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New Terdentate Ligands Containing Nitrogen and Phosphorus or Arsenic as Donor Atoms and Their Complexes with Ruthenium(II) and -(III)

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The terdentate ligands bis(2-(diphenylphosphino)ethyl)benzylamine (DPBA) and bis(2-(diphenylarsino)ethyl)benzylamine (DABA) were synthesized and characterized on the basis of their mass spectra and ^1H, ^{31}P, and ^{13}C NMR spectra. Some of the complexes of these ligands (L) with ruthenium(II) and ruthenium(III) were prepared by employing various starting materials. The reaction of $RuCl_2(PPh_3)_3$ with a twofold excess of L in acetone or *n*-hexane gave the neutral complex $[RuCl_2(PPh_3)(L)]$ (L = DPBA or DABA). The reaction of DPBA with $RuCl_2(PPh_3)_3$ in methanol, however, gave the cationic complex $[RuCl(DPBA)_2]Cl$. Neutral monomeric complexes of the type $[RuCl_3(L)]$ were obtained by the reaction of L with $RuCl_3(AsPh_3)_2MeOH$, in acetone. The cationic complex $[RuCl(DPBA)_2]Cl_2$ was obtained by the reaction of $RuCl_3(AsPh_3)_2MeOH$ with DPBA in methanol. Similar reactions with $RuBr_3(AsPh_3)_2MeOH$ in acetone yielded $[RuBr_2(AsPh_3)(L)]Br$ (L = DPBA or DABA) and $[RuBr_3(DABA)]$. The reaction of $RuCl_2(Me_2SO)_4$ with DPBA and DABA in acetone gave the complexes $[RuCl(Me_2SO)_2(DPBA)]Cl$ and $[RuCl_2(Me_2SO)(DABA)]$, respectively. The reaction of $RuCl_3\cdot 3H_2O$ with a twofold excess of DPBA and NH_4PF_6 in methanol gave the Ru(II) cationic species $[Ru(DPBA)_2](PF_6)_2$ whereas DABA yielded the ruthenium(III) cationic complex $[RuCl(DABA)_2]Cl_2$. The results of ^1H and ^{31}P NMR, EPR, and other spectral data of the complexes are discussed.

Introduction

The chemistry of the metal complexes[1] containing mono- or poly(tertiary phosphines or arsines)[2-12] is governed by the electronic and steric properties of the ligands and the oxidation state and coordination number of the metal ion. Sacconi and co-workers[8-11] synthesized ligands with mixed hard and soft donor atoms O, N, P, As, and S with varying degrees of σ-basicity and π-acidity and studied their effect on the magnetic and stereochemical properties of complexes. In this regard the syntheses of some of the ligands, bis(2-(diphenylphosphino)ethyl)amine, bis(2-(diphenylphosphino)ethyl)methylamine, bis(2-(diphenylphosphino)ethyl)cyclohexylamine, and bis(2-(diphenylphosphino)ethyl) sulfide, and their complexes with nickel(II) and cobalt(II) were reported.[8]

This paper reports the synthesis and characterization of two terdentate ligands, bis(2-(diphenylphosphino)ethyl)benzylamine (DPBA) and bis(2-(diphenylarsino)ethyl)benzylamine (DABA), which contain sets of mixed donor atoms, N, P and N, As, respectively. These ligands were used as chelates in the synthesis of a number of ruthenium(II) and -(III) complexes. The objective of this work has been to design and synthesize complexes with a potential for homogeneous catalysis, since platinum-group metal complexes with phosphines and arsines are good homogeneous catalysts in a number of reactions.[13] With a view to achieve considerable catalytic activity, it was considered necessary to prepare some ruthenium complexes with terdentate ligands such as DPBA and DABA, which contain a benzylamino group to provide the necessary nucleophilicity and two diphenylphosphino or -arsino groups to confer enough π-acidity so as to stabilize the low-valent metal complexes. Preliminary catalytic studies[14] on the homogeneous hydrogenation of olefins with the complex $[RuCl_2(PPh_3)(DPBA)]$ have indicated that the complex shows catalytic activity almost comparable with that of Wilkinson's catalyst $RhCl(PPh_3)_3$. The present work is confined to the synthesis and characterization of some complexes of DPBA and DABA with ruthenium(II) and -(III) ions whose catalytic activity is being investigated in our laboratory.

Experimental Section

Ruthenium trichloride trihydrate was obtained from Johnson Matthey (England). The ligands triphenylphosphine and arsine were purchased from Strem Chemicals Inc. (USA). The complexes $RuCl_2(PPh_3)_3$,[15] $RuX_3(AsPh_3)_2MeOH$ (X = Cl, Br),[15] and $RuCl_2(Me_2SO)_4$[16] were prepared by published procedures. Diethanolamine, benzyl bromide, and thionyl chloride were of AnalaR reagent grade and used without further purification. All solvents used in this work were of reagent grade that were purified and dried before use. All the preparations were carried out under an atmosphere of nitrogen. Microanalysis, melting points, infrared spectra, conductivity, and magnetic susceptibility measurements were done as reported.[17] Proton NMR spectra were recorded on both JEOL FX100 and Bruker 270-MHz spectrometers in $CDCl_3$. The phosphorus-31 NMR spectra were taken in the indicated solvents (Table III) with a JEOL FX100 spectrometer operating at 40.3 MHz in the Fourier transform mode with proton noise decoupling and a deuterium lock. The samples were placed in a 10-mm NMR tube, and a capillary filled with deuterium oxide was placed for the lock. 85% phosphoric acid was used as an external standard. Carbon-13 NMR spectra were taken in $CDCl_3$, with a JEOL FX100 spectrometer operating at 24.99 MHz. Tetramethylsilane was used as an external reference. The electronic spectra of complexes were measured in dichloromethane on a Shimadzu UV 240 spectrometer. The electron spin resonance spectra of the benzene solutions of the samples at liquid-nitrogen temperature were recorded on a Varian E-line ESR spectrometer, operating at 9.07 GHz using 100-kHz modulation frequency. The magnetic field calibration was checked with TCNE, whose g value is 2.0028. Molecular weight determinations were carried out on a Knauer vapor pressure osmometer, Model No. 1100, at 37 °C in chloroform (in the concentration range 0.01–0.1 M). Mass spectra were recorded at 70 eV on a VG Micromass 7070H mass spectrometer with a chamber temperature at 140 °C (filament current 200 μA).

The NMR spectral data of the ligands DPBA and DABA are presented in Table I. Microanalytical data, conductivity, melting point, and magnetic susceptibility data are presented in Table II. The ^{31}P NMR and the electronic spectral data are presented in Tables III and IV, respectively.

