

SOME TRANSITION METAL COMPLEXES OF NEW TERDENTATE LIGANDS: BIS[2-(DIPHENYLPHOSPHINO)ETHYL]BENZYLAMINE AND BIS[2-(DIPHENYLARSINO)ETHYL]BENZYLAMINE

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(Received 29 April 1986; accepted 4 September 1986)

Abstract—Complexes of the terdentate ligands bis[2-diphenylphosphino)ethyl]benzylamine (DPBA) and bis[2-(diphenylarsino)ethyl]benzylamine (DABA) with Co(II), Ni(II), Pd(II), Pt(II), Rh(III), Ir(III), Rh(I) and Ir(I) are reported. The ligand DPBA reacts with Co(II) ion to form two types of complexes: a high-spin, paramagnetic, tetrahedral Co(II) complex of composition $[\text{CoCl}(\text{DPBA})]\text{Cl}$ and a low-spin, paramagnetic, square-planar complex of composition $[\text{CoBr}(\text{DPBA})]\text{B}(\text{C}_6\text{H}_5)_4$. The reaction of DPBA with Ni(II) ion in methanol yields low-spin, diamagnetic, square-planar complexes of type $[\text{NiX}(\text{DPBA})]\text{Y}$ [$\text{X} = \text{Cl}, \text{Br}$ or I ; $\text{Y} = \text{Cl}$ or $\text{B}(\text{C}_6\text{H}_5)_4$]. Four-coordinate, square-planar, cationic complexes of type $[\text{MY}(\text{L})]^+$ [$\text{M} = \text{Pd}(\text{II}), \text{Pt}(\text{II}), \text{Rh}(\text{I})$ or $\text{Ir}(\text{I})$; $\text{Y} = \text{Cl}$ or $\text{P}(\text{C}_6\text{H}_5)_3$; $\text{L} = \text{DPBA}$ or DABA], were obtained on reaction of L with various starting materials containing these metal ions. Reaction of DPBA and DABA with rhodium and iridium trichlorides gave octahedral, neutral complexes of general formula $[\text{MCl}_3(\text{L})]$ ($\text{M} = \text{Rh}$ or Ir , $\text{L} = \text{DPBA}$ or DABA). All the complexes were characterized on the basis of their elemental analysis, molar-conductance data, magnetic susceptibilities, electronic spectra, IR spectral measurements, and ^1H and ^{31}P - $\{^1\text{H}\}$ NMR spectral data.

During the past few years, transition metal complexes of tertiary phosphines and arsines have been studied extensively, because of their chemistry and utility as catalysts in a number of reactions.^{1,2} The chemistry of the metal complexes is governed³⁻¹³ by the electronic and steric properties of the ligands and the oxidation state and coordination number of the metal ion.

The metal complexes of mixed donor ligands containing N, P, As and O have also gained considerable importance due to their catalytic activity in various homogeneous reactions.¹⁴⁻¹⁶

In our earlier communication¹⁷ we reported the synthesis of two new terdentate ligands containing N and P or As as donor atoms, bis[2-(diphenylphosphino)ethyl]benzylamine (DPBA) and bis[2-(diphenylarsino)ethyl]benzylamine (DABA) and their complexes with Ru(II) and (III). These ligands which have a hard donor amino group confer the

necessary nucleophilicity and the soft donor phosphino or arsino groups stabilize the low-valent metal centers. Both of these properties are very important in homogeneous catalytic reactions.^{18,19}

In the present paper the synthesis and characterization of complexes of Co(II), Ni(II), Pd(II), Pt(II), Rh(III), Ir(III), Rh(I) and Ir(I) with the ligands DPBA and DABA are reported.

RESULTS AND DISCUSSION

Reaction of the ligand DPBA with cobalt(II) salt in a 1:1 ratio in methanol gave stable, paramagnetic, tetracoordinate complexes of formulation $[\text{CoX}(\text{DPBA})]\text{Y}$ [$\text{X} = \text{Cl}$, $\text{Y} = \text{Cl}(\text{I})$; $\text{X} = \text{Br}$, $\text{Y} = \text{B}(\text{C}_6\text{H}_5)_4(2)$]. The molar-conductance values (Table 1) of complexes 1 and 2 are indicative of 1:1 electrolytes,²⁰ suggesting a four-coordinate geometry for Co(II) in these complexes.

The far-IR spectrum of complexes 1 and 2 exhibit intense bands at 310 and 265 cm^{-1} , respectively, for

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Table 1. Analytical and other physical data of the complexes

