Ni(II), Pd(II), and Pt(II) Complexes of Two New Ditertiary Phosphines, 1-Diphenylphosphino-2-bis(*m*- or *p*-fluorophenyl) Phosphinoethane

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Abstract

New complexes of the type *cis*-$[MX_2(P-P')]$ (M = Ni, Pd and Pt; X = Cl, Br, I or NCS and P–P' = (m-$FC_6H_4)_2PCH_2CH_2PPh_2$ or (p-$FC_6H_4)_2PCH_2CH_2PPh_2$) have been synthesized and characterized on the basis of $^{31}P\{^1H\}$ NMR, ^1H NMR, IR and UV spectroscopy, elemental analysis and magnetic susceptibility measurements. All these complexes are found to be low spin, diamagnetic and square planar. $^{31}P\{^1H\}$ spectra of these complexes exhibit extraordinarily large downfield coordination chemical shifts. $J(^{31}P-^{31}P')$ and $J(^{195}Pt-^{31}P)$ couplings are discussed. Ring contribution (ΔR) values for palladium and platinum complexes are calculated from ^{31}P NMR data.

Introduction

Recently there has been considerable interest in the synthesis of bidentate phosphine ligands with: (a) large backbones, in order to examine the precise role that length and nature of the backbone plays in determining the stereochemistry of the complexes with transition metals [1–4], and (b) chemically and magnetically different phosphorus nuclei attached to the same chelate backbone, due to the utility of ^{31}P NMR as a probe for the investigation and elucidation of the factors that determine the stereochemistry and reactivity of the resulting transition metal complexes [5–9].

This paper deals with the synthesis and characterisation of nickel(II), palladium(II) and platinum-(II) complexes of two new unsymmetrical ditertiary phosphines, $R_2PCH_2CH_2PPh_2$ where R = m-FC_6H_4 or p-FC_6H_4. This study was undertaken in order to prepare more soluble complexes so that the ^{31}P NMR studies which were previously precluded, due to poor or insufficient solubility of resulting complexes, can be carried out. In an earlier communication we reported the preparation of two new unsymmetrical ditertiary phosphines **1a** and **1b** [10]. This paper

1a

1b
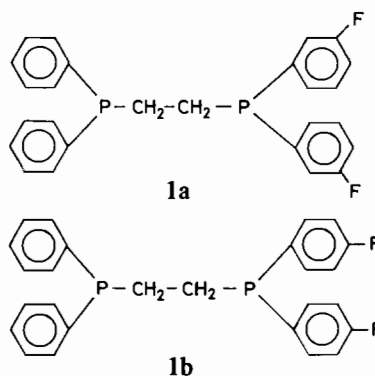
describes the synthesis of their metal complexes with Ni(II), Pd(II) and Pt(II).

Experimental

Elemental analyses were obtained from the microanalytical laboratories of the Department of Chemistry, University of Delhi and Australian National University, Canberra.

Far IR spectra were recorded in CsI on a 621 grating spectrophotometer. ^1H NMR were recorded in $CDCl_3$ solution on a Varian A-60 instrument using TMS as internal indicator. $^{31}P\{^1H\}$ NMR spectra were measured in the FT mode on a Bruker WH-90 instrument operating at spectrometer frequency 36.43 MHz. The chemical shifts are referred externally to 85% H_3PO_4. All these ^{31}P NMR spectra were obtained from University of Texas at Austin, U.S.A.

Reactions involving ditertiary phosphines were carried out in an atmosphere of purified nitrogen using standard Schlenk tube techniques. Solvents were dried in the usual way [24, 25] and degassed by distillation through a stream of nitrogen.

Preparation of Complexes

[Ni(1a)Cl₂]

$NiCl_2 \cdot 6H_2O$ (0.42 g, 1 mmol) was dissolved in butanol-1 (30 ml) on refluxing for 1 h to produce a green solution. The ligand **1a** (0.43 g, 1 mmol) was

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TABLE I. Elemental Analysis, IR and UV Data