Synthesis of the Ligands DPBA and DABA. The ligands DPBA and DABA were prepared by employing the reaction between the alkali-metal diphenylphosphides[18] or diphenylarsenides[19] and the appropriate organic polyhalide. The overall reaction process is

$$PhCH_2Br + HN(CH_2CH_2OH)_2 \xrightarrow[\text{ethanol}]{K_2CO_3} PhCH_2N(CH_2CH_2OH)_2$$

$$PhCH_2N(CH_2CH_2Cl)_2 + 2KEPh_2\cdot 2diox \xrightarrow{\text{1,4-dioxane}} PhCH_2N(CH_2CH_2EPh_2)_2 + 2KCl$$

$$E = P, As; Ph = C_6H_5; diox = dioxane$$

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Table I. NMR Spectral Parameters of the Ligands DPBA and DABA

ligand	$\delta(^1H)$[a]	$\delta(^{31}P)$[b]	^{13}C[a]	
			δ	J(P–C), Hz
$C_6H_5CH_2N[CH_2CH_2P(C_6H_5)_2]_2$	7.20 (Ph)	−19.25	50.00 (d)	27.97
	2.58 (m), 2.10 (m) ($-CH_2CH_2-$)		25.95 (d)	13.42
	3.56 (s) ($-CH_2-$)		58.39 (s)	...
			132.15–139.6	18.31 (J(P–C_1))
			128.27–128.91	...
$C_6H_5CH_2N[CH_2CH_2As(C_6H_5)_2]_2$	7.03 (m) (Ph)	...	50.25	...
	2.60 (m), 2.05 (m) ($-CH_2CH_2-$)		25.25	
	3.5 (s) ($-CH_2-$)		58.19	
			140.75–126.86	

[a] Chemical shifts are relative to internal Me_4Si. [b] Chemical shifts are relative to external 85% H_3PO_4, positive shifts representing deshielding.

Table II. Analytical and Other Physical Data of Ruthenium Complexes

complex	color	dec pt,[a] °C	μ_{eff},[b] μ_B	elemental anal.[c] % C	% H	% N	% others	conductivity,[d] λ_∞, Ω^{-1} cm^2 mol^{-1}
$[RuCl_2(PPh_3)(DPBA)]$ (**1**)	orange-red	230–235	diamag	65.5 (64.5)	5.1 (5.2)	1.3 (1.3)		13
$[RuCl_2(PPh_3)(DABA)]$ (**2**)	red	260–270	diamag	59.0 (60.3)	4.8 (4.7)	1.3 (1.3)		3
$[RuCl(DPBA)_2]Cl$ (**3**)	yellow	155–160	diamag	67.0 (68.0)	5.7 (5.7)	2.3 (2.3)		92
$[RuCl(Me_2SO)_2(DPBA)]Cl$ (**4**)	yellow	230–240	diamag	56.2 (55.3)	5.7 (5.9)	1.5 (1.4)		73
$[RuCl_2(Me_2SO)(DABA)]$ (**5**)	yellow	230–235	diamag	51.4 (51.7)	5.0 (5.0)	1.5 (1.5)		8
$[RuCl_3(DPBA)]$ (**6**)	green	315–320	2.10	55.4 (56.8)	4.7 (4.7)	1.7 (1.8)		40
$[RuCl_3(DABA)]$ (**7**)	red-orange	215–220	2.04	49.1 (50.7)	4.2 (4.2)	1.7 (1.7)		33
$[RuCl(DPBA)_2]Cl_2$ (**8**)	yellow	158–162	1.92	65.6 (66.1)	5.5 (5.5)	2.3 (2.2)		151
$[RuBr_2(AsPh_3)(DPBA)]Br$ (**9**)	green	260–265	1.97	53.4 (53.9)	4.5 (4.3)	1.1 (1.2)	19.3 (Br) (20.3)	102
$[RuBr_2(AsPh_3)(DABA)]Br$ (**10**)	green	240–243	2.10	49.1 (50.2)	3.9 (3.9)	1.1 (1.1)	19.0 (Br) (18.9)	88
$[RuBr_3(DABA)]$ (**11**)	purple	230–235	2.15	44.0 (43.8)	3.8 (3.7)	1.4 (1.5)	24.0 (Br) (25.0)	36
$[Ru(DPBA)_2](PF_6)_2$ (**12**)	yellow	195–200	diamag	56.2 (57.3)	4.7 (4.8)	1.8 (1.9)		193
$[RuCl(DABA)_2]Cl_2$ (**13**)	green	155–160	2.05	57.6 (58.1)	4.8 (4.8)	1.9 (1.9)		120

[a] Decomposition temperatures. [b] The magnetic susceptibility was measured on a Faraday balance at room temperature (300 K). [c] Calculated values are given in parentheses. [d] Conductivity measurements were done in DMF at room temperature and values reported for infinite dilution.

Table III. ^{31}P NMR Data[a] for Ruthenium(II) and -(III) Complexes

complex	solvent	chem shifts,[b] δ		J(P–P), Hz		
		DPBA	PPh_3	$J(P_A-P_B)$	$J(P_A-P_C)$	$J(P_B-P_C)$
$[RuCl_2(PPh_3)(DPBA)]$ (**1**)	CD_2Cl_2	43.42 (s) 25.78 (s)	21.54 (s)			
$[RuCl_2(PPh_3)(DABA)]$ (**2**)	CD_2Cl_2		47.92 (s)			
$[RuCl(DPBA)_2]Cl$ (**3**)	CD_3OH	58.92 (t) 53.70 (t) 35.24 (t) −20.40 (s)		40	25	22
$[RuCl(Me_2SO)_2(DPBA)]Cl$ (**4**)	$CDCl_3$	42.84 (s) 27.00 (s)				
$[RuCl_3(DPBA)]$ (**6**)	CD_2Cl_2	37.30 (s)				
$[Ru(DPBA)_2Cl]Cl_2$ (**8**)	CD_3OH	58.86 (t) 48.14 (t) 34.27 (t) −19.67 (s)		40	28	22
$[RuBr_2(AsPh_3)(DPBA)]Br$ (**9**)	CD_2Cl_2	57.85 (d) 28.00 (d)		27		
$[Ru(DPBA)_2](PF_6)$ (**12**)	CD_2Cl_2	59.03 (s)				

[a] Positive chemicals shifts downfield from 85% H_3PO_4. [b] Abbreviations: s = singlet, d = doublet, t = triplet.

