complex,  $[Pt_4L_2Cl_4]Cl_4$ . The reaction of  $[M_2LCl_2]$  (M = Rh<sup>1</sup>, Ir<sup>1</sup>) with CO gas at ambient temperature resulted in the formation of the pentacoordinate CO adduct,  $[M_2LCl_2(CO)_2]$ , with trigonal bipyramidal geometry. The reaction of  $[RhCl_2(CO)(AsPh_3)_2]$ and  $[IrCl(CO)(PPh_3)_2]$  with L gave complexes of the same composition as that of the CO adduct,  $[M_2LCl_2(CO)_2]$ , with two isomeric forms in the case of iridium. The reaction of  $[Rh_2LCl_2]$  with AgClO<sub>4</sub> in acetonitrile resulted in the complete displacement of chloride, with the formation of  $[Rh_2L(NCCH_3)_2](ClO_4)_2$ . A complex of the composition [Rh<sub>2</sub>L(PPh<sub>3</sub>)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> was obtained when [RhCl(COD)]<sub>2</sub> was reacted with L in the presence of  $PPh_3$  in equimolar ratio followed by addition of  $NaBPh_4$ . The reaction of hydrated iridium trichloride gave a dinuclear octahedral complex of Ir<sup>III</sup> of composition  $[Ir_2LCl_6]$ . The geometry of the complexes was established by  ${}^{31}P{}^{1}H{}$  NMR spectral data.

The chemistry of platinum group metal ions with polydentate tertiary phosphine ligands has attracted much attention over the past two decades.<sup>1-5</sup> Their increasing importance is affirmed in many recent reports,<sup>6</sup> particularly with rhodium and iridium in the field of catalysis.<sup>7</sup> Over the past few years a number of such complexes with monoand dinucleating ligands having nitrogen and phosphorus/arsenic donor sites,<sup>8,9</sup> and in some cases their catalytic activity,<sup>10</sup> have been reported from this laboratory. This paper reports the synthesis and characterization of a number of Rh<sup>1</sup>, Ir<sup>I</sup>, Ir<sup>III</sup>, Pd<sup>II</sup> and Pt<sup>II</sup> complexes with a binucleating ligand,  $\alpha, \alpha'$ -bis(bis(2-(diphenylphosphino)ethyl)-amino)*m*-xylene, which contains two sets of NPP donor sites separated by an *m*-xylyl bridge, as shown in structure **I**.



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#### EXPERIMENTAL

# Materials

The hydrated trichlorides of rhodium and iridium, PdCl<sub>2</sub> and H<sub>2</sub>PtCl<sub>6</sub> were purchased from Alfa Inorganics and Johnson Matthey. Triphenylphosphine, triphenylarsine and AgClO<sub>4</sub> were obtained from Aldrich Chemical Co.; NaBPh4 was obtained from Ventron Corp. 1,5-Cyclooctadiene (COD), obtained from Fluka, was used as supplied.  $[RhCl(COD)]_{2}$ ,<sup>11</sup>  $[RhCl(CO)(AsPh_3)_2]$ ,<sup>12</sup> [IrCl  $(COD)]_{2}^{13}$  [IrCl(CO)(PPh\_{3})\_{2}],<sup>14</sup> [PdCl<sub>2</sub>(COD)]<sup>15</sup> and [PtCl<sub>2</sub>(COD)]<sup>16</sup> were prepared by reported procedures. CO gas was prepared by dropwise addition of concentrated  $H_2SO_4$  into sodium formate and passed through KOH and activated silica gel. The ligand  $\alpha, \alpha'$ -bis(bis(2-(diphenylphosphino)ethyl) amino)-m-xylene (L) was synthesized by the procedure developed in this laboratory.9a

All organic solvents used were of reagent grade and were purified and dried by standard procedures before use. All the preparations were carried out under dry nitrogen or argon. Deaerated solvents (where necessary) were used to precipitate the compound from solution.

# Physical measurements

Carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba Elemental Analyser Model 1106. Chloride was estimated gravimetrically using standard procedures.<sup>17</sup> A Digisun Electronics digital conductivity meter Model D1-909 was used for solution conductivity measurements. Magnetic measurements were carried out with a PAR Model 155 vibrating-sample magnetometer. IR spectra were recorded on a Nicolet 200 SX FT-IR spectrometer, as KBr pellets or in Nujol mulls pressed between polyethylene films. The  ${}^{31}P{}^{1}H$  NMR spectra were recorded on a Jeol FX-100 FT-NMR operating at 40.27 MHz in the indicated solvents using spinning 10 mm tubes with a capillary of deuterium oxide for the internal lock and 85% H<sub>3</sub>PO<sub>4</sub> as an external standard. Electronic spectra were recorded on a Shimadzu UV-160 spectrometer.