	Complex ^a	Colour	M.p. ^b (°C)	μ_{eff}^c (BM)	Elemental analysis (%) ^d				Conductivity ^e ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
					C	H	N	Others	
1	[CoCl(DPBA)]Cl	Bluish-green	105–110	4.40	63.3 (63.5)	5.3 (5.3)	2.0 (2.1)	—	84
2	[CoBr(DPBA)]B(C ₆ H ₅) ₄	Maroon-red	170–175	2.51	—	5.5 (5.6)	1.5 (1.4)	—	137(A)
3	[NiCl(DPBA)]B(C ₆ H ₅) ₄	Saffron-red	160–165	Diamag.	74.8 (75.0)	5.8 (5.8)	1.4 (1.5)	—	133(A)
4	[NiBr(DPBA)]B(C ₆ H ₅) ₄	Red	155–160	Diamag.	71.0 (71.5)	5.5 (5.6)	1.4 (1.4)	8.0(Br)	141(A)
5	[NiI(DPBA)]B(C ₆ H ₅) ₄	Blackish-red	175–177	Diamag.	67.7 (68.3)	5.4 (5.3)	1.4 (1.3)	11.9(I) (12.2)	126(A)
6	[NiCl(DPBA)]Cl	Dark red	90–95	Diamag.	63.1 (63.6)	5.3 (5.3)	2.1 (2.1)	—	100(A)
7	[PdCl(DPBA)]B(C ₆ H ₅) ₄	Yellow	120–125	Diamag.	71.8 (71.4)	6.0 (6.0)	1.3 (1.3)	—	71
8	[PdCl(DABA)]B(C ₆ H ₅) ₄	Yellow	110–120	Diamag.	66.0 (65.6)	5.1 (5.1)	1.2 (1.3)	—	85
9	[PtCl(DPBA)]Cl	Creamish-white	178–180	Diamag.	51.9 (52.7)	4.4 (4.4)	1.8 (1.7)	—	70
10	[PtCl(DABA)]Cl	Creamish-white	200–205	Diamag.	47.0 (47.5)	3.9 (3.9)	1.6 (1.6)	—	70
11	[RhCl ₃ (DPBA)]	Yellow	> 240	Diamag.	56.4 (56.7)	4.6 (4.7)	1.8 (1.9)	—	15
12	[RhCl ₃ (DABA)]	Yellow	220–224	Diamag.	50.2 (50.7)	4.3 (4.2)	1.6 (1.7)	—	5
13	[IrCl ₃ (DPBA)]	Green	> 240	Diamag.	49.9 (50.6)	4.3 (4.2)	1.7 (1.7)	—	4(D)
14	[IrCl ₃ (DABA)]	Green	> 200	Diamag.	45.6 (45.8)	3.9 (3.8)	1.5 (1.5)	—	2(D)
15	[Rh(PPh ₃)(DPBA)]Cl	Yellow	120–126	Diamag.	67.7 (68.2)	5.6 (5.7)	1.5 (1.5)	—	66
16	[Rh(PPh ₃)(DABA)]Cl	Yellow	100–105	Diamag.	62.4 (62.4)	4.9 (4.9)	1.3 (1.4)	—	65
17	[Ir(PPh ₃)(DPBA)]Cl	White	160–164	Diamag.	62.0 (62.2)	4.8 (4.9)	1.4 (1.4)	—	90

^a DPBA = bis[2-(diphenylphosphino)ethyl]benzylamine, DABA = bis[2-(diphenylarsino)ethyl]benzylamine.^b Decomposition temperature.^c BM values are after diamagnetic corrections.^d Calculated values are in parentheses.^e Conductivity measured in DMF except where mentioned: A = acetone, D = DMSO.

$\nu(\text{Co—Cl})$ and $\nu(\text{Co—Br})$ stretching frequencies, respectively, supporting the above formulation. The band at 540 cm^{-1} in both complexes **1** and **2** can be assigned to the $\nu(\text{Co—P})$ frequency. From the conductivity and far-IR data, it can be proposed that all the three donor atoms of the ligand DPBA are coordinated to the metal ion with one of the halides inside the coordination sphere of the metal ion. This is in contrast to the earlier observation made by Sacconi and Morassi¹⁰ on complexes containing similar ligands.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra (Table 2) of complexes **1** and **2** exhibit resonances at 40.38 and 33.18 ppm, respectively, indicating that the two ends of the coordinated phosphorus atoms of DPBA are magnetically equivalent. The downfield coordination chemical shift in both the complexes is considerable compared to the free ligand (Table 2).

The electronic spectrum of **1** in dichloromethane is consistent with a tetrahedral structure. The band in the visible region at 629 nm is assigned^{10,21,22} to the $^4A_2(F) \rightarrow ^4T_1(P)$ (ν_3) transition. This band is further split into a number of components, indicating the presence of considerable deviation from T_d -symmetry. The fine structure is caused²³ by spin-orbit coupling which both splits the $^4T_1(P)$ state and allows the transitions to the neighboring doublet states to gain some intensity. The magnetic moment (Table 1) also corroborates a tetrahedral, Co(II) complex, with paramagnetism near to the spin-only value.^{24,25} Complex **1** is therefore a tetrahedral Co(II) species.

The electronic spectrum of **2** in dichloromethane in the visible region shows only a broad band at 500 nm. The magnetic moment of 2.51 BM suggests **2** to be a low-spin Co(II) complex with considerable spin-orbital contribution. Taking the magnetic moment and the colour of the complex into consideration, complex **2** can be tentatively assigned a square-planar geometry with two ends of the phosphorus atoms *trans* to each other.

