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Platinum Group Metal Complexes of Bis(2-(diphenylphosphino)ethyl)benzylamine and Bis(2-(diphenylarsino)ethyl)benzylamine

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Abstract

Rh(I), Ir(I), Pd(II) and Pt(II) metal complexes of bis(2-(diphenylphosphino)ethyl)benzylamine (DPBA) and bis(2-(diphenylarsino)ethyl)benzylamine (DABA) have been synthesized using various starting materials. Reaction of $RhCl(CO)(AsPh_3)_2$ with DPBA or DABA in methanol resulted in the formation of cationic complexes of the composition, [Rh(CO)(L)]Cl (L = DPBA or DABA). Interaction of $[IrCl(COD)]_2$ with DPBA in benzene resulted in the formation of a neutral complex [IrCl(DPBA)]. Reaction of $[PdCl_2(COD)]$ with the ligand DPBA in benzene resulted in a cationic complex of the composition [PdCl(DPBA)]Cl. Interaction of $[PdCl(DPBA)]BPh_4$ with $SnCl_2$ gave the complex $[Pd(SnCl_3)(DPBA)]BPh_4$. The ligands DPBA and DABA react with $PtCl_2(COD)$ in acetone to give neutral, Pt(II) complexes of the type, $[PtCl_2L]$ (L = DPBA or DABA). All the complexes were fully characterized by elemental analysis, conductivity measurements, IR and far-IR and $^{31}P\{^1H\}$ NMR spectral data.

Introduction

Platinum group metal complexes containing donor ligands like CO, PPh_3, $AsPh_3$, 1,5-COD(cycloocta-1,5-diene) etc. have been used extensively as starting precursors for the synthesis of other complexes. It is generally assumed that the weakly bound ligands are simply replaced by the incoming nucleophiles. Recently we have reported reactions of some polydentate mixed donor (N and P or As) ligands with platinum group metal complexes of the above ligands, where in most of the cases the simple displacement of the CO, $AsPh_3$, 1,5-COD or cyclooctene was found to take place [1–4]. We now report complexes of two mixed donor terdentate ligands, bis(2-(diphenylphosphino)ethyl)benzylamine (DPBA) and bis(2-diphenylarsino)ethyl)benzylamine (DABA), which have N and P or As as donor atoms, with platinum group metal complexes having CO, $AsPh_3$ or 1,5-COD ligands.

Experimental

The complexes $RhCl(CO)(AsPh_3)_2$ [5], $[IrCl(COD)]_2$ [6], $PdCl_2(COD)$ [7], $PtCl_2(COD)$ [8] and $[PtCl(DPBA)]BPh_4$ [9] were prepared by published procedures. The ligand bis(2-(diphenylphosphino)ethyl)benzylamine (DPBA) was synthesized as reported in our earlier publication [1]. All the solvents were of Analar grade and distilled before use. All the preparations were carried out in a dry nitrogen atmosphere. Microanalysis, melting points, infrared spectra, conductivity measurements were done as reported [10]. ^1H NMR spectra were recorded on a Jeol FX 100 spectrometer operating at 100 MHz using TMS as an internal standard. The proton noise decoupled phosphorus-31 NMR spectra of the complexes were taken using the same instrument operating at 40.3 MHz in the FT mode with a deuterium lock. 85% H_3PO_4 was used as an external reference.

Preparation of Complexes

Carbonylbis(2-(diphenylphosphino)ethyl)benzylamine)rhodium(I)chloride, [Rh(CO)(DPBA)]Cl (1) and Carbonylbis(2-(diphenylarsino)ethyl)benzylamine)rhodium(I)chloride, [Rh(CO)(DABA)]Cl (2)

To a refluxing methanolic solution of $RhCl(CO)(AsPh_3)_2$ (0.200 g, 0.26 mmol) were added the ligands DPBA (0.136 g, 0.26 mmol) or DABA (0.159 g, 0.26 mmol) in equimolar quantities in two different reactions and further refluxed for 4–5 h. The solutions were then concentrated to a small volume by vacuum rotary evaporator and diethylether added to get yellow precipitates in both cases. The complexes were filtered, washed with diethylether and recrystallized from cold methanol. DPBA: yield 0.152 g (85%), melting point (m.p.) > 200 °C; DABA: yield 0.16 g (80%), m.p. > 200 °C.