The organic halide $PhCH_2N(CH_2CH_2Cl)_2$ was obtained[20] by the reaction of the corresponding alcohol $PhCH_2N(CH_2CH_2OH)_2$ with an excess of thionyl chloride (1:2 ratio). The product $PhCH_2N(CH_2CH_2Cl)_2{\cdot}HCl$, on treatment with a stoichiometric amount of 10% KOH, gave the free amine $PhCH_2N(CH_2CH_2Cl)_2$ as an insoluble oil. A dioxane solution of the above oil was added dropwise with stirring to an orange-red suspension of $KPPh_2$[18] or $KAsPh_2$[19] in dioxane, in a stoichiometric amount under ice-cold conditions. The reaction mixture was then allowed to warm for 30 min. During the course of reaction the orange-red color of

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Table IV. UV–Visible Spectral Data for Ruthenium(II) and -(III) Complexes in Dichloromethane

complex	λ_{max},[a] nm
$[RuCl_2(PPh_3)(DPBA)]$ (**1**)	475 (421), 330 (3368), 260 (35 931), 235 (21 334)
$[RuCl_2(PPh_3)(DABA)]$ (**2**)	490 (694), 400 (4885), 325 (16 954), 270 (55 172), 230 (75 862), 222 (69 655)
$[RuCl(DPBA)_2]Cl$ (**3**)	455 (4343), 440 (5791), 380 (16 216), 235 (103 488)
$[RuCl(Me_2SO)_2(DPBA)]Cl$ (**4**)	370 (769), 330 (654), 245 (3424)
$[RuCl_2(Me_2SO)(DABA)]$ (**5**)	420 (434), 355 (743), 245 (46 615), 230 (49 520)
$[RuCl_3(DPBA)]$ (**6**)	468 (1266), 402 (4241), 340 (5064), 268 (34 819), 258 (34 123), 242 (34 123)
$[RuCl_3(DABA)]$ (**7**)	515 (1199), 395 (2233), 265 (24 626), 225 (36 194)
$[RuCl(DPBA)_2]Cl_2$ (**8**)	380 (1527), 340 (872), 248 (30 785)
$[RuBr_2(AsPh_3)(DPBA)]Br$ (**9**)	340 (2211), 232 (36 486)
$[RuBr_2(AsPh_3)(DABA)]Br$ (**10**)	590 (1418), 450 (1519), 380 (2228), 262 (30 894), 230 (89 430)
$[RuBr_3(DABA)]$ (**11**)	600 (1393), 490 (1857), 450 (2461), 360 (4226), 295 (20 923), 262 (32 820), 230 (58 461)
$[Ru(DPBA)_2](PF_6)_2$ (**12**)	435 (1187), 365 (2602), 300 (6222), 245 (5724)
$[RuCl(DABA)_2]Cl_2$ (**13**)	452 (746), 305 (11 764), 245 (76 470), 230 (88 235)

[a] The molar extinction coefficient values, ϵ (in $M^{-1}\ cm^{-1}$), are given in parentheses.

the solution almost faded out. The reaction contents were then poured into ice-cold water or methanol to get a dense oil, which solidified after it was kept in a freezer for 24 h. The products when recrystallized from chloroform–methanol gave white powders with a yield of about 90% in the case of DPBA and 70% in the case of DABA. DPBA: mp 74–75 °C; mol wt 531.6 (calculated), 525 (experimental, osmometric in chloroform). Anal. Calcd for $C_{35}H_{35}NP_2$: C, 79.09; H, 6.59; N, 2.63. Found: C, 78.50; H, 6.45; N, 2.70. DABA: mp 67–68 °C; mol wt 619 (calculated), 615 (experimental, osmometric in chloroform). Anal. Calcd for $C_{35}H_{35}NAs_2$: C, 67.85; H, 5.65; N, 2.26. Found: C, 65.55; H, 5.37; N, 2.18.

Alternatively the ligands were also obtained by an in situ reaction of $PhCH_2N(CH_2CH_2Cl)_2$ in dioxane with $KEPh_2$ (E = P, As), which was previously obtained through the reaction of metallic potassium with EPh_3 (E = P, As) in dioxane. Prior to the addition of the organic halide KPh was destroyed carefully by the addition of NH_4Cl to the reaction mixture containing both KPh and $KEPh_2$. This method is more convenient than the former.

Preparation of Complexes of Ruthenium(II) and -(III). Dichloro(triphenylphosphine)(bis(2-(diphenylphosphino)ethyl)benzylamine)ruthenium(II) (1). The ligand DPBA (0.22 g, 0.42 mM) dissolved in dry acetone was refluxed for 5 min under a nitrogen atmosphere. The complex $RuCl_2(PPh_3)_3$ (0.20 g, 0.21 mM) was added in the solid state to the above refluxing mixture, when the entire solution turned orange. The reaction mixture was refluxed for an additional 2 h. The orange-red crystals that separated during the reaction were filtered, washed with cold acetone, and finally dried over P_2O_5 under vacuum; yield 0.14 g (70%).

Alternatively, the same complex was obtained by refluxing a suspension containing $RuCl_2(PPh_3)_3$ with 1 mol excess of DPBA in *n*-hexane for about 4 h. The product settled at the end of the reaction was filtered and washed with a mixture of acetone–*n*-hexane. The latter method gave better yields than the former.

Dichloro(triphenylphosphine)(bis(2-(diphenylarsino)ethyl)benzylamine)ruthenium(II) (2). This complex was prepared as in complex **1** except that the ligand DABA (0.26 g, 0.42 mM) was reacted with $RuCl_2(PPh_3)_3$ (0.20 g, 0.21 mM) for 1 h under reflux in acetone. The product obtained as red crystals gave an yield of 0.16 g (73%). The same complex was obtained by conducting the reaction in *n*-hexane and methanol.

Chlorobis(bis(2-(diphenylphosphino)ethyl)benzylamine)ruthenium(II) Chloride (3). A suspension of the complex $RuCl_2(PPh_3)_3$ (0.20 g, 0.21 mM) in methanol was refluxed with DPBA (0.22 g, 0.42 mM) for 4–5 h under a nitrogen atmosphere. The whole suspension dissolved, resulting in an yellow solution. The solution was concentrated to a small volume and the complex precipitated with ether to give an yellow precipitate, which was then filtered and washed repeatedly with ether; yield 0.18 g (70%).

Chlorobis(dimethyl sulfoxide)(bis(2-(diphenylphosphino)ethyl)benzylamine)ruthenium(II) Chloride (4). The complex $RuCl_2(Me_2SO)_4$ (0.20 g, 0.41 mM) was suspended in dry acetone and refluxed under a nitrogen atmosphere for 10 min. An acetone solution of DPBA (0.43 g, 0.81 mM) was added to this reflux and the heating continued for an additional 4 h. After the mother liquor was evaporated to half of its volume, dry ether was added when yellow needles separated. The crystals were filtered and washed with hot ether. The complex was recrystallized from an acetone–ether mixture; yield 0.31 g (90%).