Reaction of DPBA with Ni(II) halides gave diamagnetic, cationic complexes of formulation $[\text{NiX}(\text{DPBA})]^+$ [$\text{X} = \text{Cl}$ (**3**), Br (**4**) or I (**5**)], best isolated as tetraphenyl borate complexes. Complexes **3–5** are air-stable and behave as 1:1 electrolytes²⁰ in acetone (Table 1), indicating a four-coordinate geometry for Ni(II). The far-IR spectra show bands due to $\nu(\text{Ni—X})$ ($\text{X} = \text{Cl}$, Br or I) frequencies at 340, 255 and 250 cm^{-1} in complexes **3–5**, respectively, suggesting the presence of one halide group inside the coordination sphere of the metal ion and the coordination of all the donor atoms of the ligand DPBA to the metal ion. The far-IR spectra of complexes **3–5** also show $\nu(\text{Ni—P})$ stretching frequencies at 535, 510 and 500 cm^{-1} , respectively.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra (Table 2) of complexes **3–5** show sharp singlets at 22.10, 26.76 and 35.84 ppm, respectively, with a considerable downfield shift upon coordination of DPBA to form five-membered rings, indicating the magnetic equivalency of the two *trans* phosphorus atoms of the ligand DPBA. The downfield shift decreases in the order $\text{I} > \text{Br} > \text{Cl}$, in line with the decreasing po-

Table 2. $^{31}\text{P}\{-^1\text{H}\}$ NMR data^a of the complexes

Complex	Solvent	Chemical shifts ^b [δ (ppm)]			
		DPBA	PPh ₃	$J(\text{M—P})$	$J(\text{P}_A\text{—P}_B)$
DPBA	CHCl_3	−19.25(s)	—	—	—
1 $[\text{CoCl}(\text{DPBA})]\text{Cl}$	CH_2Cl_2	40.38(s)	—	—	—
2 $[\text{CoBr}(\text{DPBA})]\text{B}(\text{C}_6\text{H}_5)_4$	CH_2Cl_2	33.18(s)	—	—	—
3 $[\text{NiCl}(\text{DPBA})]\text{B}(\text{C}_6\text{H}_5)_4$	CHCl_3	22.10(s)	—	—	—
4 $[\text{NiBr}(\text{DPBA})]\text{B}(\text{C}_6\text{H}_5)_4$	CHCl_3	26.76(s)	—	—	—
5 $[\text{NiI}(\text{DPBA})]\text{B}(\text{C}_6\text{H}_5)_4$	CHCl_3	35.84(s)	—	—	—
7 $[\text{PdCl}(\text{DPBA})]\text{B}(\text{C}_6\text{H}_5)_4$	CHCl_3	32.23(s)	—	—	—
9 $[\text{PtCl}(\text{DPBA})]\text{Cl}$	CHCl_3	28.16	—	2722.16	—
11 $[\text{RhCl}_3(\text{DPBA})]$	$\text{CH}_2\text{Cl}_2/\text{CHCl}_3$	35.20(d)	—	119.6	—
13 $[\text{IrCl}_3(\text{DPBA})]$	DMSO	29.31(s)	—	—	—
15 $[\text{Rh}(\text{PPh}_3)(\text{DPBA})]\text{Cl}$	CH_3OH	25.03(d) 21.52(d)	41.29(d) 37.96(d) 35.48(d)	119.60, 119.62	24.42
16 $[\text{Rh}(\text{PPh}_3)(\text{DABA})]\text{Cl}$	CH_3OH	—	34.09(d)	118.19	—
17 $[\text{Ir}(\text{PPh}_3)(\text{DPBA})]\text{Cl}$	CH_3OH	35.69(d)	3.75(t)	—	~24

^a Positive chemical shifts downfield from 85% H_3PO_4 .

^b s = singlet, d = doublet, t = triplet.

larizability of the coordinated halide ions. This unusual downfield shift may be explained on the basis of the increased π -acidity of the coordinated halide group in passing through Cl to I. Because of the increased π -acidity of coordinated halide the σ -basicity of the coordinated phosphine increases due to a synergic effect causing an increase in the downfield shift with an increase in the π -acidity of the halogen.

The electronic spectra of complexes 3–5 in dichloromethane contain a single strong band at 490 nm ($20,408\text{ cm}^{-1}$), 505 nm ($19,802\text{ cm}^{-1}$) and 540 nm ($18,518\text{ cm}^{-1}$), respectively, in the visible region. This absorption refers to transitions which have d -orbital character $d_{xy}-d_{x^2-y^2}$, and confirms the square-planar geometry of the complexes.^{26,27} The energy of the band increases in the order $\text{I}^- < \text{Br}^- < \text{Cl}^-$ as expected from the spectrochemical series for the halides. Complexes 3–5 are thus square-planar and analogous to the complexes with the ligands bis(2-diphenylphosphinoethyl)sulphide²⁸ and bis(2-diphenylphosphinoethyl)cyclohexylamine¹⁰ with a *trans* arrangement of the phosphorus atoms.

Complex 6 is hygroscopic and behaves as a 1 : 1 electrolyte in acetone (Table 1). The far-IR spectrum shows bands at 310 and 540 cm^{-1} , which can be assigned to $\nu(\text{Ni}-\text{Cl})$ and $\nu(\text{Ni}-\text{P})$ stretching frequencies. Complex 6 displays an electronic spectrum identical to that of complex 3, due to the presence of the same cationic species, $[\text{NiCl}(\text{DPBA})]^+$, being present in both complexes. The complex shows a band at *ca* $20,000\text{ cm}^{-1}$, which is characteristic of a square-planar geometry. The geometry assigned to complex 6 is similar to that of complex 3.

The terdentate ligand DABA failed to react with Co(II) and Ni(II) metal salts.