# Synthesis of metal complexes

[Rh<sub>2</sub>LCl<sub>2</sub>] (1). To a boiling solution of [RhCl(COD)]<sub>2</sub> (0.197 g, 0.4 mmol) in acetonitrile (30 cm<sup>3</sup>) was added dropwise the ligand (0.394 g, 0.4 mmol) dissolved in benzene (20 cm<sup>3</sup>). The reaction mixture was refluxed for 3 h, during which the yellow solution changed to orange. The solvent was removed by rotary evaporation and the residue was dissolved in dichloromethane (20 cm<sup>3</sup>), filtered, and to the hot filtrate, petroleum ether (b.p. 60–80°C) (30 cm<sup>3</sup>) was added dropwise. The resulting mixture was kept at ambient condition overnight. The orange microcrystals that deposited were collected by filtration washed by petroleum ether (b.p. 40– 60°C) and dried *in vacuo*; yield 0.363 g (72%). Found: C, 60.8; H, 5.1; N, 2.0; Cl, 5.5. Calc. for  $C_{64}H_{64}Cl_2N_2P_4Rh_2$ : C, 60.9; H, 5.1; N, 2.2; Cl, 5.6%.

[Rh<sub>2</sub>LCl<sub>2</sub>(CO)<sub>2</sub>] (2). *Method A*. To a refluxing solution (15 cm<sup>3</sup>) of [RhCl(CO)(AsPh<sub>3</sub>)<sub>2</sub>] (0.311 g, 0.4 mmol) dissolved in benzene was added ligand (0.197 g, 0.2 mmol). The reaction mixture was refluxed for 4 h, during which a brown complex was separated. The complex was isolated by filtration, washed with benzene and recrystallized from dichloromethane–petroleum ether (b.p. 40–60°C); yield 0.17 g (65%). Found : C, 60.3; H, 4.8; N, 2.0; Cl, 5.4. Calc. for C<sub>66</sub>H<sub>64</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Rh<sub>2</sub>: C, 60.1; H, 4.9; N, 2.1; Cl, 5.4%.

Method B. To a dichloromethane solution of complex 1 (0.371 g, 0.25 mmol) carbon monoxide gas was passed for 2 h with stirring at ambient temperature. The solution was then concentrated to ca 15 cm<sup>3</sup> and after dropwise addition of n-hexane (10 cm<sup>3</sup>) the resulting solution was kept at room temperature overnight. The reddish-brown compound that deposited was collected by filtration and recrystallized from dichloromethane-pet-roleum ether (b.p. 40-60); yield 80%. Found: C, 60.3; H, 4.8; N, 2.0; Cl, 5.3%.

 $[Rh_2L(NCMe)_2](ClO_4)_2$  (3). The complex [Rh<sub>2</sub>LCl<sub>2</sub>] (0.252 g, 0.2 mmol) was dissolved in acetonitrile (20 cm<sup>3</sup>), and dry AgClO<sub>4</sub> (0.083 g, 0.4 mmol), dissolved in acetonitrile  $(5 \text{ cm}^3)$ , was slowly added to the solution with stirring. AgCl precipitated and the solution turned red-orange. The mixture was stirred for 1 h and then filtered. The filtrate was concentrated to  $ca 5 \text{ cm}^3$  in a rotary evaporator and petroleum ether (b.p. 60-80°C; 5 cm<sup>3</sup>) was added slowly and the resulting mixture was kept in a refrigerator for 12 h. The red-orange microcrystalline compound that separated was collected by filtration and recrystallized from acetonitrile-petroleum ether (b.p. 60-80°C); yield 0.26 g (88%). Found: C, 55.3; H, 4.8, N, 3.7. Calc. for  $C_{68}H_{70}Cl_2N_4O_8P_4Rh_2$ : C, 55.5; H, 4.8; N, 3.8%.