Dichloro(dimethyl sulfoxide)(bis(2-(diphenylarsino)ethyl)benzylamine)ruthenium(II) (5). The complex was obtained by a method similar to that used for the preparation of complex **4**, but with DABA instead of DPBA. The product was obtained as a yellow precipitate, which was recrystallized from an acetone–ether mixture to give a yield of 90–95%.

Trichloro(bis(2-(diphenylphosphino)ethyl)benzylamine)ruthenium(III) (6) and Trichloro(bis(2-(diphenylarsino)ethyl)benzylamine)ruthenium(III) (7). An acetone solution of the ligand (DPBA, 0.51 g, 0.96 mM; DABA, 0.59 g, 0.96 mM) was added to the refluxing suspension of $RuCl_3(AsPh_3)_2MeOH$ (0.40 g, 0.48 mM) in acetone under a nitrogen atmosphere. The reaction mixture was refluxed for about 4–5 h. The color of the solution remained greenish orange in the case of DPBA and orange-pink in the case of DABA. When the reaction contents were cooled, the precipitated green (DPBA) and orange-red (DABA) crystals were filtered and washed with cold acetone to remove an excess of the ligand: yield 0.30 g, (88%, DPBA), 0.32 g (84%, DABA).

Chlorobis(bis(2-(diphenylphosphino)ethyl)benzylamine)ruthenium(III) Chloride (8). To the refluxing methanolic solution of $RuCl_3(AsPh_3)_2MeOH$ (0.20 g, 0.24 mM) was added a methanol suspension of DPBA (0.26 g, 0.48 mM) under a nitrogen atmosphere. The suspension dissolved, giving a light yellow homogeneous solution. The solution was further refluxed for 5–6 h and concentrated to a small volume, when addition of ether gave a bright yellow precipitate. The product was filtered and washed with ether to remove the excess of the ligand and the displaced arsine. The complex was recrystallized to a fine yellow powder in a methanol–ether mixture; yield 0.2 g (67%).

Dibromo(triphenylarsine)(bis(2-(diphenylphosphino)ethyl)benzylamine)ruthenium(III) Bromide (9). The complex $RuBr_3(AsPh_3)_2MeOH$ (0.10 g, 0.1 mM) suspended in acetone was refluxed with an excess of DPBA (0.10 g, 0.18 mM) in the same solvent for about 6 h. The reaction mixture was concentrated to a small volume and the complex precipitated with dry ether to give a light green product. The complex was recrystallized from an acetone–ether mixture to a fine green powder; yield 0.09 g (75%).

Dibromo(triphenylarsine)(bis(2-(diphenylarsino)ethyl)benzylamine)ruthenium(III) Bromide (10) and Tribromo(bis(2-(diphenylarsino)ethyl)benzylamine)ruthenium(III) (11). To the refluxing acetone solution of the ligand DABA (0.24 g, 0.4 mM) was added the complex $RuBr_3(AsPh_3)_2MeOH$ (0.20 g, 0.2 mM) in the solid form. The complex dissolved almost immediately after the addition, resulting in a dark greenish purple solution, which was further refluxed for an additional 3–4 h. At the end of the reaction a dark purple crystalline complex separated, which was filtered after cooling the reaction contents to room temperature. This complex was analyzed as having the formula $[RuBr_3(DABA)]$. The remaining solution was evaporated on a rotavaporator to a small volume, and a green complex was isolated by the addition of *n*-hexane. The green product was analyzed as having the composition $[RuBr_2(AsPh_3)(DABA)]Br$: yield 0.10 g (40%, $[RuBr_2(AsPh_3)(DABA)]Br$), 0.09 g (47%, $[RuBr_3(DABA)]$).

Bis(bis(2-(diphenylphosphino)ethyl)benzylamine)ruthenium(II) Hexafluorophosphate (12). Ruthenium trichloride trihydrate (0.20 g, 0.76 mM) in methanol was refluxed under a nitrogen atmosphere with the ligand DPBA (0.82 g, 1.54 mM) for 4 h. Ten minutes after the addition of the ligand the whole solution turned orange-yellow. At the end of the reaction the complex was precipitated by the addition of NH_4PF_6 in methanol to give a yellow product. The complex was recrystallized from hot methanol; yield 0.85 g (77%).

Chlorobis(bis(2-(diphenylarsino)ethyl)benzylamine)ruthenium(III) Chloride (13). To the refluxing methanolic solution of ruthenium trichloride trihydrate (0.20 g, 0.76 mM) was added a twofold excess of the ligand DABA (0.94 g, 1.52 mM) and the resulting green solution refluxed for 5 h. After the mother liquor was concentrated to a small volume, the addition of ether gave a green precipitate, which was filtered and washed repeatedly with ether; yield 0.90 g (72%).

Results and Discussion

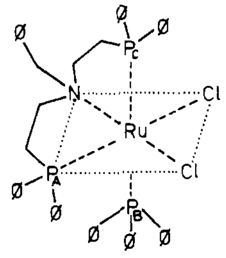
The new terdentate ligands containing mixed donor atoms, NP_2 and NAs_2, were characterized by complete elemental analysis and molecular weight determination in chloroform. The infrared spectra of these ligands were not of much help in assigning structures, but ^1H, ^{31}P, and ^{13}C NMR (Table I) and mass spectra, however, were of good use to support the proposed compositions of the ligands, $C_6H_5CH_2N[CH_2CH_2E(C_6H_5)_2]_2$ (E = P, As).

The proton NMR spectrum of DPBA exhibits resonances from the phenyl protons around δ 7.20, protons of the CH_2CH_2 bridges at δ 2.58 and 2.10, as multiplets, and a singlet at δ 3.50 due to the CH_2 proton resonance of the benzyl group. Similarly, the ligand DABA exhibits resonances of phenyl and methylene protons of the CH_2CH_2 bridges and the benzyl group at δ 7.03, 2.60 and 2.05, and 3.5, respectively. The $^{31}P\{^1H\}$ NMR spectrum of DPBA exhibits a single peak at −19.25 ppm. The $^{13}C\{^1H\}$ NMR spectra of the ligands, in addition to signals in the range 126.86–140.75 ppm, due to the diphenylphosphino or -arsino moieties and the phenyls of the benzyl groups, exhibit well-defined doublets due to coupling to ^{31}P (in DPBA) and singlets (in DABA) due to the CH_2CH_2 bridges and singlets due to CH_2 of the benzyl group. The mass spectra obtained on these compounds showed general features similar to those reported earlier[21,22] on some poly(tertiary phosphines, arsines, and phosphinoarsines) and confirm the above formulation.