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Chlorobis(2-(diphenylphosphino)ethyl)benzylamine)iridium(I), [IrCl(DPBA)] (3)

To a refluxing benzene solution of $[IrCl(COD)]_2$ (0.175 g, 0.26 mmol) was added the ligand DABA (0.140 g, 0.26 mmol) to get a yellow coloured solution. After refluxing further for 4–5 h the solution was concentrated to a small volume by rotary vacuum evaporator and the complex precipitated by the addition of petroleum ether (60–80°). The resulting yellow complex was filtered, washed with diethylether and dried. Yield 0.175 g (87%), m.p. > 200 °C.

Chlorobis(2-(diphenylphosphino)ethyl)benzylamine)palladium(II)chloride, [PdCl(DPBA)]Cl (4)

To the refluxing benzene solution of $PdCl_2(COD)$ (0.200 g, 0.70 mmol) was added the ligand DPBA (0.372 g, 0.70 mmol) and the solution further refluxed for 4–5 h. After keeping the solution overnight the precipitated pale-yellow complex was filtered, washed with benzene and diethylether and dried. Yield 0.360 g (90%), m.p. > 200 °C.

Trichlorostannatobis(2-(diphenylphosphino)ethyl)benzylamine)palladium(II)tetraphenylborate, [Pd(SnCl$_3$)(DPBA)]BPh$_4$ (5)

To the refluxing acetone solution of $[PdCl(DPBA)]BPh_4$ (0.200 g, 0.20 mmol) was added 0.038 g (0.20 mmol) of $SnCl_2$ taken in 5 ml of methanol and further refluxed for 4–5 h. The solution was then concentrated to a small volume and the yellow complex precipitated by the addition of diethylether. The complex was then dissolved in dichloromethane and evaporated to dryness. The complex was recrystallized from methanol benzene–diethylether mixture. Yield 0.125 g (62%), m.p. > 200 °C.

Dichlorobis(2-(diphenylphosphino)ethyl)benzylamine)platinum(II), PtCl$_2$(DPBA) (6) and Dichlorobis(2-(diphenylarsino)ethyl)benzylamine)platinum(II), PtCl$_2$(DABA) (7)

To the refluxing acetone solution of $PtCl_2(COD)$ (0.200 g, 0.53 mmol) were added the ligands DPBA (0.282 g, 0.50 mmol) or DABA (0.309 g, 0.53 mmol) in two different reactions. After refluxing for 4–5 h, a white precipitate settled down in both the cases. The precipitates were filtered, washed with acetone and diethylether and dried. DPBA: yield 0.345 g (80%), m.p. > 200 °C; DABA: yield 0.35 g (75%), m.p. > 200 °C.

Results and Discussion

Treatment of $RhCl(CO)(AsPh_3)_2$ with 1 mole equivalent of DPBA or DABA resulted in the formation of yellow, cationic complexes of the composition, [Rh(CO)(L)]Cl (L = DPBA (**1**); DABA (**2**)) with the complete displacement of the triphenylarsine groups. This is in contrast to the reaction of $RhCl(CO)(PPh_3)_2$ with DPBA or DABA where the carbonyl and only one of the two triphenyl phosphine groups are displaced [9] to give complexes of the type $[Rh(PPh_3)(L)]Cl$ (L = DPBA or DABA). Complexes **1** and **2** show conductance values consistent with a 1:1 electrolyte in DMF (Table I) [11].