 $[Rh_2L(PPh_3)_2](BPh_4)_2$  (4). A mixture of  $[RhCl(COD)]_2$  (0.099 g, 0.2 mmol) and triphenylphosphine (0.105 g, 0.4 mmol) and ethanol (30 cm<sup>3</sup>) was refluxed for 30 min, and the ligand L (0.197 g, 0.2 mmol) dissolved in benzene (10 cm<sup>3</sup>) was added dropwise. The solution was refluxed for

a further 2 h, during which the yellow solution changed to orange. An excess of an ethanolic solution (15 cm<sup>3</sup>) of sodium tetraphenylborate was added slowly and the resulting mixture was allowed to cool to room temperature. The yellow-orange compound that separated was isolated by filtration and washed with ethanol and diethyl ether. For recrystallization the compound was dissolved in dichloromethane  $(20 \text{ cm}^3)$  and ethanol  $(30 \text{ cm}^3)$  was added very slowly under hot conditions and the resulting solution was kept at ambient temperature overnight. The shining yellow-orange crystals that separated were collected by filtration, washed with ethanol and dried in vacuo; yield 0.32 g (68%). Found: C, 75.1; H, 5.8; N, 1.0. Calc. for  $C_{148}H_{134}B_2N_2P_6Rh_2$ : C, 75.5; H, 5.7; N, 1.2%.

 $[Ir_2LCl_2]$  (5). To a refluxing ethanolic (40 cm<sup>3</sup>) suspension of  $[IrCl(COD)]_2$  (0.134 g, 0.2 mmol) was added the ligand L (0.197 g, 0.2 mmol) dissolved in benzene (10 cm<sup>3</sup>), and the resulting solution was refluxed for 4 h. The yellow solution was concentrated to *ca* 15 cm<sup>3</sup>, filtered and to the filtrate petroleum ether (b.p. 40–60°C; 20 cm<sup>3</sup>) was added. The yellow compound that precipitated was isolated by filtration and recrystallized from dichloromethane–n-hexane; yield 0.222 g (77%). Found : C, 53.5; H, 4.3; N, 1.8; Cl, 5.1. Calc. for C<sub>64</sub>H<sub>64</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>4</sub>Ir<sub>2</sub>: C, 53.4; H, 4.4; N, 1.9; Cl, 4.9%.

[Ir<sub>2</sub>LCl<sub>2</sub>(CO)<sub>2</sub>] (6). *Method A*. This complex was prepared from complex 5 in dichloromethane following the same procedure as described for the preparation of 2 from 1 in method B. The complex was recrystallized from dichloromethane–n-hexane; yield 82%. Found: C, 52.6; H, 4.4; N, 1.7; Cl, 4.9. Calc. for C<sub>66</sub>H<sub>64</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>P<sub>4</sub>Ir<sub>2</sub>: C, 53.0; H, 4.3; N, 1.9; Cl, 4.7%.

Method B (compound 6a). To a refluxing suspension of  $[IrCl(CO)(PPh_3)_2]$  (0.312 g, 0.4 mmol) in benzene (40 cm<sup>3</sup>), ligand (0.197 g, 0.2 mmol) was added. After 10 min of addition the solution became clear and then reflux was continued for a further 4 h, during which a yellow crystalline compound separated. The compound was isolated by filtration and recrystallized from dichloromethane–n-hexane; yield 0.227 g (76%). Found : C, 53.0; H, 4.4; N, 1.7; Cl, 4.6%.

 $[Ir_2LCl_6]$  (7). A mixture of hydrated iridium trichloride (0.3 g, 1.0 mmol) and ligand L (0.492 g, 0.5 mmol) in ethanol (80 cm<sup>3</sup>) was refluxed for 10 h. During reflux a greyish-yellow precipitate separated which was isolated by filtration and washed with ethanol. The precipitate was dissolved in DMF (10 cm<sup>3</sup>) by stirring at 60°C, and filtered. On addition of ethanol (40 cm<sup>3</sup>) to the filtrate a light-yellow compound was precipitated which was isolated by filtration, washed with ethanol and dried *in vacuo*; yield 0.30 g (38%). Found : C, 48.2; H, 4.1; N, 1.6; Cl, 13.6. Calc. for  $C_{64}H_{64}Cl_6N_2P_4lr_2$ : C, 48.6; H, 4.0; N, 1.8; Cl, 13.4%.