Reactions of DPBA and DABA with palladium dichloride in a 1 : 1 mole ratio in methanol gave cationic species of the formulation $[\text{PdCIL}]^+$ [$\text{L} = \text{DPBA}$ (7) or DABA (8)], best isolated as tetraphenyl borate salts. The complexes have conductance values in accord with the presence of a 1 : 1 electrolyte (Table 1). The far-IR spectra of 7 and 8 exhibit $\nu(\text{Pd}-\text{Cl})$ frequencies at 345 and 330 cm^{-1} , respectively. Bands at 545 and 470 cm^{-1} are due to stretching modes of $\nu(\text{Pd}-\text{P})$ and $\nu(\text{Pd}-\text{As})$, respectively.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum (Table 2) of complex 7 exhibits a single resonance at 32.23 ppm, indicating the magnetic equivalence of the two phosphorus ends of the ligand DPBA and also suggests a square-planar geometry for the complex with phosphorus atoms *trans* to each other. Based on the above data, complexes 7 and 8 can be assigned a square-planar geometry similar to other known

Pd(II) complexes,^{7,29} with mono- and terdentate tertiary phosphine ligands. The electronic spectral data of complexes 7 and 8 are discussed along with complexes 9 and 10.

Treatment of K_2PtCl_4 with DPBA and DABA in a 1 : 1 mole ratio gave four-coordinate, cationic complexes of type $[\text{PtCIL}]^+$ [$\text{L} = \text{DPBA}$ (9) or DABA (10)]. These complexes appear to be square-planar, analogous to the other known complexes of similar type of tridentate ligands reported earlier.⁷ Both the complexes exhibit molar conductance values in accord with their formulation as 1 : 1 electrolytes (Table 1).

The far-IR spectra of 9 and 10 show peaks at 330 and 318 cm^{-1} , respectively, corresponding to the $\nu(\text{Pt}-\text{Cl})$ stretching frequency.³⁰ The strong peaks at 520 and 470 cm^{-1} in 9 and 10 are due to $\nu(\text{Pt}-\text{P})$ and $\nu(\text{Pt}-\text{As})$ vibrational modes, respectively.

The electronic spectra of complexes 7–10 are consistent with a square-planar geometry of the complexes. Complexes of Pd(II) and Pt(II) which are pale yellow and creamish white, respectively, show the bands characteristic of $d-d$ transition of square-planar cations. Complex 7 exhibits a band at 341 nm ($29,326\text{ cm}^{-1}$), whereas complex 8 shows a shoulder at 360 nm ($27,778\text{ cm}^{-1}$). Similarly, complexes 9 and 10 exhibit bands at 322 nm ($31,056\text{ cm}^{-1}$) and 359 nm ($27,855\text{ cm}^{-1}$) respectively. The molar extinction coefficient values are slightly higher than the conventional values for $d-d$ transitions due to the LMCT character of these bands. A comparison of the energies of the lowest-energy $d-d$ band in the corresponding complexes of DPBA and DABA showed that the expected spectrochemical order is observed, i.e. the bands in the DABA complexes are shifted to a lower energy compared to the DPBA ligand, as envisaged from ligand field considerations whenever a phosphorus donor is replaced by an arsenic donor.³¹ Comparison of the electronic spectra of complexes 3, 7 and 9 show that as the size of the metal ion increases in the triad $\text{Ni} < \text{Pd} < \text{Pt}$ the lowest-energy $d-d$ transition decreases in the order $\text{Pt} > \text{Pd} > \text{Ni}$. This hypsochromic shift to larger wavenumbers is due to the increase in the covalency of the complexes because of the increase in the size of the d -orbitals of the metal ions. Such a higher degree of metal–ligand bonding can be established in square complexes, by means of the non bonding d_{xz} , d_{yz} and p_z orbitals. The intense bands in all the complexes, around 250 nm can be assigned to the $\pi-\pi^*$ transitions of the phenyl rings.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex 9 exhibits a singlet (with ^{195}Pt satellites) at 28.16 ppm. The platinum–phosphorus coupling constant was calculated from its ^{195}Pt satellites. The spectrum

shows the two-coordinated phosphorus ends of the DPBA ligand are magnetically equivalent and *trans* to each other confirming the above formulation. A $^1J(\text{Pt-P})$ coupling constant value of 2722.16 Hz has been observed for complex **9**, which is appreciably higher when compared to those of earlier reports for similar phosphorus atoms *trans* to other phosphorus atoms in square-planar Pt(II) complexes³² of types *trans*- L_2PtCl_2 and $[\text{L}_3\text{PtCl}]^+$ [$\text{L} = \text{R}_n(\text{C}_6\text{H}_5)_{3-n}\text{P}$, where $n = 1, 2$ or 3 , and $\text{R} = \text{alkyl}$]. It has been reported in these complexes that the coupling constant value increases in every case in both the *cis* and *trans* series in going from trialkyl- to dialkylphenyl-, and to the alkyl-diphenylphosphines. This corresponds to the increasing π -acceptor character of the phosphines as the number of phenyls on the phosphorus increases. Thus, the high coupling constant of complex **9** can be ascribed to the increased $d\pi-d\pi$ bonding between P and Pt due to the presence of phenyl groups on the two phosphorus atoms.

