$\Delta_{HS} < \Delta_{LS}$. Moreover, such a crystallographic phase transition can be inferred from the lattice dynamical behavior of spin-crossover compounds, as extracted from temperature-dependent ^{57}Fe Mössbauer experiments, as will be reported elsewhere.[28] Such lattice dynamical data are consistent with the observation that the metal–ligand bond lengths decrease in going from the HS to the LS form of Fe(II) spin-crossover complexes.

The present study affords for the first time a self-consistent data set for comparison of the characteristic temperature for HS $\rightleftharpoons$ LS conversion of Fe(II) spin-crossover complexes (T_1), and the temperature at which the (trapped) HS form—produced by visible light irradiation of the LS form at low temperatures—is reannealed to the LS form (T_2). Such a comparison can be effected for complexes I, IV, and V, the three (isothiocyanato)iron(II) compounds examined in detail in the VTFTIR experiments discussed above. The present data suggest that a lower T_2 is associated with a lower T_1 for a given complex, suggesting that the lower thermal excitation required to "freeze-in" the LS form of a given complex is also required to "freeze-in" the (trapped) HS form produced by optical excitation of the LS form matrix. Clearly, the present data can only be considered as suggestive of such a relationship between T_1 and T_2, and further experiments to explore this behavior are currently under way.

Acknowledgment. The author is indebted to Dr. L. Casson, D. Mellick, and N. Blumenkrantz for assistance with some of the measurements and to Prof. J. Potenza and H. Schugar for the X-ray diffraction data on III. This research was supported in part by the Division of Materials Research of the NSF under Grant No. DMR 810 2940, and this support is herewith gratefully acknowledged.

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Synthesis and Characterization of Binuclear Platinum Group Metal Complexes of Novel Hexadentate Ligands α,α′-Bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene and α,α′-Bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene

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Received December 3, 1985

The hexadentate ligands α,α′-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene (PXBDPA) and α,α′-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene (PXBDAA) were synthesized and characterized on the basis of their ^{1}H, ^{31}P, and ^{13}C NMR spectra. Binuclear metal complexes of these ligands with Ru(II), Ru(III), Rh(I), Ir(I), Pd(II), and Pt(II) are reported. Reaction of $RuCl_2(PPh_3)_3$ with PXBDPA or PXBDAA in benzene in a 2:1 ratio gave neutral, binuclear Ru(II) complexes of the type $[Ru_2Cl_4(PPh_3)_2(L)]$ (L = PXBDPA, PXBDAA). The salt $[Ru_2Cl_2(Me_2SO)_4(PXBDPA)](PF_6)_2$ was obtained by the reaction of $RuCl_2(Me_2SO)_4$, PXBDPA, and NH_4PF_6 in an ethanol–benzene mixture. Neutral, binuclear, and octahedral complexes of the type $[Ru_2Cl_6(L)]$ (L = PXBDPA, PXBDAA) were obtained by the reaction of L with $RuCl_3(AsPh_3)_2MeOH$ in benzene. Reaction of $RuBr_3(AsPh_3)_2MeOH$ with PXBDPA or PXBDAA yielded Ru(III) complexes of the composition $[Ru_2Br_4(AsPh_3)_2(L)]Br_2$ (L = PXBDPA, PXBDAA). The reaction of $[Rh(COD)Cl]_2$ or $[Ir(COD)Cl]_2$ with PXBDPA or PXBDAA in an ethanol–benzene mixture yielded neutral, binuclear, and square-planar complexes of the type $[M_2Cl_2(L)]$ (M = Rh, Ir; L = PXBDPA, PXBDAA). Binuclear, square-planar cationic complexes of the composition $[Rh_2(S)_2(L)](PF_6)_2$ (S = PPh_3, CH_3CN; L = PXBDPA, PXBDAA) were obtained by the reaction of $[Rh(COD)Cl]_2$, L, and PPh_3 or acetonitrile in boiling ethanol. Binuclear, cationic, and square-planar complexes of Pd(II) and Pt(II) of the composition $[M_2X_2(L)]Y$ (X = Cl, Br, SCN; L = PXBDPA, PXBDAA; Y = Cl, BPh_4, PF_6) were obtained by the reaction of L with $MX_2(PhCN)_2$ (M = Pd, Pt; X = Cl, Br) in ethanol. The thiocyanato complex $[Pd_2(SCN)(PXBDPA)](BPh_4)_2$ was obtained by stirring the reaction mixture of $PdCl_2(PhCN)_2$, NH_4SCN, and PXBDPA in ethanol. All the complexes were characterized on the basis of their elemental analyses, molar conductance data, magnetic susceptibilities, infrared spectral measurements, and ^{1}H, ^{31}P, and ^{13}C NMR spectral data.

Introduction

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, and O[1-5] due to their increasing importance in the field of catalysis[6] and also in the construction of bi- and polynuclear transition-metal complexes. In our earlier communications,[3,4] we have reported the synthesis and characterization of two novel terdentate ligands containing N and P or As as donor atoms, bis(2-(diphenylphosphino)ethyl)benzylamine and bis(2-(diphenylarsino)ethyl)benzylamine, and their transition-metal complexes. We have also reported[1,2,5] the platinum group metal complexes of bis(2-(diphenylphosphino)ethyl)amine, bis(2-(diphenylarsino)ethyl)amine, and (diphenylphosphino)acetic acid.

In this paper we report the synthesis of two novel potential hexadentate ligands, α,α′-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene (PXBDPA) and α,α′-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene (PXBDAA) (I), which contain N and P or As as donor atoms. These ligands contain two terdentate moieties (PNP or AsNAs) separated by a rigid *p*-xylyl bridge capable of forming binuclear complexes in which the metal ions are held apart at a sufficient distance such that the two groups of donor atoms cannot coordinate to the same metal ion. Synthesis of binuclear complexes of d^5, d^6, and d^8 metal ions of the platinum

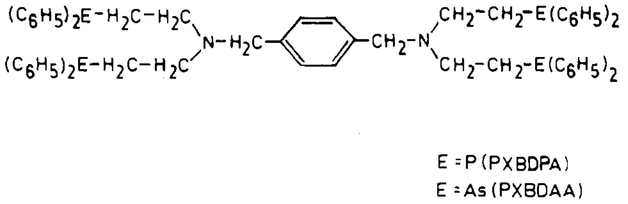

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Table I. NMR Spectral Data of the Ligands PXBDPA and PXBDAA

ligand	$\delta(^1H)^a$	$\delta(^{31}P\{^1H\})^b$	$^{13}C\{^1H\}^c$	
			δ	J(C–P), Hz
p-$C_6H_4[CH_2N(CH_2CH_2PPh_2)_2]_2$	7.1, 7.3 (Ph)	−19.1	57.5 (s) ($-CH_2-$)	...
	2.6 (m), 2.2 (m) ($-CH_2CH_2-$)		49.3 (d) ($-CH_2PPh_2$)	26.7
	3.5 (s) ($-CH_2$)		25.0 (d) ($-NCH_2$)	13.0
			139.0–128.9 (Ph)	
p-$C_6H_4[CH_2N(CH_2CH_2AsPh_2)_2]_2$	7.1, 7.3 (Ph)	...	57.5 (s) ($-CH_2-$)	...
	2.6 (m), 2.2 (m) ($-CH_2CH_2-$)		49.5 (s) ($-CH_2AsPh_2$)	...
	3.5 (s) ($-CH_2-$)		25.2 (s) ($-NCH_2-$)	...
			140.7–128.2 (Ph)	

[a] Chemical shifts are relative to internal Me_4Si; m = multiplet, s = singlet. [b] Chemical shifts are relative to external 85% H_3PO_4, positive shifts representing deshielding. [c] Chemical shifts are relative to external Me_4Si.

group with these ligands are reported.