Ruthenium(II) and -(III) Complexes. The reaction of DPBA with $RuCl_2(PPh_3)_3$ gave two different products depending upon the reaction conditions. In boiling acetone or *n*-hexane an orange-red diamagnetic complex of the composition $[RuCl_2(PPh_3)(DPBA)]$ (**1**; ϕ = Ph in all the structures shown) was obtained. The reaction was conducted with both 1:1 and 1:2 mole ratios of the starting complex and the ligand and in either case complex **1** was obtained with a 1:1 ratio of Ru(II) to ligand. In the case of the reaction of $RuCl_2(PPh_3)_3$ with DABA in acetone, *n*-hexane, or methanol only a 1:1 complex of the composition $[RuCl_2(PPh_3)(DABA)]$ (**2**) was obtained. When the reaction of $RuCl_2(PPh_3)_3$ was carried out in boiling methanol with a twofold excess of DPBA, a yellow solid of the composition $[RuCl(DPBA)_2]Cl$ (**3**) was obtained.

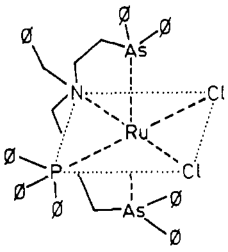
Complexes **1** and **2** have low conductivity in DMF solutions, suggesting their formulation as nonelectrolytes.[23] The far-infrared spectra of complexes **1** and **2** display evidence that they contain at least one triphenylphosphine in the coordination sphere of the metal ion, as supported by the presence of an intense band at 530 cm^{-1} assigned to ν(M–P). A band at 510 cm^{-1} in complex **1** is assigned to ν(M–P) of the ligand DPBA. The cis disposition of the chlorides in the complexes is indicated by the presence of strong absorption bands at 320 and 270 cm^{-1} in complex **1** and at 310 and 290 cm^{-1} in complex **2**. On the basis of the infrared information two types of structures with cis chlorides and meridionally or facially coordinated DPBA or DABA can be proposed for complexes **1** and **2**. A distinction between these two possibilities can however be made based on the proton NMR spectra of complexes. Thus the ^1H NMR spectrum of complex **1** is consistent with a facial arrangement of the terdentate ligand and cis-disposed chlorides. The resonance signal corresponding to methylene protons attached to the $(C_6H_5)_2P$–group is split into two multiplets with chemical shifts at δ 3.35 and 3.10. This splitting can be explained on the basis of different chemical environments for two P-binding sites, and this is possible in a facially disposed DPBA structure in which the phosphine ends are coordinated trans to two different ligands (Cl and PPh_3). This is in contrast to the meridional DPBA, in which both of the phosphine ends keep in a mutually trans configuration. The absorption due to the methylene protons of the bridged chains bonded to the nitrogen end appears as a broad multiplet centered at δ 2.80. A singlet due to benzyl methylene protons appears at δ 4.80. There is a significant downfield shift in all these resonances when compared to those of the free ligand. The phenyl proton resonance appears as a broad well-resolved multiplet centered around δ 7.10.

The $^{31}P\{^1H\}$ NMR spectrum of complex **1** displays three signals at 43.42, 25.78, and 21.54 ppm (Table III). The peak on the low-field side at 43.42 ppm is assigned to the phosphorus P_A of the coordinated DPBA, which is trans to chloride whereas the peaks at 25.78 and 21.54 ppm are assigned to the phosphorus atoms P_C and P_B (structure I; ϕ = Ph in all structures), respectively. The difference in chemical shifts of the two phosphorus nuclei of the chelated DPBA is understandable since one of the phosphorus atoms is trans to PPh_3 and other trans to chloride.[24] The proposed structure of complex **1** is shown in I.



I

In contrast to complex **1** the ^1H NMR spectrum of complex **2** is consistent with the meridional disposition of the ligand DABA. The signal corresponding to methylene protons attached to the $(C_6H_5)_2As$–group gives a multiplet centered at δ 3.30 and is not split into two multiplets as in the case of complex **1**. This indicates that both of the arsine ends of the ligand DABA coordinate in a mutually trans configuration. The resonance signal corresponding to the methylene protons of the bridged chains bonded toward the nitrogen end appear as a multiplet centered at δ 2.90. A resonance singlet due to benzyl methylene protons appears at δ 4.71. The phenyl protons appear as a broad multiplet around δ 7.00. The $^{31}P\{^1H\}$ NMR spectrum of complex **2** displays a signal at 47.92 ppm, corresponding to the coordinated phosphorus atom of triphenylphosphine, which is trans to chloride in the complex. The structure of complex **2** is shown in II.



II

The conductivity of complex **3** corresponds[23] to a 1:1 electrolyte (Table II). The infrared, conductivity, and microanalytical data are in accord with the formulation of this complex as the cationic species $[RuCl(DPBA)_2]^+$. The far-infrared spectrum of complex **3** exhibits intense bands at 510 and 530 cm^{-1}, which can be assigned to the ν(Ru–P) stretching mode of the bound DPBA ligand. An absorption band in the metal–chloride region at 315 cm^{-1} is consistent with the presence of a coordinated chloride in the coordination sphere of the metal ion. The ^1H NMR spectrum of complex **3** is not much use in the interpretation of structure as it displays very broad signals. The $^{31}P\{^1H\}$ NMR spectrum (Table III) suggests that one of the DPBA ligands, which is potentially terdentate, is coordinated to the metal atom through nitrogen and only one of its phosphorus atoms. The spectrum shows a higher field phosphorus resonance having a chemical shift of −20.40 ppm, very similar to that of the phosphorus atom of free DPBA, and the signal can therefore be assigned[25-27] to the

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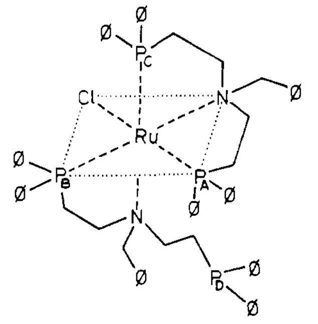
uncoordinated phosphorus atom P_D (structure III) of the complex.



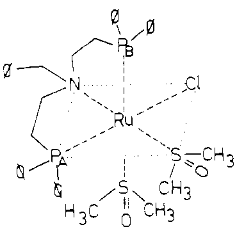
III

There are three apparent triplets on the downfield side, with the center peak having higher intensity than the other two peaks. The higher intensity of the middle peak is due to the merging of two component peaks of a quartet which is expected for this complex. The three triplets, centered at 58.92, 53.70, and 35.24 ppm, are assigned to the phosphorus atoms P_A, P_B, and P_C (structure III) with coupling constants $J(P_A{-}P_B) = 40$ Hz, $J(P_A{-}P_C) = 25$ Hz, and $J(P_B{-}P_C) = 22$ Hz. A J(P–P) value of 20–40 Hz is typical for the coupling constant of nonequivalent phosphorus nuclei cis to one another in ruthenium(II)–tertiary phosphine complexes.[28,29] The structure of complex **3** is shown in III.