The reaction of rhodium trichloride with the ligands DPBA and DABA in 1:1 mole ratios in boiling methanol gave diamagnetic, yellow Rh(III) complexes of formulation $[\text{RhCl}_3\text{L}]$ [$\text{L} = \text{DPBA}$ (**11**) or DABA (**12**)]. Complexes **11** and **12** have low molar-conductivity values in DMF solutions²⁰ (Table 1), indicating the nonelectrolytic nature of the complexes. Hence, an octahedral geometry has been assigned to complexes **11** and **12**. Such complexes can exist as facial or meridional isomers. The far-IR spectrum of **11** shows bands due to $\nu(\text{Rh-Cl})$ stretching frequencies at 316, 295 and 262 cm^{-1} , whereas complex **12** exhibits $\nu(\text{Rh-Cl})$ frequencies at 312, 293 and 281 cm^{-1} . These frequencies are in much closer agreement with the $\nu(\text{Rh-Cl})$ frequencies for a facial type of isomer.^{6,7,33} The far-IR spectra of **11** and **12** also show bands due to $\nu(\text{Rh-P})$ and $\nu(\text{Rh-As})$ frequencies at 540 and 480 cm^{-1} , respectively.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex **11** shows a doublet centered at 35.20 ppm, with $^1J(\text{Rh-P}) = 119.6\text{ Hz}$, suggesting the magnetic equivalence of the two phosphorus ends of the ligand DPBA.

The electronic spectra of complexes **11** and **12** show bands at 411 nm ($24,331\text{ cm}^{-1}$), 429 nm ($23,310\text{ cm}^{-1}$) and 377(sh) nm ($26,525\text{ cm}^{-1}$), respectively, in conformity with an octahedral Rh(III) species.³⁴ These $d-d$ bands with LMCT character can be assigned to the transitions from the $^1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ upper states. The intense bands in the UV region can be assigned to the $\pi-\pi^*$ transitions and LMCT bands. A facial configuration with *cis* phosphorus or arsenic atoms of the ligands is proposed for complexes **11** and **12**.

Treatment of hydrated iridium trichloride with DPBA and DABA in methanol gave neutral, octahedral complexes of type $[\text{IrCl}_3\text{L}]$ [$\text{L} = \text{DPBA}$ (**13**) or DABA (**14**)]. Both the complexes exhibit very low conductance values (Table 1) in DMSO, indicative of a non-ionic nature of the complexes. Hence, they appear to be octahedral, iridium(III) complexes with the ligands occupying three coordination positions. Here also, such complexes can exist either in facial or meridional configurations.

The far-IR spectra of both the complexes show a broad intense signal at 320 cm^{-1} due to $\nu(\text{Ir-Cl})$ mode. Peaks at 510 and 475 cm^{-1} in **13** and **14** can be assigned to $\nu(\text{Ir-P})$ and $\nu(\text{Ir-As})$ frequencies, respectively.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex **13** exhibits a single peak at 29.31 ppm, confirming the equivalency of the phosphorus atoms of the ligand DPBA.

Due to solubility reasons, the electronic spectra of concentrated solutions of **13** and **14** could not be taken.

A meridional configuration or a facial configuration of the ligands is proposed for **13** and **14**.

Square-planar, cationic complexes of type $[\text{Rh}(\text{PPh}_3)\text{L}]^+$ [$\text{L} = \text{DPBA}$ (**15**) or DABA (**16**)] were synthesized by reacting the Rh(I) complex $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ with the ligands DPBA and DABA, respectively. The reaction in boiling acetone or methanol resulted in displacement of one of the coordinated triphenylphosphine groups and carbon monoxide from the starting complex, to give diamagnetic complexes of the above formulation. The molar-conductance values (Table 1) of both the complexes are in accord with their formulation as 1:1 electrolytes. The far-IR spectra of the complexes do not show any band around 300 cm^{-1} , indicating the total absence of the chloride ion inside the coordination sphere of the metal ion. Both the complexes show bands characteristic of a $\nu(\text{Rh-P})$ stretch, due to the coordinated PPh_3 at 510 cm^{-1} . The complexes also display strong bands at 540 and 470 cm^{-1} , due to $\nu(\text{Rh-P})$ and $\nu(\text{Rh-As})$ modes, respectively.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex **15** gave a well-resolved spectrum (Fig. 1), consistent with a square-planar, four-coordinate $[\text{Rh}(\text{PPh}_3)(\text{DPBA})]^+$ cation. It exhibits a pair of doublets centered at 25.03 and 21.52 ppm, which can be assigned to the two equivalent *trans* phosphorus atoms (P_A) (structure I) of the ligand DPBA, with $^1J(\text{Rh-P}_A) = 119.62\text{ Hz}$. The doublet of doublet can be explained on the basis of the splitting of two equivalent phosphorus atoms (P_A) by a rhodium nucleus ($I = 1/2$) to give a doublet which in turn is split again by the phosphorus atom (P_B) into

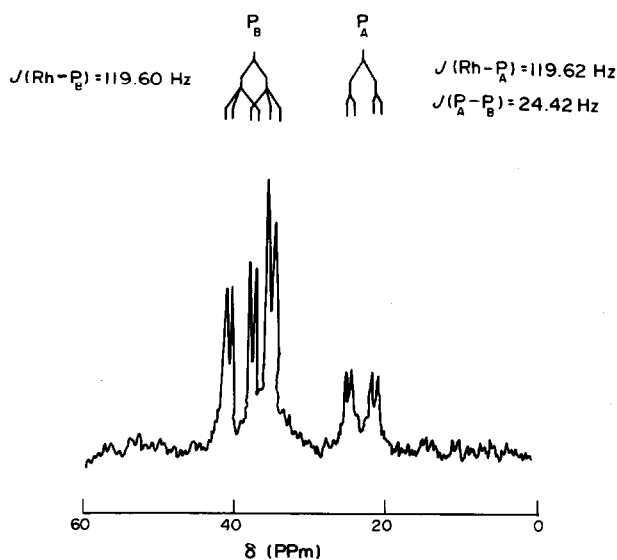


Fig. 1. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex $[\text{Rh}(\text{PPh}_3)(\text{DPBA})]\text{Cl}$.