Experimental Section

The hydrated trichlorides of ruthenium, rhodium, and iridium, $PdCl_2$, and K_2PtCl_4 were purchased from Alfa Inorganics and Johnson Matthey. Triphenylphosphine and triphenylarsine were obtained from Aldrich Chemical Co.; NH_4PF_6 and $NaBPh_4$ were obtained from Ventron Corp. 1,5-Cyclooctadiene (COD) obtained from Fluka was used as supplied. The complexes $RuCl_2(PPh_3)_3$,[7] $RuX_3(AsPh_3)_2MeOH$ (X = Cl, Br),[7] $RuCl_2(Me_2SO)_4$,[8] $[Rh(COD)Cl]_2$,[9] $[Ir(COD)Cl]_2$,[10] and $[M(PhCN)_2Cl_2]$ (M = Pd, Pt)[11,12] were prepared by standard procedures. Diethanolamine and thionyl chloride were of AnalaR reagent grade and were used without further purification. Potassium metal was obtained from Robert-Johnson. α,α'-Dibromo-p-xylene was prepared by a published procedure.[13] All organic solvents used in this work were of reagent grade and were purified and dried before use. All the preparations were carried out in an atmosphere of dry nitrogen, and the compounds obtained were dried under vacuum.

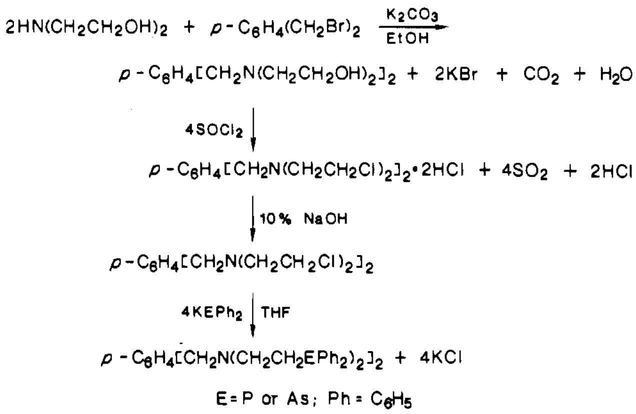
Microanalyses, melting points, and conductivity and magnetic susceptibility measurements were done as reported.[14] Infrared, far-infrared, and electronic spectra and molecular weight measurements were done as reported.[3,4] The proton NMR spectra were recorded at 100 MHz on a JEOL FX100 spectrometer using tetramethylsilane as reference. The $^{31}P\{^1H\}$ NMR spectra were taken in indicated solvents (Table III) by using a JEOL FX100 spectrometer operating at 40.3 MHz in the Fourier transform mode. The samples were placed in 10-mm NMR tubes, and a capillary of deuterium oxide was used for the lock. H_3PO_4 (85%) was used as an exteneral standard. $^{13}C\{^1H\}$ NMR spectra of the ligands were taken in $CDCl_3$ by using a JEOL FX100 operating at 24.99 MHz. Tetramethylsilane was used as an external reference.

The NMR spectral data of the ligands PXBDPA and PXBDAA are presented in Table I. Microanalytical, conductivity, and magnetic suscepetibility data are presented in Table II. The ^{31}P NMR data are presented in Table III.

Synthesis of Ligands PXBDPA and PXBDAA. The new hexadentate mixed donor (N, P or N, As) binucleating ligands PXBDPA and PXBDA were synthesized as shown in Scheme I.

The compound α,α'-bis(diethanolamine)-p-xylene, p-$C_6H_4[CH_2N(CH_2CH_2OH)_2]_2$ was prepared by the reaction of α,α'-dibromo-p-xylene (19.8 g, 0.075 mol) with diethanolamine (15.77 g, 0.15 mol) and potassium carbonate (10.42 g, 0.075 mol) in 150 mL of absolute alcohol. The organic halide p-$C_6H_4[CH_2N(CH_2CH_2Cl)_2]_2$ was obtained[15] by the reaction of the above corresponding alcohol with an excess of thionyl chloride (1:4 ratio). The product p-$C_6H_4[CH_2N(CH_2CH_2Cl)_2]_2\cdot 2HCl$ on treatment with a stoichiometric amount of 10% NaOH gave the free amine p-$C_6H_4[CH_2N(CH_2CH_2Cl)_2]_2$ as an insoluble oil, which was dried before use. The free amine was dissolved in 15 mL of anhydrous THF and added dropwise with stirring to an orange-red solution of $KEPh_2$ (E = P or As; Ph = C_6H_5)[16,17] taken in 150 mL of anhydrous THF, under cold conditions (15–20 °C) until a sharp decoloration occurred. The solution was then heated to reflux for 30 min and after cooling was poured into three times its volume of ice-cold water when a pale yellow oil separated. The mixture was ice-cooled until the oil crystallized completely. The ligands PXBDPA and PXBDAA, when recrystallized from a chloroform–ethanol mixture, gave white crystalline products with an yield of about 82% in the case of PXBDPA and 70% in the case of PXBDAA. PXBDPA: mp 165 °C; mol wt 985 (calculated), 980 (experimental, osmometric in chloroform). Anal. Calcd for $C_{64}H_{64}N_2P_4$: C, 78.03; H, 6.55; N, 2.84. Found: C, 78.31; H, 6.48; N, 2.80. PXBDAA: mp 145 °C; mol wt 1160 (calculated), 1150 (experimental). Anal. Calcd for $C_{64}H_{64}N_2As_4$: C, 66.22; H, 5.50; N, 2.41. Found: C, 66.06; H, 5.58; N, 2.38.

Scheme I



Preparation of Metal Complexes. Tetrachlorobis(triphenylphosphine)(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-p-xylene)diruthenium(II), $[Ru_2Cl_4(PPh_3)_2(PXBDPA)]$ (1). The complex $RuCl_2(PPh_3)_3$ (0.384 g, 0.4 mmol) and ligand PXBDPA (0.197 g, 0.2 mmol), were dissolved in 30 mL of dry benzene and stirred at room temperature for 3 h under a nitrogen atmosphere. The red-orange precipitate that separated out was filtered and washed with benzene and diethyl ether. The complex was recrystallized from a chloroform–ethanol mixture and dried in vacuo: yield, 0.29 g (80%); mp 214–218 °C.

Tetrachlorobis(triphenylphosphine)(μ-bis(bis(2-(diphenylarsino)ethyl)amino)-p-xylene)diruthenium(II), $[Ru_2Cl_4(PPh_3)_2(PXBDAA)]$ (2). This complex was prepared as for **1** except that PXBDPA was replaced by an equimolar quantity of PXBDAA (0.232 g, 0.2 mmol). The resulting pink complex was recrystallized from a chloroform–ethanol mixture and dried in vacuo: yield, 0.28 g (71%); mp 250–254 °C.

Dichlorotetrakis(dimethyl sulfoxide)(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-p-xylene)diruthenium(II) Hexafluorophosphate, $[Ru_2Cl_2(Me_2SO)_4(PXBDPA)](PF_6)_2$ (3). To a refluxing ethanolic solution of $RuCl_2(Me_2SO)_4$ (0.194 g, 0.4 mmol) was added the ligand PXBDPA (0.197 g, 0.2 mmol) dissolved in 30 mL of benzene. After the solution was refluxed for 4 h, the orange solution was filtered and concentrated to 25 mL. Addition of NH_4PF_6 (0.069 g, 0.42 mmol) in 10 mL of ethanol to the above solution yielded a yellow crystalline complex. The complex was filtered, washed with hot ethanol–benzene and diethyl ether, and recrystallized from a chloroform–ethanol mixture: yield, 0.27 g (70%); mp 240–245 °C.