[Pd<sub>2</sub>LCl<sub>2</sub>]Cl<sub>2</sub> (8). To a refluxing suspension of [PdCl<sub>2</sub>(COD)] (0.143 g, 0.5 mmol) in benzene (30 cm<sup>3</sup>) was added the ligand L (0.246 g, 0.25 mmol) dissolved in benzene (10 cm<sup>3</sup>), and the reflux continued for 1 h. The solution was then concentrated to half its original volume and kept at ambient temperature overnight. The lemon-yellow complex that precipitated was isolated by filtration, washed with cold benzene and dried *in vacuo*; yield 0.25 g (75%). Found : C, 57.6; H, 4.7; N, 1.9; Cl, 10.7%. Calc. for C<sub>64</sub>H<sub>64</sub>Cl<sub>4</sub>N<sub>2</sub>P<sub>4</sub>Pd<sub>2</sub>: C, 57.4; H, 4.8; N, 2.1; Cl, 10.6%.

 $[Pt_2LCl_2]Cl_2$ (9). То suspension of а [PtCl<sub>2</sub>(COD)] (0.15 g, 0.4 mmol) in chloroform (20  $cm^3$ ) the ligand L (0.197 g, 0.2 mmol) dissolved in chloroform (10 cm<sup>3</sup>) was added with stirring at ambient temperature. Within 20 min a clear, lightvellow solution was formed. The stirring was continued for 1 h and the solution was then concentrated to ca 10 cm<sup>3</sup> in a rotary evaporator. Diethyl ether (15 cm<sup>3</sup>) was added slowly to precipitate the complex. The complex was recrystallized from dichloromethane-n-hexane; yield 0.242 g (80%). Found : C, 50.4; H, 4.4; N, 1.7; Cl, 9.1. Calc. for C<sub>64</sub>H<sub>64</sub>Cl<sub>4</sub>N<sub>2</sub>P<sub>4</sub>Pt<sub>2</sub>: C, 50.6; H, 4.2; N, 1.8; Cl, 9.3%.

[Pt<sub>4</sub>LCl<sub>4</sub>]Cl<sub>4</sub> (10). To a refluxing solution of ligand L (0.295 g, 0.3 mmol) in benzene (20 cm<sup>3</sup>) was added slowly a solution of [PtCl<sub>2</sub>(COD)] (0.225 g, 0.6 mmol) dissolved in boiling benzene (75 cm<sup>3</sup>). The reaction mixture was refluxed for 1 h, during which a white compound was precipitated. It was isolated by filtration, washed with hot benzene and dichloromethane, and dried *in vacuo*; yield 0.35 g (77%). Found: C, 50.3; H, 4.2; N, 1.7; Cl, 9.5. Calc. for  $C_{128}H_{128}Cl_8N_4P_8Pt_4$ : C, 50.6; H, 4.2; N, 1.8; Cl, 9.3%.

## **RESULTS AND DISCUSSION**

The reaction between the dimeric  $Rh^{1}$  complex  $[RhCl(COD)]_{2}$  and ligand L in a 1:1 molar ratio in acetonitrile resulted in the formation of a complex of composition  $[Rh_{2}LCl_{2}]$  (1). The reaction of L with  $[RhCl(CO)(AsPh_{3})_{2}]$  in a 1:2 molar ratio in benzene resulted in the complete displacement of AsPh<sub>3</sub> with the formation of a dinuclear complex of composition  $[Rh_{2}LCl_{2}(CO)_{2}]$  (2). The same complex (2) was also obtained when CO gas was passed through a dichloromethane solution of complex 1 at ambient temperature. The reaction of AgClO<sub>4</sub> with complex 1 in acetonitrile gave an acetonitrile adduct,  $[Rh_2L(NCCH_3)_2]$  (ClO<sub>4</sub>)<sub>2</sub> (3). A complex of composition  $[Rh_2L(PPh_3)_2](BPh_4)_2$  (4) was obtained by the reaction of L with a refluxing ethanolic solution of a mixture of  $[RhCl(COD)]_2$  and  $PPh_3$  (molar ratio 1:2), followed by the addition of a slight excess of sodium tetraphenylborate to the solution. A dinuclear Ir<sup>I</sup> complex of composition  $[Ir_2LCl_2]$  (5) was obtained when the ligand L was reacted with [IrCl(COD)<sub>2</sub>]<sub>2</sub> in a 1:1 molar ratio in ethanol. The reaction of CO gas with 5 in dichloromethane resulted in the formation of a CO adduct  $[IrLCl_2(CO)_2]$  (6). A complex (6a) of the same composition as 6 was obtained when the ligand L was reacted with Vaska's compound, [IrCl(CO)  $(PPh_3)_2$ , in benzene. The reaction of hydrated iridium trichloride with L in ethanol under reflux resulted in the formation of a dinuclear octahedral complex of composition  $[Ir_2LCl_6]$  (7). A dinuclear complex of  $Pd^{II}$ ,  $[Pd_2LCl_2]Cl_2$  (8), was obtained by the reaction of  $[PdCl_2(COD)]$  with the ligand L in benzene. The reaction between  $[PtCl_2(COD)]$  and ligand L gave bi- as well as tetranuclear complexes depending on the condition of the reactions; that in chloroform at ambient temperature gave  $[Pt_2LCl_2]Cl_2$  (9), whereas the same reaction in refluxing benzene resulted in the formation of  $[Pt_4L_2Cl_4]Cl_4$  (10).