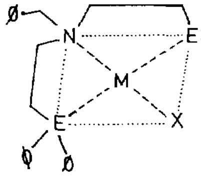
TABLE I. Analytical and NMR Spectral Data of the Complexes

Compound	Elemental analysis (%)[a]			^{31}P NMR[b]		^{1}H NMR[f] δ (ppm)	Conductivity[g] λ_∞ (Ω^{-1} cm^2 mol^{-1})
	C	H	N	δ (ppm)	J(M–P) (Hz)		
[Rh(CO)(DPBA)]Cl (**1**)	61.9 (61.5)	5.0 (5.0)	2.0 (1.9)	30.0[c]		7.4(m)(Ph); 3.3(m), 2.9(m) ($-CH_2CH_2-$); 4.3(s)($-CH_2-$)	74
[Rh(CO)(DABA)]Cl (**2**)	55.0 (54.9)	4.5 (4.5)	1.8 (1.7)			7.4(m)(Ph); 3.2(m), 2.8(m) ($-CH_2CH_2-$); 4.2(s)($-CH_2-$)	78
[IrCl(DPBA)] (**3**)	54.6 (54.1)	4.6 (4.5)	1.8 (1.8)	17.5[d]		7.2(m)(Ph); 3.2(m), 2.8(m) ($-CH_2CH_2-$); 4.1(s)($-CH_2-$)	5
[PdCl(DPBA)]Cl (**4**)	59.2 (59.1)	4.9 (4.9)	2.0 (1.9)	31.3[d]		7.40(m)(Ph); 3.30(m); 2.90(m) ($-CH_2CH_2-$), 4.5(s)($-CH_2-$)	71
$[Pd(SnCl_3)(DPBA)]BPh_4$ (**5**)	59.9 (59.5)	4.7 (4.7)	1.2 (1.2)	31.6[e]	47.6		90
$[PtCl_2(DPBA)]$ (**6**)	52.7 (52.3)	4.4 (4.3)	1.8 (1.8)	−2.6[d]	2730.4	7.3(m)(Ph); 2.80(m), 2.45(m) ($-CH_2CH_2-$); 3.45(s)($-CH_2-$)	3
$[PtCl_2(DABA)]$ (**7**)	47.5 (47.3)	4.0 (4.0)	1.6 (1.6)			7.3(m)(Ph), 2.75(m), 2.40(m) ($-CH_2CH_2-$); 3.42(s)($-CH_2-$)	6

[a] Found values are given in parentheses. [b] Positive chemical shifts downfield from 85% H_3PO_4. [c] in CH_2Cl_2. [d] in $CHCl_3$. [e] in acetone. [f] Chemical shifts in $CDCl_3$ are relative to internal Me_4Si. [g] Conductivity measurements were done in DMF at room temperature and values reported for infinite dilution.

The infrared spectra of complexes **1** and **2** exhibit intense bands at 1980 and 1950 cm^{-1}, respectively, indicating the coordination of the carbonyl group to the metal ion. The proton (^1H) NMR spectrum of **1**, exhibits resonances from the phenyl protons as a multiplet around 7.4 δ and resonances from the protons of the CH_2CH_2 bridges as broad multiplets centered at 3.3 δ and 2.9 δ. The peak at 2.9 δ may be due to the resonance of CH_2 protons attached to the amine center, whereas the peak at 3.2 δ is due to the CH_2 protons bonded to the $-PPh_2$ end. Both the resonances appear as complex, asymmetric multiplets possibly due to the interaction of neighbouring methylene protons followed by the coupling of ^{31}P nuclear spin. There is also a singlet at 4.3 δ which is assigned to the methylene protons of the benzyl group of the ligand DPBA. Similarly the ^1H NMR spectrum of **2** exhibits phenyl protons resonances at around 7.4 δ as a multiplet owing to the presence of a large number of magnetically non-equivalent phenyl protons. The methylene protons attached to the nitrogen center from the CH_2CH_2 bridges exhibit resonance at 2.8 δ and those attached to the arsenic moiety at 3.2 δ as multiplets. A singlet at 4.2 δ is assigned to the CH_2 protons of the benzyl group. There is considerable downfield shift in all these resonances when compared to those of the free ligands [1], owing to the coordination of all donor atoms of the potential terdentate ligands DPBA and DABA to the metal ion.