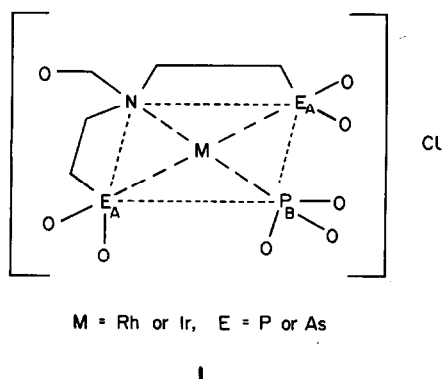
two doublets. There are three more doublets in the downfield region centered at 41.29, 37.96 and 35.48 ppm, that are assigned to the phosphorus atom (P_B), which is first split by the rhodium nucleus and in turn by the two equivalent phosphorus atoms (P_A) of the ligand (Fig. 1). The coupling constants are $J(\text{Rh}-\text{P}_\text{B}) = 119.60$ Hz and $^2J(\text{P}_\text{A}-\text{P}_\text{B}) = 24.42$ Hz. The chemical shifts are in agreement with the earlier reported work.³⁵

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex **16** exhibits a doublet centered at 34.09 ppm (Table 2) with $^1J(\text{Rh}-\text{P}) = 118.19$ Hz, which can be assigned to the coordinated phosphorus atom of the lone triphenylphosphine group.

The spectra in and near the visible region of **15** and **16** show weak $d-d$ transition bands with LMCT character at 384 nm ($26,042\text{ cm}^{-1}$) and 451 nm ($22,172\text{ cm}^{-1}$), and 364 nm ($27,510\text{ cm}^{-1}$) and 299 nm ($33,388\text{ cm}^{-1}$), respectively, which are typical³⁶ of many d^8 complexes. A similar trend of the band shifting to the longer wavelengths has been observed in the case of DABA complex. The bands in the high-energy region can be attributed to the $\pi-\pi^*$ and charge-transfer bands.

The proposed structures of **15** and **16** are shown in I.

Reactions of DPBA with $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ in boiling acetone resulted in displacement of one of the two coordinated triphenylphosphine groups and CO, to give a cationic Ir(I) complex of type $[\text{Ir}(\text{PPh}_3)(\text{DPBA})]^+$ (**17**). The molar conductance of **17** (Table 1) is indicative of a 1:1 electrolyte. The cationic formulation of complex **17** is also supported by the complete absence of the $\nu(\text{Ir}-\text{Cl})$ stretching frequency around 300 cm^{-1} in the far-



IR spectrum of the complex. The intense peaks at 515 and 545 cm^{-1} can be assigned to the $\nu(\text{Ir}-\text{P})$ modes of coordinated PPh_3 and the ligand DPBA, respectively.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex **17** also corroborates the above formulation. The spectrum exhibits two resonances, a downfield doublet centered at 35.69 ppm, and a triplet centered at 3.75 ppm. The doublet due to the splitting of a P_A by P_B (structure I) is assigned to the equivalent phosphorus atoms (P_A) of the ligand DPBA. The appearance of a triplet, which can be assigned to the phosphorus atom (P_B) of the triphenylphosphine, is due to the splitting of P_B by the two equivalent phosphorus atoms (P_A). The small coupling constant $J(\text{P}_\text{A}-\text{P}_\text{B})$ of ~ 24 Hz, may be due to the presence of P_A and P_B *cis* to each other. The proposed structure of **17** is shown as structure I.

The ^1H NMR spectra of complexes **7-12**, **16** and **17** could be obtained satisfactorily in CDCl_3 . All the complexes exhibited broadened resonance signals due to phenyl and methylene protons, with

considerable downfield shift, when compared to those of free ligand¹⁷ [DPBA: phenyl = 7.2 δ (m); —CH₂CH₂— = 2.58 δ (m), 2.10 δ (m) and —CH₂— = 3.56 δ (s); DABA: phenyl = 7.0(m); —CH₂CH₂— = 2.60 δ (m), and 2.05 δ (m) —CH₂ = 3.50 δ (s)]. The phenyl resonances in the complexes occur as an asymmetric multiplet between 7.2 and 7.5 δ . The methylene protons of the benzyl group occur as a singlet between 3.6 and 4.9 δ . The methylene protons of CH₂CH₂ bridges occur as broadened, complex asymmetric multiplets, between 2.8 and 3.9 and 2.3 and 2.9 δ , corresponding to the methylene protons attached to diphenylphosphino or arsino group and amine center, respectively. The complex asymmetric multiplets are possibly due to the interaction of neighbouring methylene protons followed by the coupling of the ³¹P nuclear spin (in DPBA). For the remaining complexes the ¹H NMR could not be obtained satisfactorily owing to either the paramagnetic nature of the complexes or insufficient solubility.