Conductivity measurements in DMF show that the complexes 1, 2 and 5–7 are non-electrolytes (Table 1),<sup>18</sup> indicating that the chloride ions in these complexes are coordinated to metal ions. Complexes 3, 4 and 8 are 1:2 electrolytes. These results indicate that  $ClO_4^-$ ,  $BPh_4^-$  and two chloride ions in complexes 3, 4 and 8, respectively, are not involved in coordination. The conductivity of complex 9, however, is less than the required value for a 1:2 electrolyte (discussed later). Complex 10 is a 1:4 electrolyte. Magnetic susceptibility measurements show that all the compounds are diamagnetic.

Some selected IR bands of the reported complexes are shown in Table 1. The IR spectra of all the complexes exhibit medium to strong band(s) in the range 500–530 cm<sup>-1</sup>, which may be assigned to v(M-P).<sup>8,9</sup> In all complexes except **3** and **4**, weak to medium band(s) appeared in the range 295–345 cm<sup>-1</sup>, which can be assigned to v(M-CI).<sup>8,9</sup> The strong band(s) in the range 1955–2010 cm<sup>-1</sup> in complexes **2**, **6** and **6a** is due to v(CO).<sup>19,20</sup> In complex **3** a strong broad band centred at 1100 cm<sup>-1</sup> and a sharp band at 620 cm<sup>-1</sup> are assigned to the  $v_3$  and  $v_4$  frequencies, respectively, for the uncoordinated  $ClO_4^{-,21}$  The presence of CH<sub>3</sub>CN in complex **3** is confirmed by a weak band at 2265 cm<sup>-1</sup> due to v(C=N).<sup>21</sup>

#### Geometrv

The  ${}^{31}P{}^{1}H$  NMR data of all complexes, shown in Table 2, are useful for geometrical assignment. Complex 1 shows a doublet centred at  $\delta$  30.88 at 245 K with a coupling constant of 70 Hz. These data indicate that all phosphorus atoms are equivalent and bound to rhodium (free ligand shows a singlet at  $\delta - 20.89^{9a}$ ; the doublet is due to coupling of the phosphorus atom with the <sup>103</sup>Rh nucleus having S = 1/2. The coupling constant<sup>5a,8d</sup> and  $\delta$ value<sup>8b-d</sup> are also in the range found for many other complexes with nitrogen/phosphorus donor atoms, where phosphorus atoms of PPh<sub>2</sub> are trans to each other. These data therefore suggest a binuclear square planar structure with NPPCl coordination of each metal ion for complex 1, as shown in structure II. The  ${}^{31}P{}^{1}H$  NMR spectrum of 2 at 245 K shows a doublet at  $\delta$  31.16 with a coupling constant of 90 Hz. Molar conductance measurement indicates that the chloride ions are coordinated to the metal centre. From these data it appears that the complex is binuclear pentacoordinated and all phosphorus atoms are equivalent. With such an arrangement trigonal bipyramidal (TBP) or square pyramidal (SP) configurations are possible. Since TBP is the predominant geometry observed for fivecoordinate complexes of Co<sup>I</sup>,<sup>2d,5a,22</sup> Rh<sup>I</sup> and Ir<sup>I</sup>, this geometry may be assigned to complex 2. However, with the present data it is difficult to differentiate between two possibilities: (i) an NPP moiety in the trigonal plane and (ii) PP at the axial position and nitrogen at the trigonal plane with chloride and CO; since the latter possibility requires less strain in the P-N-P bond angle, TBP geometry with phosphorus atoms at the axial positions may be the most probable geometry for complex 2, as shown in structure III. The  ${}^{31}P{}^{1}H{}$  NMR spectrum of complex 3 shows a doublet at  $\delta$  32.58 with a coupling constant of 107 Hz. These data are consistent with a binuclear square planar geometry with phosphorus atoms in trans positions, as shown in structure II. The  ${}^{31}P{}^{1}H$  NMR spectrum of 4 displays a doublet of triplets and a doublet of doublets centred at  $\delta$  30.33 and 35.86, respectively. The splitting pattern can be explained by considering the binuclear complex with square planar geometry shown in structure II. The signal due to phosphorus atoms of PPh<sub>2</sub> groups is split by the <sup>103</sup>Rh nucleus into a doublet  $(J_{(Rh-P)} = 135.6 \text{ Hz})$  and in turn this doublet is split by the phosphorus atom of the PPh<sub>3</sub> group into two doublets  $(J_{(P-P)} = 23.2 \text{ Hz})$ . The phosphorus atom of PPh<sub>3</sub> is split by the rhodium nucleus into a doublet  $(J_{(Rh-P)} = 88 \text{ Hz})$  and then further split by the two equivalent phosphorus atoms of PPh<sub>3</sub> groups to give a doublet of triplets.