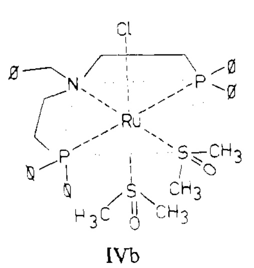
The displacement reactions of coordinated Me_2SO in the complex $RuCl_2(Me_2SO)_4$ with DPBA and DABA in acetone gave products of the compositions $[RuCl(Me_2SO)_2(DPBA)]Cl$ (**4**) and $[RuCl_2(Me_2SO)(DABA)]$ (**5**), respectively. Complex **4** showed conductivity consistent with a 1:1 electrolyte in DMF solution,[23] whereas complex **5** behaved as a nonelectrolyte (Table II). In the reaction of $RuCl_2(Me_2SO)_4$ with DPBA and DABA, displacement of the weakly coordinated O-bonded Me_2SO group takes place first, leaving the S-bonded Me_2SO groups in the complex. In the case of DPBA, two Me_2SO groups and one chloride are displaced. However, with DABA three of the four Me_2SO groups are displaced, yielding the neutral complex **5**. The infrared spectra of both complexes show a strong band at 1090 cm^{-1}, which can be assigned to the S=O stretch of S-bonded Me_2SO.[16,30] A strong band at 320 cm^{-1} can be assigned to ν(Ru–Cl) in complex **4**. In complex **5** the peak at 320 cm^{-1} may be due to ν(Ru–Cl) of the trans-disposed chlorides. From the available data, metal–sulfur stretching frequencies come in the region 400–500 cm^{-1}.[16,30-32] Intense bands at 440 and 490 cm^{-1} in complex **4** may be due to the metal–sulfur absorptions of the cis-disposed S-bonded Me_2SO groups but, however, in complex **5** the broad peak around 470 cm^{-1} may be due to the overlapping of the metal–arsine and metal–sulfur absorptions.

The ^1H NMR spectra of complexes **4** and **5** are well-resolved and provide information to support the configuration assigned to these complexes. The methyl resonance of the O-bonded Me_2SO group was reported[16] to appear close to that of free Me_2SO around δ 2.72 whereas for S-bonded Me_2SO groups the signal appears about 1 ppm downfield from the free Me_2SO resonance. Complexes **4** and **5** exhibit resonance peaks at δ 3.10 and 3.18, respectively, for the methyl protons of the S-coordinated Me_2SO groups. Besides these peaks, the ^1H NMR spectrum of complex **4** contains peaks corresponding to the DPBA ligand. The two multiplets centered at δ 2.80 and 3.35 correspond to the methylene protons of the bridging chain and the singlet at δ 4.80 to that of benzyl group. In complex **5** the multiplets centered at δ 2.60 and 3.40 can be assigned to the methylene protons of the bridging chain whereas a singlet at δ 4.80 is assigned to that of benzyl group. The phenyl protons in both complexes are observed in the region around δ 7.00.

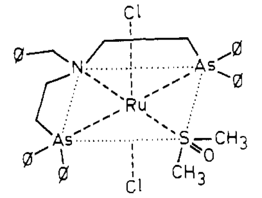
The $^{31}P\{^1H\}$ NMR spectrum of complex **4** displays two resonance absorptions due to two magnetically inequivalent phosphorus nuclei of DPBA at 42.84 and 27.00 ppm. The inequivalence of the two phosphorus atoms in the chelated DPBA may be due to the trans disposition of one of the phosphorus atoms to Cl (42.84 ppm) and other to Me_2SO (27.00 ppm). The structures of complexes **4** and **5** are shown in IVa and V, respectively. When the $^{31}P\{^1H\}$ NMR spectrum of complex **4** was taken in a more polar solvent like methanol, the spectrum displayed only a sharp singlet peak at 47.05 ppm, showing the equivalency of the two phosphorus atoms of the ligand DPBA. This behavior may be due to some sort of rearrangement taking place in the geometry of the molecule, and in the probable arrangement the phosphorus atoms of the ligand DPBA, which are trans to different groups (Cl and Me_2SO), rearrange to become trans to each other (meridional configuration, IVb), making them magnetically equivalent.



IVa



IVb



V

Reactions of DPBA and DABA with Wilkinson's green complex $RuCl_3(AsPh_3)_2MeOH$ in acetone resulted in the complete displacement of triphenylarsine groups to give neutral complexes of the type $[RuCl_3L]$ (L = DPBA (**6**), DABA (**7**)). The complexes exhibit paramagnetic susceptibilities of 2.10 (**6**) and 2.04 μ_B (**7**), respectively, corresponding approximately to one unpaired electron, expected for low-spin ruthenium(III) complexes. Complexes **6** and **7** are highly soluble in most of the common organic solvents. The conductivity data on **6** and **7** in DMF solution (Table II) shows that the complexes are nonelectrolytes.

Complexes **6** and **7** can exist either as facial or meridional isomers. The far-infrared spectrum of complex **6** exhibits three ν(Ru–Cl) frequencies at 290, 315, and 330 cm^{-1} in closer agreement with Ru–Cl frequencies reported[5,33] for *mer*-$[RuCl_3L_3]$ (L = mono(tertiary phosphine)). Similar bands at 280, 300, and 315 cm^{-1} are observed in the far-infrared spectrum of complex **7**. There are also intense bands at 510 and 485 cm^{-1} in complexes **6** and **7**, which can be assigned to ν(Ru–P) and ν(Ru–As) vibrational modes, respectively.

The ^1H NMR spectra of complexes **6** and **7** contain broadened resonance signals owing to the presence of the paramagnetic ruthenium(III) center. The resonance of the methylene protons of the benzyl group appears as a broad signal at δ 5.70 with considerable downfield shift in complex **6**. Two broad unresolved multiplets corresponding to two types of methylene protons of the ethyl chain appear at δ 5.35 and 4.95. The phenyl proton resonance absorption takes place at δ 7.25. The ^1H NMR spectrum of complex **7** was very much broadened, and as such not much structural information could be gathered from the spectrum. The $^{31}P\{^1H\}$ NMR spectrum of complex **6** (Table III) contains a singlet

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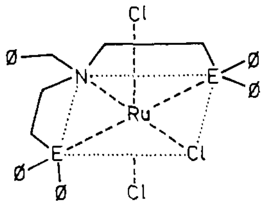
at 37.30 ppm corresponding to the magnetically equivalent coordinated phosphorus atoms of the ligand DPBA and is in conformity with the assigned structure of the complex.