Hexachloro(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-p-xylene)diruthenium(III), $[Ru_2Cl_6(PXBDPA)]$ (4). To a refluxing solution of the ligand PXBDPA (0.197 g, 0.2 mmol) in 30 mL of benzene was added $RuCl_3(AsPh_3)_2MeOH$ (0.341 g, 0.4 mmol) and the contents refluxed for 3 h. The precipitated yellow-brown complex was filtered and washed

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Table II. Analytical and Other Data for Ru(II), Ru(III), Rh(I), Ir(I), Pd(II), and Pt(II) Complexes

complex	μ_{eff},[a] μ_B	elemental anal.[b] % C	% H	% N	% Cl/Br	λ_∞,[c] Ω^{-1} cm^2 mol^{-1}
$Ru_2Cl_4(PPh_3)_2$(PXBDPA) (**1**)	*d*	64.20	5.12	1.46	7.58	22
		(64.79)	(5.11)	(1.51)	(7.65)	
$Ru_2Cl_4(PPh_3)_2$(PXBDAA) (**2**)	*d*	58.87	4.57	1.32	7.01	20
		(59.18)	(4.66)	(1.38)	(6.98)	
[$Ru_2Cl_2(Me_2SO)_4$(PXBDPA)]$(PF_6)_2$ (**3**)	*d*	46.32	4.69	1.43	3.74	102
		(46.47)	(4.76)	(1.50)	(3.81)	
Ru_2Cl_6(PXBDPA) (**4**)	1.96	54.48	4.56	1.96	15.07	24
		(54.90)	(4.60)	(2.00)	(15.19)	
Ru_2Cl_6(PXBDAA) (**5**)	1.99	48.35	4.01	1.73	13.33	21
		(48.78)	(4.09)	(1.78)	(13.50)	
[$Ru_2Br_4(AsPh_3)_2$(PXBDPA)]Br_2 (**6**)	2.08	52.71	4.14	1.20	20.13	105
		(52.69)	(4.15)	(1.22)	(21.03)	
[$Ru_2Br_4(AsPh_3)_2$(PXBDAA)]Br_2 (**7**)	2.10	48.93	3.73	1.08	18.79	101
		(49.12)	(3.87)	(1.14)	(19.10)	
Rh_2Cl_2(PXBDPA) (**8**)	*d*	60.59	5.17	2.18	5.65	26
		(60.91)	(5.11)	(2.22)	(5.61)	
Rh_2Cl_2(PXBDAA) (**9**)	*d*	52.92	4.40	1.88	4.87	22
		(53.46)	(4.48)	(1.94)	(4.93)	
[$Rh_2(PPh_3)_2$(PXBDPA)]$(PF_6)_2$ (**10**)	*d*	59.69	4.70	1.33		130
		(59.88)	(4.72)	(1.39)		
[$Rh_2(PPh_3)_2$(PXBDAA)]$(PF_6)_2$ (**11**)	*d*	54.62)	4.38	1.15		132
		(55.06)	(4.34)	(1.28)		
[$Rh_2(CH_3CN)_2$(PXBDPA)]$(PF_6)_2$ (**12**)	*d*	52.01	4.43	3.39		128
		(52.25)	(4.51)	(3.58)		
[$Rh_2(CH_3CN)_2$(PXBDAA)]$(PF_6)_2$ (**13**)	*d*	46.77	4.10	3.15		125
		(46.97)	(4.19)	(3.22)		
Ir_2Cl_2(PXBDPA) (**14**)	*d*	53.19	4.44	1.80	5.00	23
		(53.36)	(4.47)	(1.94)	(4.90)	
Ir_2Cl_2(PXBDAA) (**15**)	*d*	47.39	4.00	1.71		21
		(47.55)	(3.99)	(1.73)		
[Pd_2Cl_2(PXBDPA)]Cl_2 (**16**)	*d*	57.15	4.76	2.01	10.07	129
		(57.37)	(4.81)	(2.09)	(10.58)	
[Pd_2Cl_2(PXBDAA)]Cl_2 (**17**)	*d*	50.60	4.21	1.79	9.31	123
		(50.71)	(4.25)	(1.85)	(9.35)	
[Pd_2Br_2(PXBDPA)]$(BPh_4)_2$ (**18**)	*d*	64.61	5.09	1.33	3.35	105
		(64.57)	(5.03)	(1.34)	(3.40)	
[$Pd_2(SCN)_2$(PXBDPA)]$(BPh_4)_2$ (**19**)	*d*	66.82	5.35	1.28		117
		(67.38)	(5.25)	(1.33)		
[Pt_2Cl_2(PXBDPA)]$(PF_6)_2$ (**20**)	*d*	44.20	3.76	1.58	3.98	126
		(44.27)	(3.71)	(1.61)	(4.08)	
[Pt_2Cl_2(PXBDAA)]$(PF_6)_2$ (**21**)	*d*	39.92	3.32	1.40	3.28	101
		(40.20)	(3.37)	(1.46)	(3.37)	

[a] Magnetic susceptibility measured on a Faraday balance at room temperature. [b] Calculated values in parentheses. [c] Molar conductance in DMF at 30 °C. Values reported for infinite dilution. [d] Diamagnetic.

Table III. $^{31}P\{^1H\}$ NMR Data for Ru(II), Ru(III), Rh(I), Ir(I), Pd(II), and Pt(II) Complexes[a]

complex	chem shifts, δ PXBDPA	PPh_3	J(M–P), Hz	$J(P_A–P_B)$, Hz
$Ru_2Cl_2(PPh_3)_2$(PXBDPA) (**1**)	24.9 (d)	47.5 (t)	...	26.9
$Ru_2Cl_2(PPh_3)_2$(PXBDAA) (**2**)	...	51.3 (s)	...	
[$Ru_2Cl_2(Me_2SO)_4$(PXBDPA)]$(PF_6)_2$ (**3**)	30.3 (P_B)	...	...	...
	59.4 (P_A)			
Ru_2Cl_6(PXBDPA)[b] (**4**)	29.2 (s)	...	...	...
[$Ru_2Br_4(AsPh_3)_2$(PXBDPA)]Br_2[b] (**6**)	28.9 (s)	...	...	...
Rh_2Cl_2(PXBDPA) (**8**)	35.5 (bs)[c]	...	...	...
[$Rh_2(PPh_3)_2$(PXBDPA)]$(PF_6)_2$ (**10**)	37.7 (d, d)	35.9 (t, t)	136.7 (J(Rh–P_A))	26.9
			124.3 (J(Rh–P_B))	26.9
[$Rh_2(PPh_3)_2$(PXBDAA)]$(PF_6)_2$ (**11**)	...	33.5 (d)	117.2	...
[$Rh(CH_3CN)_2$(PXBDPA)]$(PF_6)_2$	36.7 (d)	...	144.60	...
Ir_2Cl_2(PXBDPA) (**14**)	16.7 (s)	...	...	...
[Pd_2Cl_2(PXBDPA)]Cl_2 (**16**)	33.0 (s)	...	...	...
[Pd_2Br_2(PXBDPA)]$(BPh_4)_2$[b] (**18**)	34.6	...	...	...
[$Pd_2(SCN)_2$(PXBDPA)]$(BPh_4)_2$[b] (**19**)	40.3 (s)	...	...	...
[Pt_2Cl_2(PXBDPA)]$(PF_6)_2$[b] (**20**)	28.6	...	2744.0	...