Complex	UV-vis spectral data" $\hat{\lambda}_{max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	Selected IR bands (cm <sup>-1</sup> )			Conductivity,
		v(M—P)	v(M—Cl)	Others	$- \Lambda_{\rm M}^{\rm a} (\Omega^{-1})$ cm <sup>2</sup> mol <sup>-1</sup> )
$[Rh_2LCl_2] (1)$	440sh (580), 364 (2000), 310 (9200), 273 (17,300)	525 (s)	295 (m)		107
$[Rh_2LCl_2(CO)_2]$ (2)	358 (200), 314 (10,300), 274 (20,700)	520 (s)	300 (m)	1955 (s) <sup>c</sup>	16 <sup>7</sup>
$[Rh_{2}L(NCCH_{3})_{2}](ClO_{4})_{2} (3)^{h}$	430sh (300), 360 (1650), 338 (2250), 258sh (19,600), 238 (22,600)	530 (s)		1100 (br) <sup>d</sup> 620 (s), <sup>d</sup> 2265 (w) <sup>e</sup>	2404
$[Rh_{2}L(PPh_{3})_{2}][BPh_{4}]_{2}$ (4)	450sh (600), 376 (2400), 312 (19,500), 278 (24,850)	500 (s) 525 (s)			1429
$[Ir_2LCl_2]$ (5)	356 (1800), 305sh (5550), 272 (13,100)	520 (s)	320 (w)		14/
$[Ir_2LCl_2(CO)_2]$ (6)	387 (1600), 338 (2400), 305sh (6650), 273 (14,800)	515 (s)	312 (w)	1965 (s) <sup>c</sup>	22 <sup>f</sup>
$[Ir_2LCl_2(CO)_2]$ (6a)	385 (1500), 335 (2300), 304 (7000), 273 (15,100)	515 (s), 530 (m)	312 (w) 320 (w)	1965 (s) <sup>c</sup> 2010 (s) <sup>c</sup>	12 <sup>,r</sup>
$[\mathrm{Ir}_{2}\mathrm{LCl}_{6}] (7)$	378 (2150), 272 (16,400)	510 (s)	310 (w) 325 (m)	()	17 <sup>,r</sup>
$[Pd_{2}LCl_{2}]Cl_{2} (8)$	363 (10,450), 296 (15,000), 274 (17,400)	510 (s)	325 (m)		136 <sup><i>q</i></sup>
$[Pt_2LCl_2]Cl_2 (9)$	295sh (7200), 272 (13,750)	500 (s) 512 (m)	330 (w) 345 (w)		110
[Pt <sub>4</sub> L <sub>2</sub> Cl <sub>4</sub> ]Cl <sub>4</sub> (10)	300 (14,500), 272 (22,400)	480 (m) 500 (s) 522 (m)	335 (w) 302 (w)		280"

Table 1. UV-vis, IR and conductivity data of the reported complexes

"UV-vis spectra and conductivity measurements were done in DMF at room temperature.

<sup>*b*</sup> Acetonitrile was used as solvent.

<sup>c</sup> v(CO).

<sup>*d*</sup> Due to  $ClO_4^-$ .

 $v(C \equiv N).$ 

/Non-electrolyte.