The $^{31}P\{^1H\}$ NMR spectrum of **1** exhibits a singlet at 30.0 δ due to the *trans* disposed magnetically equivalent phosphorus atoms of the ligand DPBA. The presence of a singlet instead of a doublet (due to coupling with Rh nucleus, $S = 1/2$) can be attributed to the rapid intramolecular exchange of the Rh–P bonds and this exchange process could not be stopped even after cooling the sample to −20 °C. The geometry of complexes **1** and **2** can therefore be assigned as shown in Scheme 1.



Scheme 1. M = Rh(I), X = CO; M = Ir(I), Pd(II); X = Cl, $SnCl_3$; E = P, As.

In the reactions of $[Ir(Cl(COD)]_2$, $[PdCl_2(COD)]$ and $[PtCl_2(COD)]$ with the ligands DPBA and DABA, displacement of diolefin took place.

Reaction of $[IrCl(COD)]_2$ with the ligand DPBA in benzene gave a neutral complex of the composition [IrCl(DPBA)] (**3**). Complex **3** is non-conducting in DMF solvent (Table I). The far-infrared spectrum of **3** exhibits an intense band at 310 cm^{-1} indicative of a ν(Ir–Cl) stretching mode. The ^1H NMR spectrum of **3** also exhibits considerable downfield resonances of phenyl protons as a multiplet centered at 7.2 δ. The methylene protons attached to the nitrogen center are observed at 2.8 δ and those of the CH_2 protons attached to the $-PPh_2$ group at 3.2 δ as broad multiplets and CH_2 protons of the benzyl group as a singlet at 4.1 δ. The $^{31}P\{^1H\}$ NMR spectrum exhibits an intense singlet at 17.5 δ indicating the magnetic equivalence and *trans* coordination of the two phosphorus ends of the ligand DPBA. A square-planar geometry with the donor atoms (N, P or As of the ligands) coordinated to the metal ion was proposed as is shown in Scheme 1.

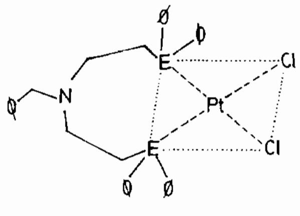
Reaction of $PdCl_2(COD)$ with the ligand DPBA in benzene resulted in the formation of a square-planar, cationic complex [PdCl(DPBA)]Cl (**4**) which has also been synthesized by the reaction of $PdCl_2$ with DPBA in methanol [12]. Complex **4** is a 1:1 electrolyte and exhibits an intense ν(Pd–Cl) stretching mode at 345 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of **4** displays a singlet at 31.3 δ similar to that of the δ value of the complex synthesized from $PdCl_2$ [9, 12]. The assigned geometry of the complex is similar to that of Scheme 1.

Interaction of $[PdCl(DPBA)]BPh_4$ [9] with $SnCl_2$ in methanol–acetone mixture gave a complex with a $SnCl_3^-$ ligand coordinated to the metal ion $[Pd(DPBA)(SnCl_3)]BPh_4$ (**5**). Complex **5** is a 1:1 electrolyte [11] in DMF (Table I). The $^{31}P\{^1H\}$ NMR of the complex exhibits a triplet centered at 31.6 δ with $J(^{119}Sn-^{31}P) = 47.6$ Hz confirming the presence of a coordinated $SnCl_3^-$ ligand and also its *cis* disposition [13] to the two *trans* phosphorus atoms of the ligand DPBA as shown in Scheme 1.