[a] $^{31}P\{^1H\}$ chemical shifts relative to external 85% H_3PO_4 in CD_2Cl_2 unless specified. Key: s = singlet; d = doublet; t = triplet; bs = broad singlet. [b] In Me_2SO. [c] See text.

with warm benzene and diethyl ether. The complex was recrystallized from a DMF–ethanol mixture and dried in vacuo: yield, 0.22 g (81%); mp 231–235 °C.

Hexachloro(μ-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene)diruthenium(III), [Ru_2Cl_6(PXBDAA)] (5). The complex was prepared in a manner similar to that used for **4**, with $RuCl_3(AsPh_3)_2MeOH$ (0.341 g, 0.4 mmol) and PXBDAA (0.232 g, 0.2 mmol) used instead of PXBDPA. The red complex obtained was recrystallized from a DMF–ethanol mixture and dried in vacuo: yield, 0.24 g (76%); mp 280–285 °C.

Tetrabromobis(triphenylarsine)(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene)diruthenium(III) Bromide, [$Ru_2Br_4(AsPh_3)_2$-

(PXBDPA)]Br_2 (6), and Tetrabromobis(triphenylarsine)(μ-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene)diruthenium(III) Bromide, [$Ru_2Br_4(AsPh_3)_2$(PXBDAA)]Br_2 (7). Complexes **6** and **7** were prepared in a manner similar to that used for complex **4**, except that the ligands PXBDPA (0.197 g, 0.2 mmol) and PXBDAA (0.232 g, 0.2 mmol) were respectively reacted with $RuBr_3(AsPh_3)_2MeOH$ (0.394 g, 0.4 mmol). An yellow-brown compound was obtained in the case of **6** and a dark-green complex obtained in the case of **7**. For **6**: yield, 0.33 g (73%); mp 230–233 °C. For 7: yield 0.33 g (69%); mp 240–245 °C.

Dichloro(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene)dirhodium(I), [Rh_2Cl_2(PXBDPA)] (8), and Dichloro(μ-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene)dirhodium(I), [Rh_2Cl_2(PXBDAA)] (9). To a boiling suspension of $[Rh(COD)Cl]_2$ (0.0986 g, 0.2 mmol) in 30 mL of ethanol was added the PXBDPA (0.197 g, 0.2 mmol) or PXBDAA (0.232 g, 0.2 mmol) in 5 mL of benzene, and an orange solution was obtained in both cases. The solutions for the synthesis of **8** and **9** after being refluxed for 3 h were concentrated to a small volume. Addition of petroleum ether (40–60 °C) precipitated an orange crystalline complex in each case. The complexes **8** and **9** were filtered, washed with petroleum ether and diethyl ether, recrystallized from an ethanol–ether mixture, and dried in vacuo. For **8**: yield, 0.21 g (84%); mp 205–208 °C. For **9**: yield, 0.22 g (78%); mp 195–198 °C.

Bis(triphenylphosphine)(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene)dirhodium(I) Hexafluorophosphate, [$Rh_2(PPh_3)_2$(PXBDPA)]$(PF_6)_2$ (10), and Bis(triphenylphosphine)(μ-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene)dirhodium(I) Hexafluorophosphate, [$Rh_2(PPh_3)_2$(PXBDAA)]$(PF_6)_2$ (11). To a suspension of $[RhCl(COD)]_2$ (0.074 g, 0.15 mmol) in 30 mL of ethanol was added triphenylphosphine (0.786 g, 0.3 mmol). On addition of PPh_3, $[RhCl(COD)]_2$ dissolved quickly to give a homogeneous yellow solution. To this refluxing solution was added PXBDPA (0.147 g, 0.15 mmol) or PXBDAA (0.174 g, 0.15 mmol) in 5 mL of benzene. After the solutions were refluxed for 3 h, an equimolar amount of NH_4PF_6 in ethanol was added giving an orange crystalline complex [$Rh_2(PPh_3)_2$(PXBDPA)]$(PF_6)_2$ (**10**) or a red-orange complex [$Rh_2(PPh_3)_2$(PXBDAA)]$(PF_6)_2$ (**11**), respectively. The complexes were filtered, washed with hot ethanol and diethyl ehter, recrystallized from a dichloromethane–ethanol mixture, and dried in vacuo. For **10**: yield, 0.25 g (83%); mp 200–205 °C. For **11**: yield, 0.25 g (77%); mp 224–228 °C.

Bis(acetonitrile)(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene)dirhodium(I) Hexafluorophosphate, [$Rh_2(CH_3CN)_2$(PXBDPA)]$(PF_6)_2$ (12), and Bis(acetonitrile)(μ-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene)dirhodium(I) Hexafluorophosphate, [$Rh_2(CH_3CN)_2$(PXBDAA)]$(PF_6)_2$ (13). To a refluxing ethanolic solution of $[Rh(COD)Cl]_2$ (0.074 g, 0.15 mmol) and 2 mL of acetonitrile was added the PXBDPA (0.147 g, 0.15 mmol) or PXBDAA (0.174 g, 0.15 mmol) in equimolar quantities in two different reactions, and the mixture was further refluxed for 3 h. Then NH_4PF_6 was added in 1:2 ratio to the above solutions to give the yellow-orange complex [$Rh_2(CH_3CN)_2$(PXBDPA)]$(PF_6)_2$ (**12**) or the orange complex [$Rh_2(CH_3CN)_2$(PXBDAA)]$(PF_6)_2$ (**13**), respectively. The complexes were filtered and washed with hot ethanol–benzene and diethyl ether. The complexes were recrystallized from a dichloromethane–ethanol mixture and dried in vacuo. For **12**: yield, 0.17 g (73%); mp 215–220 °C. for **13**: yield, 0.18 g (70%); mp 218–221 °C.

Dichloro(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene)diiridium(I), [Ir_2Cl_2(PXBDPA)] (14), and Dichloro(μ-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene)diiridium(I), [Ir_2Cl_2(PXBDAA)] (15). To a refluxing ethanolic suspension of $[IrCl(COD)]_2$ (0.099 g, 0.15 mmol) was added PXBDPA (0.147 g, 0.15 mmol) or PXBDAA (0.174 g, 0.15 mmol) in benzene, and the resulting yellow solution in both cases was refluxed for 3 h. The solutions were then filtered and concentrated to a small volume and the complexes were precipitated by the addition of petroleum ether (40–60 °C) as yellow products [Ir_2Cl_2L] (L = PXBDPA (**14**), PXBDAA (**15**) in both cases. The complexes were filtered, washed with petroleum ether (40–60 °C) and diethyl ether, recrystallized from ethanol–ether, and dried in vacuo. For **14**: yield, 0.160 g (74%), mp 256–260 °C. For **15**: yield, 0.168 g (69%), mp 180–185 °C.

Dichloro(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene)dipalladium(II) Chloride, [Pd_2Cl_2(PXBDPA)]Cl_2 (16), and Dichloro(μ-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene)dipalladium(II) Chloride, [Pd_2Cl_2(PXBDAA)]Cl_2 (17). To an ethanolic solution of $PdCl_2(PhCN)_2$ (0.115 g, 0.3 mmol) was added PXBDPA (0.147 g, 0.15 mmol) or PXBDAA (0.174 g, 0.15 mmol) taken in 5 mL of benzene, and the resulting solution was further stirred for an additional hour. Each solution was filtered and concentrated to a small volume by a vacuum rotary evaporator and petroleum ether (40–60 °C) was added to get a either lemon yellow precipitate [Pd_2Cl_2(PXBDPA)]Cl_2 (**16**) or a yellow complex [Pd_2Cl_2(PXBDAA)]Cl_2 (**17**). The complexes were filtered, washed with petroleum ether and diethyl ether, and recrystallized from an ethanol–ether mixture. For **16**: yield, 0.17 g (85%); mp 178–186 °C. For **17**: yield, 0.18 g (78%); mp 230–235 °C.