The ESR spectrum of complex **6** exhibits a rhombic distortion with three g values at 2.37, 2.23, and 1.80. No hyperfine splitting due to nuclear interaction of other nuclei was observed. In the absence of a detailed quantitative analysis, it was not however possible to assign from the ESR spectrum the detailed **g** tensor values, viz. g_1, g_2, and g_3, to g_x, g_y, or g_z. The peak at the low-field side ($g = 2.37$) is more intense than the peaks at the higher field side. This pattern of the ESR spectrum was attributed[34] to the compressed rhombic distortion in the complex. The ESR spectrum of complex **7** however gives only two g values at 2.25 and 1.77 corresponding to $g_\perp$ and $g_\parallel$, respectively. Here the molecule may be axially distorted. The structures of complexes **6** and **7** are shown in VI.



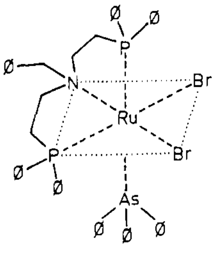
VI (E = P, As)

The reaction of $RuCl_3(AsPh_3)_2MeOH$ and DPBA under reflux in methanol gave the cationic complex $[RuCl(DPBA)_2]Cl_2$ (**8**). The conductivity of the complex in DMF corresponds[23] to a 1:2 electrolyte (Table II). The paramagnetism of this complex suggests that it is a low-spin ruthenium(III) complex. The far-infrared spectrum bands at 330 and 510 cm^{-1} can be assigned to the ν(Ru–Cl) and ν(Ru–P) modes, respectively. The cation $[RuCl(DPBA)_2]^{2+}$ can be assigned a structure similar to that of complex **3** (structure III).

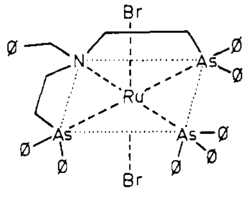
The ^1H NMR spectrum of complex **8** gives a very broad unresolved spectrum due to the broadening by the paramagnetic Ru(III) center. The $^{31}P\{^1H\}$ NMR spectrum however displays features similar to that of complex **3** (Table III). There are three triplets centered at 58.86, 48.14, and 34.27 ppm on the downfield side, which correspond to the phosphorus atoms P_A, P_B, and P_C of the ligands (structure III). The coupling constant values are also similar to those of complex **3**, with $J(P_A–P_B) = 40$ Hz, $J(P_A–P_C) = 28$ Hz, and $J(P_B–P_C) = 22$ Hz. A singlet on the high-field side at −19.67 ppm can be assigned to the uncoordinated phosphorus atom of the bidentate ligand. The ESR investigation of complex **8** gave a poorly resolved spectrum with the g_{av} value 2.16. The structure assigned to complex **8** is similar to that of complex **3**, as shown in III.

The reaction between $RuBr_3(AsPh_3)_2MeOH$, and DPBA or DABA in boiling acetone resulted in the formation of $[Ru(AsPh_3)(L)Br_2]Br$ (L = DPBA (**9**), DABA (**10**)). The complex $[RuBr_3(DABA)]$ (**11**) was also obtained from the reaction mixture containing $RuBr_3(AsPh_3)_2MeOH$ and a twofold excess of DABA. On the basis of conductivities in DMF (Table II) complexes **9** and **10** are formulated as 1:1 electrolytes[23] and **11** is a nonelectrolyte. Complexes **9–11** are paramagnetic, low-spin ruthenium(III) species (Table I). The far-infrared spectrum of complex **9** exhibits strong bands at 265 and 235 cm^{-1}, which can be assigned to the ν(Ru–Br) modes of the cis bromides. Complex **10** exhibits only one ν(Ru–Br) mode at 225 cm^{-1}, indicating the trans disposition of the bromides. The infrared spectra also display ν(Ru–As) frequencies of the $AsPh_3$ group at 460 cm^{-1} in both **9** and **10**. The ν(Ru–P) and ν(Ru–As) modes of the coordinated DPBA and DABA are exhibited at 510 and 475 cm^{-1} in complexes **9** and **10**, respectively. **9** and **10** give very broad unresolved ^1H NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum of complex **9** shows two doublets centered at 57.85 and 28.00 ppm, which shows the inequivalence of the two coordinated phosphorus atoms. The difference in chemical shifts of two phosphorus atoms of chelated DPBA may be due to the disposition of one of the phosphorus atoms trans to $AsPh_3$, a π-acid (doublet at 28.00 ppm), and the other to Br^-, a σ-base (doublet at 57.85 ppm). The coupling constant $J(P_A–P_B) = 27$ Hz shows that the phosphorus atoms are cis to each other.[28,29]

The ESR spectrum of complex **9** gives three values for its **g** tensor, 2.44, 2.26, and 1.71, corresponding to g_1, g_2, and g_3. Here also the molecule shows a compressed rhombic distortion, since the three g values are different and the peak at low-field side ($g = 2.44$) is more intense than the peaks at higher field side. The ESR spectrum of complex **10** is not well-resolved and hence a g_{av} value of 2.25 is calculated. Complexes **9** and **10** have cis and trans bromides, and the structures are shown in VII and VIII, respectively.



VII



VIII

The far-infrared spectrum of complex **11** exhibits ν(Ru–Br) frequencies at 250, 210, and 200 cm^{-1}. The spectrum exhibits only one intense band at 475 cm^{-1}, which corresponds to the ν(Ru–As) mode of the DABA ligand. Well-resolved ^1H NMR and ESR spectra could not be obtained for the complex. A geometry similar to that of complex **7** can be assigned to complex **11**.

The reaction between hydrated ruthenium trichloride and the ligand DPBA in boiling methanol in the presence of NH_4PF_6 gave the cationic Ru(II) complex $[Ru(DPBA)_2]^{2+}$, which was isolated as its hexafluorophosphate salt **12**. The complex exhibited conductance for a 1:2 electrolyte (Table II). The complex is diamagnetic, in conformity with the spin-paired Ru(II) $(t_{2g})^6$ configuration.

The far-infrared spectrum of complex **12** shows no bands around 300 cm^{-1} that can be assigned to ν(Ru–Cl) modes, confirming the complete absence of chlorides in the coordination sphere of the metal ion. The bands at 510 and 535 cm^{-1} are assigned to ν(Ru–P) modes.