Some of the earlier workers³⁷ have observed a large downfield chemical shift, upon coordination of tertiary phosphines to form five-membered chelate rings, in ³¹P NMR. A similar effect of a large downfield shift has been observed upon coordination of the ligand DPBA to form five-membered chelate rings in the present work. By ³¹P-{¹H} NMR studies it has been confirmed that both the phosphorus ends of the ligand DPBA coordinate to the metal atom in all the complexes.

EXPERIMENTAL

The compounds CoX₂·xH₂O (X = Cl or Br) and NiX₂·xH₂O (X = Cl, Br or I) used were BDH Analar grade. Rhodium trichloride, iridium trichloride trihydrate, palladium dichloride and potassium tetrachloroplatinate were purchased from Strem Chemicals (U.S.A.). The complexes RhCl(CO)(PPh₃)₂ and IrCl(CO)(PPh₃)₂ were prepared by published procedures.³⁸ All solvents used in this work were of reagent grade, and were purified and dried before use. All preparations were carried out in an atmosphere of dry nitrogen.

The ligands DPBA and DABA were synthesized as reported earlier.¹⁷ Microanalysis, melting points, conductivity and magnetic-susceptibility measurements were done as reported,^{39,40} and are given in Table 1. Far-IR spectra of the complexes in the 600–100-cm⁻¹ region were obtained using Nujol mulls pressed between polyethylene plates. The IR spectra were recorded on a Nicolet FT-IR model 200SX spectrometer. The electronic spectra (900–

190 nm) were recorded in dichloromethane and chloroform using Shimadzu UV 240 and Beckman DU-7 spectrophotometers. Proton NMR spectra in CDCl₃ were recorded at 100 MHz on a JEOL FX-100 spectrometer using tetramethyl silane as reference. The proton-decoupled ³¹P NMR spectra were taken in the indicated solvents (Table 2) using a JEOL FX-100 spectrometer operating at 40.3 MHz in the Fourier transform mode. The samples were placed in a 10-mm NMR tube and a capillary of deuterium oxide for the lock. 85% phosphoric acid was used as an external standard.

Preparation of the metal complexes

Chlorobis(2 - (diphenylphosphino)ethyl)benzyl - aminecobalt(II)chloride, [CoCl(DPBA)]Cl. To a refluxing methanolic solution of CoCl₂·6H₂O (0.10 g, 0.42 mM), the ligand DPBA (0.22 g, 0.42 mM) was added under a nitrogen atmosphere to get a green solution. After refluxing the reaction contents for 4–5 h, the solution was evaporated to dryness by a roto-evaporator *in vacuo*, to get a bluish-green precipitate, which was then washed with water and CCl₄, and dried over P₂O₅ *in vacuo*. The compound was recrystallized from an acetone-*n*-hexane mixture. Yield 0.161 g (58%).

Bromobis(2 - (diphenylphosphino)ethyl)benzyl - aminecobalt(II)tetraphenylborate, [CoBr(DPBA)]B(C₆H₅)₄. To a refluxing methanolic solution of CoBr₂ (0.10 g, 0.45 mM) the ligand DPBA (0.24 g, 0.92 mM) was added, when a maroon-red solution was formed. After 4–5 h of refluxing 2 mol of NaBPh₄ was added to the cooled solution, when a shining red precipitate was obtained. The product was filtered, washed with methanol and diethyl ether, and recrystallized from an acetone-methanol mixture. Yield 0.130 g (60%).

Chlorobis(2 - (diphenylphosphino)ethyl)benzyl - aminenickel(II)tetraphenylborate, [NiCl(DPBA)]B(C₆H₅)₄, *bromobis(2-(diphenylphosphino)ethyl)benzylaminenickel(II)tetraphenylborate*, [NiBr(DPBA)]B(C₆H₅)₄, and *iodobis(2-(diphenylphosphino)ethyl)benzylaminenickel(II)tetraphenylborate*, [NiI(DPBA)]B(C₆H₅)₄. To refluxing methanolic solutions of NiCl₂·6H₂O (0.10 g, 0.42 mM), NiBr₂·3H₂O (0.10 g, 0.46 mM), and NiI₂ (0.10 g, 0.32 mM), the ligand DPBA was added, 0.22 g (0.42 mM) in the case of the chloride, 0.24 g (0.46 mM) in the case of the bromide, and 0.17 g (0.32 mM) in the case of the iodide, under an N₂ atmosphere and further refluxed for 4–5 h. To the cooled solutions a 2-mol excess of NaB(C₆H₅)₄ was added to get a saffron-red compound in the case of the chloro complex 3, shining red in the case of the bromo complex 4, and blackish-red in the case of the

iodo complex 5. The products were filtered, washed with methanol and ether, and dried. The complexes 3–5 were recrystallized from an acetone–methanol mixture. Yield 0.31 g (78%) in the case of 3, 0.36 g (80%) in the case of 4, and 0.28 g (83%) in the case of 5.

Chlorobis(2 - (diphenylphosphino)ethyl)benzyl - aminenickel(II)chloride, $[\text{NiCl}(\text{DPBA})]\text{Cl}$. The procedure adapted for this complex is analogous to that described above for complexes 3–5, except that after refluxing the reaction contents for 4–5 h the solution was evaporated to dryness to get a red precipitate, which was washed and dried and stored in a vacuum desiccator because of its hygroscopicity. Yield 0.18 g (65%).