Dibromo(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene)dipalladium(II) Tetraphenylborate, [$PdBr_2$(PXBDPA)]$(BPh_4)_2$ (18). A mixture of $PdCl_2(PhCN)_2$ (0.115 g, 0.3 mmol) and LiBr (0.312 g, 3.6 mmol in 30 mL of ethanol was stirred for 3–4 h. To the resulting dark orange solution was added PXBDPA (0.147 g, 0.15 mmol) in 5 mL of benzene to give a yellow solution. The solution was then warmed (60 °C) for 30 min, and $NaBPh_4$ (0.11 g, 0.32 mmol) in ethanol was added to get a lemon yellow crystalline complex. The complex was filtered, washed with hot ethanol, benzene, and diethyl ether, recrystallized from DMF–ethanol, and dried in vacuo: yield, 0.23 g (78%); mp 225–230 °C.

Bis(thiocyanato)(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene)dipalladium(II) Tetraphenylborate, [$Pd_2(SCN)_2$(PXBDPA)]$(BPh_4)_2$ (19). This complex was prepared as for **18**, except that $PdCl_2(PhCN)_2$ (0.115 g, 0.3 mmol) was stirred with NH_4SCN (0.274 g, 3.6 mmol) in ethanol for 2 h before addition of the ligand PXBDPA (0.147 g, 0.15 mmol). The yield of the yellow complex was 0.23 g (80%); mp 210–215 °C.

Dichloro(μ-bis(bis(2-(diphenylphosphino)ethyl)amino)-*p*-xylene)diplatinum(II) Hexafluorophosphate, [Pt_2Cl_2(PXBDPA)]$(PF_6)_2$ (20), and Dichloro(μ-bis(bis(2-(diphenylarsino)ethyl)amino)-*p*-xylene)diplatinum(II) Hexafluorophosphate, [Pt_2Cl_2(PXBDAA)]$(PF_6)_2$ (21). To a yellow ethanolic solution of $PtCl_2(PhCN)_2$ (0.142 g, 0.3 mmol) was added PXBDPA (0.147 g, 0.15 mmol) or PXBDAA (0.174 g, 0.15 mmol) in 5 mL of benzene, and the solution was stirred for an hour, yielding colorless solution. An equimolar amount of NH_4PF_6 in ethanol was added to the resulting solution to get the colorless complex $[PtCl_2L](PF_6)_2$ (L = PXBDPA (**20**), PXBDAA (**21**)). The complexes were filtered, washed with hot ethanol, benzene, and diethyl ether, and recrystallized from a DMF–ethanol mixture. For **20**: yield, 0.21 g (82%); mp 243–248 °C. For **21**: yield, 0.198 g (72); mp 240–242 °C.

Results and Discussion

The hexadentate ligands PXBDPA and PXBDAA, containing mixed donor atoms NP_2 and NAs_2, were characterized fully by elemental analysis, infrared and ^1H, ^{31}P, and ^{13}C NMR spectra and molecular weight measurements in chloroform. Although the infrared spectral data is not of much use, the NMR data is quite useful to support the proposed composition of the ligands as $p\text{-}C_6H_4[CH_2N(CH_2CH_2EPh_2)_2]_2$ (E = P, As; Ph = C_6H_5).

The proton NMR spectrum of PXBDPA exhibits resonance signals due to aromatic protons around δ 7.2 corresponding to the phenyl protons of the xylyl group and diphenylphosphino groups. The resonance of the protons of the CH_2CH_2 bridges are observed at δ 2.2 ($-CH_2$ protons attached to an amine center) and δ 2.6 ($-CH_2$ protons attached to the diphenylphosphino group) as multiplets due to the interaction with the neighboring methylene protons followed by the coupling of ^{31}P nuclear spin. A singlet at δ 3.5 is assigned to the CH_2 proton resonance of the xylyl group. The ligand PXBDAA also exhibits resonances of the phenyl and methylene protons of the CH_2CH_2 bridges and xylyl group at δ 7.2 and 2.2 and δ 2.6 and 3.5, respectively.

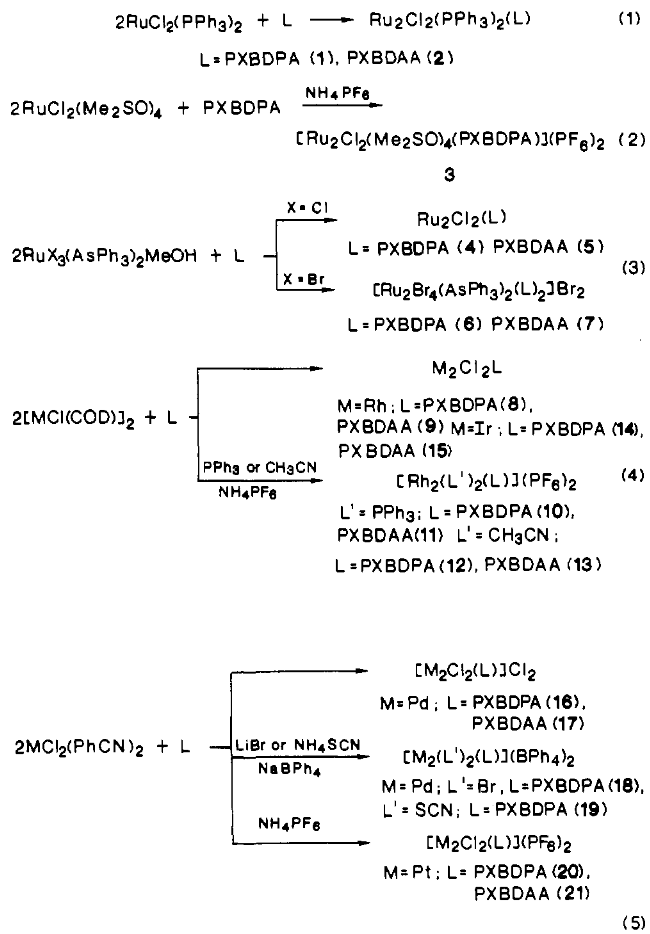
The $^{31}P\{^1H\}$ NMR spectrum of the ligand PXBDPA in CH_2Cl_2 exhibits a single peak at δ −19.1, indicating the magnetic equivalence of all the phosphorus donor atoms. The $^{13}C\{^1H\}$ NMR spectra of the ligands PXBDPA and PXBDAA exhibit signals in the range δ 128.2–140.5 due to the phenyl carbon atoms of diphenylphosphino or -arsino moieties and the phenyls of the xylyl group. The ^{13}C NMR spectra of the ligands also exhibit well-defined doublets due to coupling to ^{31}P (in PXBDPA), singlets (in PXBDAA) (Table I) due to the CH_2CH_2 bridges, and singlets in both cases due to the CH_2 of the xylyl group.

The above spectral data are consistent with the proposed structure of the ligands (I).

Platinum Group Metal Complexes. The ligands PXBDPA and PXBDAA have two terdentate moieties (NP_2 or NAs_2) separated by a *p*-xylyl bridge, and form binuclear complexes with Ru(II), Ru(III), Rh(I), Ir(I), Pd(II), and Pt(II) (Scheme II).