The ^1H NMR spectrum of complex **12** consists of a well-resolved phenyl multiplet centered around δ 7.10 and methylene multiplets around δ 3.05 and 2.70. The ^1H NMR spectrum of the complex also contains an unusual AB quartet centered at δ 4.15, due to the methylene protons of the benzyl group. The origin of this quartet may be explained on the basis of magnetic inequivalency induced in the two methylene protons by the restricted rotation of the benzyl group flanked by the bulky phenyl groups attached to the cis-phosphorus atoms of the coordinated phosphines. The ^{31}P NMR spectrum of complex **12** gives a sharp singlet at 59.03 ppm, suggesting the equivalence of all four phosphorus atoms of the two DPBA ligands. It has been observed in $^{31}P\{^1H\}$ NMR studies that there is a large downfield shift upon coordination of the ligand DPBA to form five-membered chelate rings as noted by earlier workers.[26,27,35] A facial or meridional geometry can be proposed for complex **12**, with all the donor atoms of the ligand DPBA coordinating to the metal ion.

The reaction of $RuCl_3{\cdot}3H_2O$ with DABA in methanol gave the cationic complex $[RuCl(DABA)_2]Cl_2$ (**13**), whose conductance is consistent with a 1:2 electrolyte (Table II). Complex **13** shows paramagnetism of 2.05 μ_B, the value expected for a ruthenium(III) low-spin complex. Complex **13** displays a very strong band due to ν(Ru–Cl) at 310 cm^{-1} and a band at 480 cm^{-1} due to the ν(Ru–As) mode. The ^1H NMR spectrum is not well resolved and

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is considerably broadened due to the paramagnetic Ru(III) center. The ESR spectrum gives three values for its **g** tensor, 2.55, 2.40, and 1.73, corresponding to g_1, g_2, and g_3 in accord with a compressed rhombic distorted configuration. The structure of complex **13** (structure III) is similar to that of complex **8** with only one of the arsine ends of the ligand DABA coordinating to the metal atom and the other end free. The other DABA acts as a terdentate ligand.

The electronic spectral data for complexes **1**–**13** are presented in Table IV. The molar extinction coefficient values are all higher than the conventional values for d–d transitions due to charge-transfer character of the bands. In the case of Ru(II) complexes with spin-paired $(t_{2g})^6$ ground configurations, two d–d bands are observed in the range 420–490 nm and 330–380 nm. Complexes **6**–**11** and **13** are distorted-octahedral Ru(III) species with spin-paired $(t_{2g})^5$ ground configuration. The bands in the range 500–600 nm in the complexes may be assigned to the d–d transition with LMCT character. The intense bands around 230 nm in both Ru(II) and Ru(III) complexes can be assigned to the $\pi-\pi^*$ transitions of the phenyl rings whereas the other higher energy bands may be due to LMCT or the charge transfer involving P or As lone pairs and the phenyl rings.

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Supplementary Material Available: A detailed discussion of ^1H, ^{31}P, and ^{13}C NMR spectra with figures and mass spectra with fragmentation schemes of the ligands DPBA and DABA and the $^{31}P\{^1H\}$ NMR spectrum of complex **3** (9 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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A New Mixed-Ligand Diruthenium(II) Compound. Synthesis and Characterization of $[Ru_2Cl(Me_2PCH_2PMe_2)_2(PhNpy)_2][BPh_4]$

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The title compound was prepared by reacting $Ru_2Cl(O_2CCH_3)_2(PhNpy)_2(PhNHpy)$, which was obtained from an in situ reaction of $Ru_2Cl(O_2CCH_3)_4$ and 2-anilinopyridine (PhNHpy), and (dimethylphosphino)methane (dmpm) in the presence of chlorotrimethylsilane in toluene. The compound was isolated as a crystalline mass by cooling a methanolic solution of the complex in the presence of $Na[BPh_4]$. The crystals of composition $[Ru_2Cl(dmpm)_2(PhNpy)_2][BPh_4]\cdot 1.5MeOH$ belong to the monoclinic system, space group $P2_1/n$, with the following unit cell dimensions: a = 14.064 (5) Å, b = 24.047 (8) Å, c = 18.642 (4) Å, $\alpha = \gamma$ = 90°, β = 110.52 (2)°, V = 5905 (3) Å^3, Z = 4. The cationic species $[Ru_2Cl(dmpm)_2(PhNpy)_2]^+$ consists of a diruthenium(II) core held by two dmpm and two $PhNpy^-$ ligands. The orientation of the $PhNpy^-$ ligands is unidirectional. The ruthenium that is bonded to pyridine nitrogens has an axial Cl^- ligand while the axial site on the other ruthenium is vacant because of two pendant phenyl rings on the amine nitrogen atoms. The Ru–Ru distance is 2.340 (2) Å. The Ru–Cl, average Ru–P, and average Ru–N distances are 2.480 (5) Å, 2.396 [5] Å, and 2.122 [12] Å, respectively. The average torsion angle in N–Ru–Ru–N and P–Ru–Ru–P is 19.84°. The compound is moderately stable in air in the solid state and is soluble in common organic solvents. The complex is paramagnetic and has a magnetic moment of 2.6 μ_B (at 308 K), corresponding to two unpaired spins. The metal–metal bond order is 2.0 according to the $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^4$ ground-state electronic configuration. The electronic spectrum of an acetonitrile solution of the complex exhibits a band at 395 nm (ϵ = 2600 M^{-1} cm^{-1}) and a shoulder at 320 nm. Cyclic voltammetry of the compound in acetonitrile displays two metal-centered one-electron oxidative processes at +0.332 (ΔE_p = 64 mV) and +1.195 V (ΔE_p = 74 mV) at v = 100 mV s^{-1}. A ligand-centered reduction is observed at −0.632 V (ΔE_p = 95 mV). A linear correlation is observed between the redox potentials of the Ru(III)Ru(II)/Ru(II)Ru(II) couples and the position of the lowest energy bands in the electronic spectra among diruthenium(II) compounds.

Introduction

The present work stems from our current exploration of the chemistry of diruthenium complexes having ruthenium–ruthenium multiple bonds. The systems that have been most thoroughly studied[1-9] are the diruthenium tetracarboxylates, in which the metal atoms are in different formal oxidation states. These compounds are all paramagnetic with three unpaired spins. Recent development in this field has shown that many other types of Ru(II)Ru(III) compounds can be made and that the reactivity pattern and the general nature of these Ru(II)Ru(III) complexes are quite different from those of other dimetallic species. One example is the reactivity of triarylphosphines toward tetrakis(amidato) species $Ru_2Cl(ArCONH)_4$ in which aryl group migration from PAr_3 onto the metal center takes place along with a synergic formation of a P to amidato oxygen bond.[10,11] The resulting complex is an edge-sharing bioctahedral Ru(III)Ru(III) species with an Ru–Ru single bond. The reactions between three-atom-bridging ligands of the type 2-hydroxypyridine and its derivatives, as well as 2-anilinopyridine, which have N,O- and

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