Chlorobis(2 - (diphenylphosphino)ethyl)benzyl - aminepalladium(II)tetraphenylborate, $[\text{PdCl}(\text{DPBA})]\text{B}(\text{C}_6\text{H}_5)_4$, and *chlorobis(2 - (diphenylarsino)ethyl)benzylaminepalladium (II) tetraphenylborate*, $[\text{PdCl}(\text{DABA})]\text{B}(\text{C}_6\text{H}_5)_4$. After refluxing the yellow methanolic solutions of PdCl_2 (0.10 g, 0.56 mM) and the ligands [DPBA (0.30 g, 0.56 mM) or DABA (0.35 g, 0.56 mM)] for 4–5 h, the reaction contents were cooled and a 2-mol excess of $\text{NaB}(\text{C}_6\text{H}_5)_4$ in methanol was added, when a yellow precipitate was obtained in both cases. The complexes were filtered, washed with hot methanol and diethyl ether, and recrystallized from a dichloromethane–methanol mixture. Yield 0.29 g (52%) (DPBA), and 0.3 g (51%) (DABA).

Chlorobis(2 - (diphenylphosphino)ethyl)benzyl - amineplatinum(II)chloride, $[\text{PtCl}(\text{DABA})]\text{Cl}$, and *chlorobis(2 - (diphenylarsino)ethyl)benzylamineplatinum (II) chloride*, $[\text{PtCl}(\text{DABA})]\text{Cl}$. To an acetone solution of the ligand [DPBA (0.128 g, 0.24 mM) and DABA (0.149 g, 0.24 mM)] the compound K_2PtCl_4 (0.100 g, 0.24 mM) in 2–3 cm³ of water was added, and the solution slightly warmed for 2–3 h. The resulting pale yellow solutions in both the cases were concentrated to a small volume and the complexes precipitated by the addition of diethyl ether to get a creamish white precipitate in both cases. The complexes were filtered, washed, dried and recrystallized from an acetone–diethyl ether mixture. Yield 0.192 g (88%) (DPBA), and 0.180 g (88%) (DABA).

Trichlorobis(2 - (diphenylphosphino)ethyl)benzyl aminerhodium(III), $[\text{RhCl}_3(\text{DPBA})]$, and *trichlorobis(2 - (diphenylarsino)ethyl)benzylaminerhodium (III)*, $[\text{RhCl}_3(\text{DABA})]$. To the refluxing methanolic solution of RhCl_3 (0.10 g, 0.47 mM), the ligand [DPBA (0.253 g, 0.47 mM) or DABA (0.294 g, 0.47 mM)] in 5 cm³ benzene was added slowly over a period of 1 h, under an N_2 atmosphere. A silky yellow precipitate settled down in both the cases after refluxing for 4–5 h. The pre-

cipitates were filtered, washed and recrystallized from a dichloromethane–diethyl ether mixture. Yield 0.14 g (40%) (DPBA), and 0.158 g (40%) (DABA).

Trichlorobis(2 - (diphenylphosphino)ethyl)benzyl - amineiridium(III), $[\text{IrCl}_3(\text{DPBA})]$, and *trichlorobis(2 - (diphenylarsino)ethyl)benzylamineiridium (III)*, $[\text{IrCl}_3(\text{DABA})]$. To a refluxing methanolic solution of the ligand [DPBA (0.302 g, 0.56 mM), or DABA (0.35 g, 0.56 mM)] was added $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (0.10 g, 0.28 mM), and the solution further refluxed for 4–5 h, when a greyish green complex was obtained in the case of 13 and a greenish complex in the case of 14. The products were filtered, washed with methanol and diethyl ether, and recrystallized from hot dimethylsulphoxide. Yield 0.10 g (45%) (DPBA), and 0.115 g (44%) (DABA).

Triphenylphosphinebis(2 - (diphenylphosphino)ethyl)benzylaminerhodium(I)chloride, $[\text{Rh}(\text{PPh}_3)(\text{DPBA})]\text{Cl}$, and *triphenylphosphinebis(2 - (diphenylarsino)ethyl)benzylaminerhodium(I) chloride*, $[\text{Rh}(\text{PPh}_3)(\text{DABA})]\text{Cl}$. To a refluxing acetone solution of the ligand DPBA (0.125 g, 0.21 mM) and a methanolic solution of DABA (0.130 g, 0.21 mM), was added the Rh(I) complex $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (0.150 g, 0.21 mM). After 3–4 h of refluxing the yellow homogeneous solutions in both the cases were concentrated to a small volume and the complexes precipitated by diethyl ether. The yellow products were filtered, washed with diethyl ether and recrystallized from a methanol–diethyl ether mixture. Yield 0.180 g (89%) (DPBA), and 0.125 g (57%) (DABA).

Triphenylphosphinebis(2 - (diphenylphosphino)ethyl)benzylamineiridium(I)chloride, $[\text{Ir}(\text{PPh}_3)(\text{DPBA})]\text{Cl}$. $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (0.100 g, 0.12 mM) was added to a refluxing methanolic solution of DPBA (0.068 g, 0.12 mM) and further refluxed for 3–4 h. The solution was then concentrated and diethyl ether added to get a creamish white precipitate which was filtered, washed with ether and recrystallized from a dichloromethane–diethyl ether mixture. Yield 0.055 g (57%).

Acknowledgement—One of us (V.V.S.R.) thanks CSIR, New Delhi, India, for financial support.

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