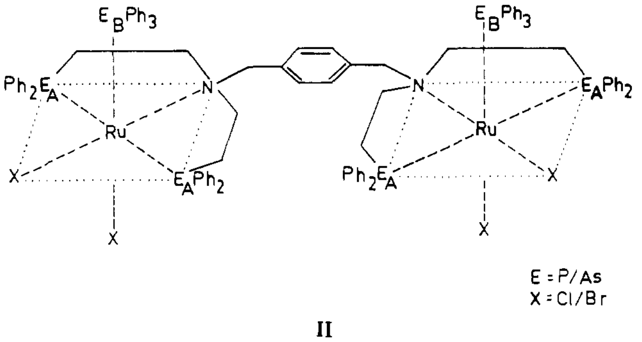
The reaction of $RuCl_2(PPh_3)_3$ and PXBDPA or PXBDAA at room temperature in benzene solution gives diamagnetic Ru(II) complexes of composition [$Ru_2Cl_4(PPh_3)_2$(L)], where L = PXBDPA (**1**) and PXBDAA (**2**). When the above reaction was conducted in refluxing benzene, polymeric products are formed. Complexes **1** and **2** are nonelectrolytes[18] in DMF solvent (Table

Scheme II



II). The presence of two bands in the ν(Ru–Cl) region at 266 and 311 cm^{-1} in complex **1** and 321 and 350 cm^{-1} in complex **2** indicate a cis diposition of the two chlorides in the complexes.[19]

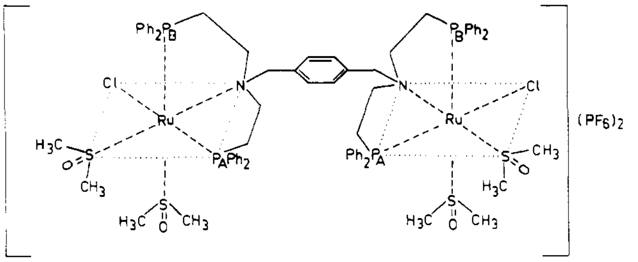
The complexes with cis chlorides and one triphenylphosphine group can have a meridional or a facial disposition of the ligands PXBDPA and PXBDAA. However, the $^{31}P\{^{1}H\}$ NMR spectrum of **1** supports a meridional disposition of the ligands (II). The $^{31}P\{^{1}H\}$ NMR spectrum of **1** displays an AB$_2$ spectrum with a doublet centered at δ 24.9 and a triplet centered at δ 47.5, with an intensity ratio of 2:1, respectively, indicating the magnetic equivalence of the two phosphorus ends of the ligand PXBDPA (doublet at δ 24.9) and also the presence of a triphenylphosphine group (triplet at δ 47.5). The resonance signal due to P$_A$ atoms is split by the P$_B$ atom of the PPh$_3$ to give a doublet, and the resonance signal due to P$_B$ is split into a triplet by the two equivalent P$_A$ toms of the ligand PXBDPA. A J(P$_A$–P$_B$) value of 26.9 Hz is also typical for the coupling constant of nonequivalent phosphorus nuclei cis to one another in ruthenium(II)–tertiary phosphine complexes.[20–22] The $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** exhibits a singlet at a more downfield value δ 51.3, indicating the presence of a PPh$_3$ group and its trans disposition to an electronegative chloride group. The structures of complexes **1** and **2** are proposed to be binuclear octahedral, with each terdentate moiety of PXBDPA or PXBDAA coordinating meridionally (II).



II

The displacement reaction of a coordinated Me$_2$SO in the complex RuCl$_2$(Me$_2$SO)$_4$ with PXBDPA and NH$_4$PF$_6$ in a refluxing 1:1 ethanol–benzene mixture gives a complex of the composition [Ru$_2$Cl$_2$(Me$_2$SO)$_4$(PXBDPA)](PF$_6$)$_2$ (**3**). In the reaction of RuCl$_2$(Me$_2$SO)$_4$ with PXBDPA the weakly coordinated O-bonded Me$_2$SO groups are displaced first, leaving the S-bonded Me$_2$SO groups coordinated to the metal ion. The conductivity of complex **3** (Table II) in DMF solvent is in accord with a 2:1 electrolyte.[18] The infrared spectrum of **3** shows a strong band at 1096 cm^{-1} due to ν(S=O) of the S-bonded Me$_2$SO[8,14,23,24] but no band around 900 cm^{-1} due to O-bonded Me$_2$SO. We find ν(Ru–Cl) in **3** at 345 cm^{-1} and ν(P–F)[19] at 840 cm^{-1}. A peak at δ 2.9 in the ^{1}H NMR spectrum of **3** was assigned to a methyl resonance, which further corroborates the coordination of Me$_2$SO through S.[8]

The $^{31}P\{^{1}H\}$ NMR spectrum of **3** shows two resonance signals at δ 30.3 and 59.4 for two magnetically inequivalent phosphorus nuclei of PXBDPA. This inequivalence of the two phosphorus atoms of the chelated ligand PXBDPA is due to the trans disposition of one of the phosphorus atoms (P$_A$) to chloride (δ 59.4) and other (P$_B$) to a Me$_2$SO group (δ 30.3). The absence of J(P$_A$–P$_B$) coupling might be due to the fast intramolecular exchange of the phosphorus donor atoms of the ligand with concomitant loss of J(P–P),[25,26] and this exchange process could not be stopped even after the sample was cooled to 200 K. On the basis of the above spectral data, a binuclear, octahedral structure (III) with facial disposition of the ligand PXBDPA is proposed for complex **3**.



III

Reaction of PXBDPA or PXBDAA with RuCl$_3$(AsPh$_3$)$_2$MeOH in refluxing benzene results in displacement of the triphenylarsine groups to give paramagnetic, neutral complexes of the composition [Ru$_2$Cl$_6$(L)], where L = PXBDPA (**4**) and PXBDAA (**5**). The μ_{eff} of these complexes (Table II) calculated from the magnetic susceptibility data is 1.96 μ_B for **4** and 1.99 μ_B for **5**, corresponding to one unpaired electron per metal center, as expected for low-spin, ruthenium(III) complexes.

Complexes **4** and **5** can exist either as facial or meridional isomers. The far-infrared spectra of complexes **4** and **5** exhibit two ν(Ru–Cl) stretching bands at 298 and 333 cm^{-1} and 302 and 335 cm^{-1}, respectively, in close agreement with Ru–Cl frequencies reported earlier,[19,27] in accordance with a facial isomer (three

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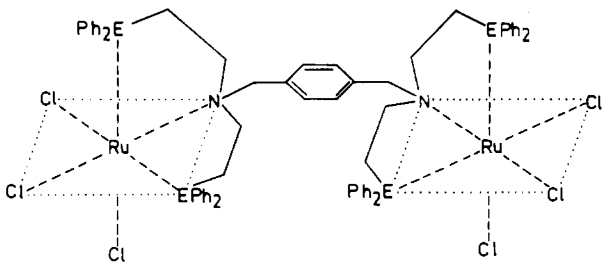
absorption bands are observed for a meridional isomer). The ^{31}P{^{1}H} NMR spectrum of **4** shows a singlet at δ 29.2. The ^{31}P NMR results can be explained on the basis of either a meridional or facial coordination of each of the terdentate moiety (NP_2) of the ligand PXBDPA. On the basis of the far-infrared spectral data, however, a facial coordination of each of the terdentate moieties of PXBDPA and PXBDAA is suggested for **4** and **5** (IV).