<sup>*g*</sup> 1 : 2 electrolyte.

<sup>*h*</sup> I : 4 electrolyte.

s, strong; m, medium; w, weak; br, broad.

The coupling constant value due to two inequivalent phosphorus atoms indicates that they are in cis positions.<sup>2c.8d,f</sup> Other coupling constants are also in accord with the reported values.5a,8d,23 The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **5** shows a singlet at  $\delta$ 31.24, indicating that all the phosphorus atoms are equivalent; therefore, a binuclear square planar geometry, similar to complex 1, is proposed. Complex 6 is a non-electrolyte and its  ${}^{31}P{}^{1}H{}$  NMR spectrum shows a singlet at  $\delta$  30.92; these data are similar to those of complex 2 and suggest a TBP geometry with phosphorus atoms in axial positions. The  ${}^{31}P{}^{1}H{}$  NMR spectrum of **6a**, like **6**, shows a strong singlet at  $\delta$  30.90 in addition to two doublets of equal intensity centred at  $\delta$  4.96 and -5.05, with a coupling constant of 23.1 Hz. This observation can be interpreted by considering complex 6a in two geometrical isomeric forms, the major one ( $\delta$ 30.90) showing the same geometry as that of 6. In the other form (minor), two types of phosphorus atoms with *cis* disposition  $(J_{(P-P)} = 23.1 \text{ Hz})$  are present. The high field doublet at  $\delta - 5.05$  can be assigned to the phosphorus atom trans to CO because of its strong trans influence<sup>8g,24</sup> and a TBP geometry with facial disposition of ligand, as shown in structure IV, is proposed for this form of 6a. The absorption peak at 2010  $cm^{-1}$  in the IR spectrum is assigned to v(CO) trans to the phosphorus atom of PPh<sub>2</sub>.<sup>25,26</sup> The  ${}^{31}P{}^{1}H$  NMR spectrum of 7 displays a singlet at  $\delta$  23.07. This compound is a nonelectrolyte (Table 1) and shows two IR bands at 310 and 325 cm<sup>-1</sup> due to v(Ir—Cl). These results suggest a dinuclear octahedral geometry for 7, with phosphorus atoms trans to each other in the square





 $M = Rh(I), X = Cl(1), NCMe(3), PPh_3(4)$  M = Ir(I), X = Cl(5), M = Pd(II), X = Cl(8),M = Pt(II), X = Cl(9),





(II)









(VII)

plane, as shown in structure V. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of complex 8 exhibits a singlet at  $\delta$  33.06. These data, together with the molar conductance value and IR data, are consistent with a dinuclear square planar structure for 8, as shown in structure II. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 9, shown in Fig. 1, contains two singlets at  $\delta$  42.26 and 28.52, with satellites resulting from the coupling of the phosphorus atom with the <sup>195</sup>Pt nucleus. The  $J_{(PLP)}$  coupling constants are 3623 and 2734 Hz for the signals at  $\delta$  42.26 and 28.52, respectively. The  $\delta$  value of 42.26, with a Pt–P coupling constant value of 3623 Hz, is in the range reported for phosphorus atoms *trans* to chloride.<sup>8f,g,27</sup> The resonance signal at  $\delta$  28.52 and its coupling constant value of 2734 Hz agree with the reported data for phosphorus atoms *trans* to each other.<sup>8c,e,f,28</sup> The absence of splitting of the signals indicates that the non-equivalent phosphorus atoms are not coordinated to the same metal ion. These data can be explained by considering complex 9 in two forms, as shown in structures I (major) and VI (minor). The lower molar conductance value (110  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>) is due to the contribution of the neutral form (minor) of the