Interaction of $PtCl_2(COD)$ with the ligands DPBA and DABA gave neutral, square-planar complexes of the type $[PtCl_2(L)]$ (L = DPBA (**6**); DABA (**7**)). Complexes **6** and **7** are non-conducting (Table I). The infrared spectra of **6** and **7** show ν(Pt–Cl) stretching as intense bands at 330 and 315 cm^{-1} and 320 and 310 cm^{-1}, respectively due to the *cis* coordination of the two chloro groups to the metal ion. The ^1H, $^{31}P\{^1H\}$ NMR and above spectral and conductivity data support the above formulation for **6** and **7** in which the nitrogen donor atom is uncoordinated to the metal ion in contrast to that of a similar complex [PtCl(DPBA)]Cl which has been synthesized [9] by the reaction of K_2PtCl_4 with DPBA in water–acetone mixture where all the donor atoms of the terdentate ligand DPBA are coordinated to the metal ion. The ^1H NMR spectra of **6** and **7** exhibit the resonances due to methylene group CH_2 protons of the benzyl group which is attached to the nitrogen center at 3.45 δ and 3.42 δ, respectively. These values are almost similar to the chemical shift values of the CH_2 protons of the benzyl group of the free ligands DPBA and DABA

[1] (3.56 δ for DPBA and 3.50 δ for DABA) and it can therefore be presumed that the nitrogen donor atom is uncoordinated to the metal ion and thus the potential terdentate ligands act as bidentate ligands in the complexes. The steric effect and the less coordinating tendency of the tertiary nitrogen could account for the presumed detachment of the nitrogen donor [14]. The ^{1}H NMR also exhibits resonances due to the CH_2CH_2 bridges less downfield in comparison to that of complexes **1**–**3** where all the donor atoms participate in coordination. Complexes **6** and **7** exhibit multiplets at 2.80 δ (DPBA) and 2.75 δ (DABA) due to the CH_2 protons of the CH_2CH_2 bridges attached to the $-EPh_2$ end (E = P, As) and CH_2 protons attached to the nitrogen end gives resonance signal at 2.45 δ (DPBA) and 2.40 δ (DABA) also as multiplets. The protons of the phenyl exhibit resonances around 7.3 δ as complex multiplets for **6** and **7**.

The $^{31}P\{^1H\}$ NMR spectrum of complex **6** exhibits a sharp singlet at −2.6 δ (with ^{195}Pt satellites) indicating the magnetic equivalence of the two phosphorus ends of the ligand DPBA. The ^1J(Pt–P) coupling constant as calculated from its ^{195}Pt satellites is 2730.4 Hz. The comparatively low downfield chemical shift of the ^{31}P resonance might be due to the formation of a large chelate ring [15] corroborating the bidentate nature of the ligand DPBA. Based on the above information a square-planar geometry with uncoordinated nitrogen is proposed for **6** and **7** as shown in Scheme 2.



Scheme 2. E = P, As.

The ^{31}P NMR chemical shifts (δ) of all the complexes reveal that there is a good correlation between the size of the metal ion and chemical shifts [15]. The ^{31}P NMR chemical shifts of coordinated complexes are generally observed downfield as compared to that of the free ligand due to the strong σ-donor bond from phosphorus to metal with a small d_π–d_π back donation [15]. As the size of the metal ion increases and electronegativity decreases the δ values are shifted less downfield due to the weak metal–phosphorus σ-bond and a strong metal to ligand d_π–d_π back bonding interaction [16]. This is also observed in the present work with δ values decreasing in the order Rh > Ir and Pd > Pt (Table I). In addition to the above reasons the other factor effecting the downfield shift in the Pt(II) complex of DPBA, $PtCl_2$(DPBA) (**6**), is the large chelate ring size [15]. It has been observed [16] that the *cis*-^1J(Pt–P) value of 2730.4 Hz in complex **6** can also be attributed to the large size chelate ring in the complex.

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