E =P/As

IV

Interaction of $RuBr_3(AsPh_3)_2MeOH$ and PXBDPA or PXBDAA in refluxing benzene results in the displacement of one $AsPh_3$ and a Br^- group to give a Ru(III), cationic species of the composition $[Ru_2Br_4(AsPh_3)_2(L)]Br_2$ (L = PXBDPA (**6**), PXBDAA (**7**)). The conductivity of complexes **6** and **7** in DMF solvent corresponds to a 2:1 electrolyte (Table II). The μ_{eff} values of 2.08 μ_B for **6** and 2.10 μ_B for **7** indicate that these complexes are paramagnetic to the extent of one unpaired electron. Weak ν(Ru–Br) bands at 254 and 281 cm^{-1} in **6** and 242 and 263 cm^{-1} in **7** suggest a cis disposition of the bromides in both the complexes.

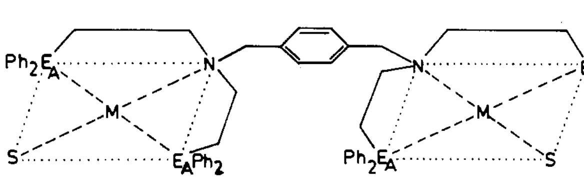
The ^{31}P{^{1}H} NMR spectrum of complex **6** displays a singlet at δ 28.8. On the basis of the chemical shift, a meridional configuration in which the two phosphorus atoms of the ligands are trans to each other is proposed. A more downfield shift of ^{31}P resonance is expected in a facial isomer if the phosphorus atom is trans to a bromide group as reported earlier.[3,20,28,29] A binuclear octahedral geometry, in which each terdentate moiety of PXBDPA or PXBDAA coordinates meridionally to the metal ion, is proposed for complexes **6** and **7** (II).

It is thus observed that the presence of a bulky triphenylphosphine or -arsine group inside the coordination sphere of the metal ion makes the ligands PXBDPA or PXBDAA coordinate meridionally, whereas a facial configuration results with the presence of only chlorides and Me_2SO groups inside the coordination sphere of the metal ion.

Binuclear rhodium(I) complexes of the type $[Rh_2Cl_2L]$ (L = PXBDPA (**8**), PXBDAA (**9**)) have been prepared by halogen bridge splitting and the displacement of 1,5-cyclooctadiene from $[Rh(COD)Cl]_2$ by the ligands PXBDPA or PXBDAA in boiling ethanol. Complexes **8** and **9** are nonelectrolytes in DMF solvent (Table II). Weak bands in the far-infrared spectra at 286 cm^{-1} in **8** and 277 cm^{-1} in **9** confirm the presence of a coordinated chloride.

The ^{31}P{^{1}H} NMR spectrum of complex **8** recorded at 300 K consists of a broad resonance signal centered at δ 35.5 (Table III). The broad peak is attributed to intramolecular rearrangement of the ligand. The ^{31}P{^{1}H} NMR spectrum when recorded at 200 K gives a doublet at δ 35.0 with ^{1}J(Rh–P) v 70.0 Hz. The structure of complexes **8** and **9** is consistent with a square-planar geometry about Rh(I) with PXBDPA or PXBDAA acting as a sexadentate, bimetallic donor (V).

Four-coordinate, square-planar, cationic complexes of the composition $[Rh_2(PPh_3)_2L](PF_6)_2$ (L = PXBDPA (**10**), PXBDAA (**11**)) were synthesized by the reaction of $[Rh(COD)Cl]_2$ with PPh_3 and PXBDPA or PXBDAA in boiling ethanol. Complexes **10** and **11** are 2:1 electrolytes in DMF solvent (Table II). The complexes show no peaks due to ν(Rh–Cl).



E = P/As
M = Rh, Ir, Pd, Pt
S = Cl, Br, SCN, $PPh_3(P_B)$, CH_3CN

V

The ^{31}P{^{1}H} NMR spectrum of complex **10** displays a AM_2X pattern[28] of doublet of triplets and a doublet of doublets, which is expected for a cation with the above formulation. The doublet of triplets is centered at δ 35.9 and the doublet of doublets at δ 37.7 (Table III). This splitting pattern can be explained by assuming that in each cation $[Rh_2(PPh_3)_2(PXBDPA)]^{2+}$ the Rh(1) ions have square-planar geometries with the ligand acting as a sexadentate, binucleate donor binding to three coordination sites on each metal ion and a PPh_3 bound trans to nitrogen of PXBDPA (V). The phosphorus atom P_A of the ligand is split by the rhodium nucleus into a doublet ($^{1}J(Rh–P_A)$ = 136.7 Hz) and then in turn this doublet is split by P_B of the PPh_3 group into two doublets ($^{2}J(P_A–P_B)$ = 26.9 Hz). Similarly the phosphorus atom P_B is split by the rhodium nucleus into a doublet ($^{1}J(Rh–P_B)$ = 124.3 Hz) and in turn by the two equivalent phosphorus atoms P_A to give a doublet of triplets. The low value of $J(P_A–P_B)$ indicates the presence of P_A and P_B in the cis position, and all the coupling values are in accordance with the earlier reports.[30]

The ^{31}P{^{1}H} NMR spectrum of complex **11** displays a doublet centered at δ 33.5 with ^{1}J(Rh–P) = 117.2 Hz, indicating the presence of a PPh_3 group. The proposed structures of **10** and **11** are shown in V.

Complexes of the composition $[Rh_2(CH_3CN)_2(L)](PF_6)_2$ (L = PXBDPA (**12**), PXBDAA (**13**)) were prepared by the reaction of $[RhCl(COD)]_2$ with CH_3CN and the ligands PXBDPA and PXBDAA in boiling ethanol. The cations so formed were isolated as PF_6^- salts. The conductivity data of these complexes supports a 2:1 electrolytic nature of the complexes (Table II). The infrared spectra of **12** and **13** show two weak broad bands at 2318 and 2282 cm^{-1}, respectively, characteristic of ν(C≡N) of a coordinated acetonitrile group.[19,31] The presence of acetonitrile group in the coordination sphere was further supported by the observation of a methyl proton resonance at δ 2.3 in the ^{1}H NMR spectrum of **12** and at δ 2.3 in **13**.

The ^{31}P{^{1}H} NMR spectrum of **12** consists of a doublet centered at δ 39.6 with ^{1}J(Rh–P) = 144.6 Hz, confirming a trans coordination of the two phosphorus ends of the ligand PXBDPA. On the basis of the above spectral data, a dinuclear structure with square-planar Rh(I) in which acetonitrile groups are bound trans to nitrogen atoms of PXBDPA and PXBDAA is proposed for **12** and **13** (V).

Complexes of the type $[Ir_2Cl_2L]$ (L = PXBDPA (**14**), PXBDAA (**15**)) were prepared in a manner similar to that of rhodium analogues by the displacement of COD from $[Ir(COD)Cl]_2$ with PXBDPA or PXBDAA in boiling ethanol. The conductivity data (Table II) of **14** and **15** indicate that the complexes are neutral. The presence of coordinated chlorides is supported by the observation of a weak band in the far-IR spectrum, at 319 cm^{-1} in **14** and 325 cm^{-1} in **15**.

The ^{31}P{^{1}H} NMR spectrum of **14** displays only a singlet at δ 16.7. A binuclear geometry similar to that of the rhodium analogue as in structure V is proposed for complexes **14** and **15**.