Complex	Solvent	Chemical shifts, $\delta$	$J_{(M-P)}$ (Hz)	$J_{(P-P)}$ (Hz)
[Rh <sub>2</sub> LCl <sub>2</sub> ] (1)	CH <sub>2</sub> Cl <sub>2</sub>	30.88 (d) <sup>b</sup>	70	
$[Rh_{2}LCl_{2}(CO)_{2}]$ (2)	CH <sub>2</sub> Cl <sub>2</sub>	31.16 (d) <sup>6</sup>	90	
$[Rh_2(NCMe)_2](ClO_4)_2$ (3)	NCMe	32.58 (d)	107	
$[Rh_{2}L(PPh_{3})_{2}](BPh_{4})_{2}$ (4)	$CH_2Cl_2$	30.33 (dt), 35.86 (dd)	136, 88	23.2
$[Ir_2LCl_2]$ (5)	$CH_2Cl_2$	31.24 (s)		
$[lr_2LCl_2(CO)_2]$ (6)	$CH_2Cl_2$	30.92 (s)		
$[Ir_{2}LCl_{2}(CO)_{2}]$ (6a)	$CH_2CI_2$	-5.05 (d), 4.96 (d), 30.90 (s)		23.1
$[Ir_{2}LCl_{6}]$ (7)	DMF	23.07 (s)		
$[Pd_{3}LCl_{2}]Cl_{2}$ (8)	DMF	33.06 (s)		
$[Pt_2LCl_2]Cl_2$ (9)	CHCl <sub>3</sub>	28.52 (s), 42.26 (s)	2734, 3623	
$[Pt_4L_2Cl_4]Cl_4$ (10)	DMSO	1.82 (t), 29.0 (d), 43.29 (s)	3608, 2720, 3710	17.1

Table 2.  ${}^{31}P{}^{1}H$  NMR data for the reported complexes"

<sup>*a*31</sup>P{<sup>1</sup>H} NMR chemical shifts relative to external 85%  $H_3PO_4$  at room temperature.

<sup>*h*</sup> At 245 K.

s, singlet; d, doublet; t, triplet.



Fig. 1.  ${}^{31}P{}^{1}H{}$  NMR spectrum of complex 9 in CHCl<sub>3</sub>.

complex. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of complex **10**, shown in Fig. 2, contains a triplet at  $\delta$  1.82, a doublet at 29.0 and a singlet at 43.29 with Pt–P coupling constants, calculated from its <sup>195</sup>Pt satellites, of 3710, 2720 and 3608 Hz, respectively. The lower P–P coupling constant value (17.1 Hz), calculated from the doublet and triplet, indicates that the non-equivalent phosphorus atoms are in *cis* disposition.<sup>8d,f</sup> On comparison with complex **9** and



Fig. 2.  ${}^{31}P{}^{1}H$  NMR spectrum of  $[Pt_4L_2Cl_4]Cl_4$  in DMSO.

with other reported results,<sup>8c.e.f.28</sup> the doublet at  $\delta$ 29.0 with coupling constant of 2720 Hz can be assigned to the phosphorus atoms  $(P_A)$  trans to each other. The high field triplet ( $\delta$  1.82) can be assigned to a phosphorus atom ( $P_B$ ) trans to the nitrogen;<sup>8d,g</sup> the  $J_{(Pt-P_n)}$  value of 3608 Hz is typical of a phosphorus atom trans to an amine.8d.28 The coupling of two  $P_A$  atoms and one  $P_B$  atom results in a doublet for  $P_A$  and a triplet for  $P_B$ , consistent with the observation (Fig. 2). The low-field singlet at  $\delta$  43.29 and its coupling constant value of 3710 Hz are very similar to those discussed for structure V of complex 9 and can be assigned to phosphorus atom  $P_{\rm C}$ trans to chloride.8d,e,27,29 On the basis of the above data, structure VII is proposed for complex 10. The presence of three v(Pt-P) and two v(Pt-Cl)vibrations in the IR spectrum of the complex also supports the proposed structure. Such a multinuclear structure for a Pt<sup>II</sup> complex with an NP<sub>2</sub> ligand was reported earlier.8d

The electronic spectral data of all the complexes are given in Table 1. All the square planar complexes reported here have an  $nd^8$  electronic configuration and show lowest energy bands in the range 430-450 nm for Rh<sup>1</sup> (1, 3 and 4), 356 nm for Ir<sup>I</sup> (5), 363 nm for Pd<sup>II</sup> (8), and 295 and 300 nm for Pt<sup>II</sup> (9 and 10) which can be assigned to a d-dtransition.<sup>8c,d,f</sup> Pentacoordinate complexes with TBP geometry, however, show lowest energy bands at 350 nm for Rh<sup>I</sup> (2), 387 and 385 nm for Ir<sup>I</sup> (6 and 6a). The octahedral Ir<sup>III</sup> complex 7 shows the lowest energy band at 378 nm, assigned to the  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  transition. The other high energy bands are due to  $\pi - \pi^*$  transitions and ligand-to-metal charge transfer character. Acknowledgement—We thank Professor P. Natarajan for his kind interest and encouragement.

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