Square-planar Pd(II) complexes of the composition $[Pd_2Cl_2L]Cl_2$ (L = PXBDPA (**16**), PXBDAA (**17**)) were prepared from the benzonitrile complex $PdCl_2(PhCN)_2$ and the ligand PXBDPA or PXBDAA in ethanol at room temperature. The conductivity

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of complexes **16** and **17** (Table II) are in accord with 2:1 electrolytes in DMF solvent.[18] The far-IR spectra of **16** and **17** displayed bands at 332 and 346 cm^{-1}, respectively, corresponding to ν(Pd–Cl).[19,32]

The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **16** consists of a singlet at δ 33.0. Pd(II) forms square-planar complexes in a majority of the cases as five-coordination could not be achieved in most of the nitrogen–phosphorus or nitrogen–arsenic ligands.[33] A binuclear, square-planar geometry (V) for **16** and **17** is proposed, analogous to other known $[(\mathrm{L})_{3-n}\mathrm{MX}]^+$ (M = Pd(II), Pt(II), Ni(II); L = terdentate tris(tertiary phosphine), R_3P; n = 0, 3) complexes.[34,35]

The complexes $[\mathrm{Pd_2Br_2(PXBDPA)}](\mathrm{BPh_4})_2$ **18** and $[\mathrm{Pd_2(SCN)_2(PXBDPA)}](\mathrm{BPh_4})_2$ **19** were prepared by the interaction of $\mathrm{PdBr_2(PhCN)_2}$ or $\mathrm{Pd(SCN)_2(PhCN)_2}$ in ethanol with PXBDPA, and the cations so formed were best isolated as tetraphenylborate salts. Both complexes show conductance values (Table II) indicating their formulations as 2:1 electrolytes. The far-IR spectrum of complex **18** shows a weak band at 230 cm^{-1}, which may be assigned to ν(Pd–Br).[19,32] The presence of coordinated SCN$^-$ group in complex **19** is supported by a strong band in the IR spectrum at 2050 cm^{-1}, characteristic of an N-bonded thiocyanate group.[36,37] The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of **18** and **19** exhibit singlets at δ 34.6 and 40.3, respectively, confirming the square-planar geometry of the complexes (V).

The ^{31}P chemical shifts of complexes **16**, **18**, and **19** (Table III) increase as the halogen changes from chloride to bromide and to a pseudohalogen (SCN) in the coordination sphere of the metal ion. The ^{31}P chemical shifts move more downfield as the halogen changes from Cl$^-$ to Br$^-$ to SCN$^-$ (order of increasing polarizability of the ligand) as was observed earlier.[4] As the π-acidic character of the halide increases in passing through Cl to I, the σ-basicity of the coordinated phosphorus increases due to a synergic effect causing an increase in the downfield shift with an increase in the π-acidity of the halogen.

Reaction of $\mathrm{PtCl_2(PhCN)_2}$ and PXBDPA or PXBDAA in ethanol yielded square-planar cationic complexes of the composition $[\mathrm{Pt_2Cl_2L}]^{2+}$ (L = PXBDPA (**20**), PXBDAA (**21**)) best isolated as $\mathrm{PF_6}^-$ salts. Conductivity data indicate that both complexes are 2:1 electrolytes in DMF solvent. The far-IR spectra of **20** and **21** show weak absorption bands at 332 and 324 cm^{-1}, respectively, corresponding to ν(Pt–Cl).[38]

The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **20** displays a singlet at δ 28.6 with ^{195}Pt satellites. The ^1J(Pt–P) coupling constant calculated from its ^{195}Pt satellites is 2744 Hz, which is appreciably higher when compared to those of earlier reports for similar phosphorus atoms trans to one another in monodentate, square-planar Pt(II) complexes,[39] of the type *trans*-$\mathrm{L_2PtCl_2}$ and $[\mathrm{L_3PtCl}]^+$ (L = $\mathrm{R}_n(\mathrm{C_6H_5})_{3-n}\mathrm{P}$, where n = 1–3 and R = alkyl). This was also reported earlier[4] for the cationic complex [PtCl(DPBA)]$^+$, where DPBA = bis(2-(diphenylphosphino)ethyl)benzylamine and can be ascribed to the increased d_π–d_π bonding between P and Pt due to the presence of phenyl groups on the two phosphorus atoms. A binuclear, square-planar geometry similar to V is proposed for **20** and **21**.

In the complexes of Rh(I), Ir(I), Pd(II), and Pt(II) with the ligand PXBDPA, the ^{31}P resonance is shifted to a high-field side (Table III) as one descends in a given group, i.e. from Rh to Ir and Pd to Pt, which is consistent with the earlier reports.[40,41] A large downfield chemical shift upon coordination of PXBDPA to form five-membered chelate rings has been observed in ^{31}P NMR as was evidenced earlier.[40]

The metal–phosphorus and metal–arsenic stretching frequencies of the coordinated P or As of the ligands PXBDPA, PXBDAA, $\mathrm{PPh_3}$, and $\mathrm{AsPh_3}$ in the far-IR spectra of the complexes are observed in the regions 504–540 cm^{-1} and 470–480 cm^{-1}, respectively. The metal–nitrogen stretching frequencies in all the complexes could not be assigned decisively, since the critical region of ν(M–N) in each case was complicated by the presence of bands due to the other ligand vibrations.

The ^{1}H NMR spectra of all the complexes displayed broadened resonance signals due to phenyl and methylene protons and were of not much help in assigning the geometries. There is a considerable downfield shift in the resonances of various protons, when compared to those of free ligand. In the complexes, the phenyl resonances occur in the range δ 7.4–6.6, the benzylic protons occur in the range δ 4.8–4.2, the methylene protons attached to phosphorus and arsenic donor atoms occur in the range δ 3.4–2.8, and methylene protons attached toward a nitrogen donor atom occur between δ 2.8 and 2.1.

Registry No. **1**, 105501-88-0; **2**, 105501-89-1; **3**, 105517-93-9; **4**, 105501-90-4; **5**, 105517-94-0; **6**, 105501-91-5; **7**, 105501-92-6; **8**, 105501-93-7; **9**, 105501-94-8; **10**, 105501-96-0; **11**, 105501-98-2; **12**, 105502-00-9; **13**, 105502-02-1; **14**, 105502-03-2; **15**, 105502-04-3; **16**, 105502-05-4; **17**, 105502-06-5; **18**, 105502-08-7; **19**, 105502-10-1; **20**, 105502-12-3; **21**, 105502-14-5; PXBDPA, 105502-15-6; PXBDAA, 105517-95-1; $\mathrm{RuCl_2(PPh_3)_3}$, 15529-49-4; $\mathrm{RuCl_2(Me_2SO)_4}$, 89395-66-4; $\mathrm{RuCl_3(AsPh_3)_2MeOH}$, 15692-70-3; $\mathrm{RuBr_3(AsPh_3)_2MeOH}$, 15692-69-0; $\mathrm{[Rh(COD)Cl]_2}$, 12092-47-6; $\mathrm{[IrCl(COD)]_2}$, 12112-67-3; $\mathrm{PdCl_2(PhCN)_2}$, 14220-64-5; $\mathrm{PtCl_2(PhCN)_2}$, 14873-63-3; $\mathrm{HN(CH_2CH_2OH)_2}$, 111-42-2; p-$\mathrm{C_6H_4(CH_2Br)_2}$, 623-24-5; p-$\mathrm{C_6H_4[CH_2N(CH_2CH_2OH)_2]_2}$, 19926-06-8; p-$\mathrm{C_6H_4[CH_2N(CH_2CH_2Cl)_2]_2{\cdot}2HCl}$, 105502-16-7; p-$\mathrm{C_6H_4[CH_2N(CH_2CH_2Cl)_2]_2}$, 105502-17-8; $\mathrm{KPPh_2}$, 15475-27-1; $\mathrm{KAsPh_2}$, 21498-51-1.

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