Compound[a]	Colour	Melting point (decomposition)	Analysis (found (calc.))			ν (M−X) (cm^{-1})	λ (nm) in acetone
			% C	% H	% P		
[Ni(1a)Cl$_2$]	red	206−208	55.4 (55.1)	3.9 (3.6)	10.9 (10.5)	326, 340	465
[Ni(1a)Br$_2$]	brown	220−221	47.8 (47.3)	3.4 (3.1)	9.5 (9.2)	264, 290	475
[Ni(1a)I$_2$]	mauve	256−257	41.8 (41.5)	2.9 (2.6)	8.3 (8.2)	−	490
[Ni(1a)(NCS)$_2$]	yellow	225−226	55.2 (55.0)	3.6 (3.4)	10.2 (9.8)	−	440
[Pd(1a)Cl$_2$]	light-yellow	264−266	51.0 (50.9)	3.5 (3.6)	10.1 (9.7)	285, 310	
[Pd(1a)Br$_2$]	yellow	256−257	44.6 (44.9)	3.1 (2.9)	8.8 (8.6)	235, 265	
[Pd(1a)I$_2$]	yellow	270−271	39.3 (39.5)	2.8 (2.8)	7.8 (7.6)		
[Pd(1a)(NCS)$_2$]	yellow	249−250	51.2 (50.8)	3.3 (3.4)	9.4 (9.5)		
[Pt(1a)Cl$_2$]	white	280−282	44.6 (44.3)	3.1 (3.2)	8.8 (8.6)	290, 315	
[Pt(1a)Br$_2$]	yellow	250−252	39.6 (39.3)	2.8 (2.6)	7.9 (7.6)	225, 275	
[Pt(1a)I$_2$]	yellow	268−270	35.4 (35.4)	2.6 (2.5)	7.0 (6.8)		
[Ni(1b)Cl$_2$]	red	225−227	55.4 (55.0)	3.9 (3.5)	11.0 (10.4)	320, 344	472
[Ni(1b)Br$_2$]	orange	258−260	47.8 (47.6)	3.4 (3.0)	9.5 (9.1)	260, 285	480
[Ni(1b)I$_2$]	mauve	230−232	41.8 (41.3)	2.9 (2.7)	8.3 (8.0)	−	495
[Ni(1b)(NCS)$_2$]	yellow	270−271	55.2 (54.9)	3.6 (3.5)	10.2 (9.8)	−	455
[Pd(1b)Cl$_2$]	pale-yellow	250−253	51.0 (51.2)	3.6 (3.3)	10.1 (9.9)	285, 305	
[Pd(1b)Br$_2$]	yellow	274−275	44.6 (44.9)	3.1 (2.9)	8.8 (8.5)	230, 262	
[Pd(1b)I$_2$]	yellow	257−258	39.3 (39.2)	2.8 (2.5)	7.8 (7.9)		
[Pd(1b)(NCS)$_2$]	yellow	286−287	51.2 (51.2)	3.3 (3.3)	9.4 (9.0)		
[Pt(1b)Cl$_2$]	white	261−263	44.6 (44.2)	3.1 (3.2)	8.8 (8.5)	286, 312	
[Pt(1b)BR$_2$]	yellow	276−278	39.6 (39.4)	2.8 (2.4)	7.8 (7.6)	222, 270	
[Pt(1b)I$_2$]	brown	280−281	35.4 (35.1)	2.5 (2.1)	7.0 (6.8)	−	

[a] 1a = (m-FC$_6$H$_4$)$_2$PCH$_2$CH$_2$PPh$_2$, 1b = (p-FC$_6$H$_4$)$_2$PCH$_2$CH$_2$PPh$_2$.

added to it, producing a deep red solution. It was refluxed for 2 h. On cooling, red crystals were deposited which were collected in a sintered glass funnel and recrystallized from CH_2Cl_2 and n-hexane. Nickel bromide, iodide and thiocyanate complexes were obtained in the same manner.

[Pd(1a)Cl₂]

Palladium dichloride (0.35 g, 2 mmol) dissolved in acetonitrile (40 ml) was refluxed for 4 h to produce a brown solution. To this solution ligand 1a (0.88 g, 2 mmol) was added and the solution was refluxed for an additional 3 h. The solvent was removed by vacuum and the residue was treated with animal charcoal in CH_2Cl_2. It was filtered and dried. The yellow powder was crystallized from $CHCl_3$ and n-hexane.

[Pd(1a)X₂] (X = Br, I, NCS)

These complexes were prepared by metathetical exchange reactions treating [Pd(1a)Cl₂] with an excess of the corresponding potassium or ammonium salt in boiling acetone. The resulting complexes were filtered and dried under vacuum. The complexes were extracted with CH_2Cl_2.

[Pt(1a)(Cl₂)]

[PtCl₂(PhCN)₂] (0.47 g, 1 mmol) and ligand 1a (0.43 g, 1 mmol) were stirred for 9 h in benzene (30 ml) at 60 °C. The initial yellow colour gradually turned light-yellow and finally colourless. The solvent was removed by pumping. The residue was crystallized from CH_2Cl_2 and EtOH to give a white crystalline compound.

[Pt(1a)X₂] (X = Br or I)

These complexes were prepared by a metathetical exchange reaction using the same procedure as adopted for palladium complexes. The resulting complexes were crystallized from $CHCl_3$ and petroleum ether. Complexes with ligand 1b were prepared by analogous procedure.

Results and Discussion

The complexes of Ni(II), Pd(II) and Pt(II) with 1a and 1b were prepared as described in the literature [11] and have been found to be more soluble in common organic solvents as compared to known ditertiary phosphine complexes. The melting point and analytical data for these complexes are given in Table I.

$^{31}P\{^1H\}$ NMR spectra of the ligand 1a and 1b at 161.98 Hz exhibit an AB quartet confirming the non-equivalence of both the phosphorous nuclei. It has been observed that the phosphorous nucleus attached to p-FC₆H₆ group is more shielded than that attached

to phenyl group, whereas the phosphorus nucleus attached to m-FC₆H₆ group is less shielded than that attached to phenyl group [10]. This discrepancy may be attributed to the fact that the transmission of electronic effects from the m-position in the phenyl ring to the phosphorous nuclei is different than that from the p-position [12].

$^{31}P\{^1H\}$ NMR data obtained for complexes are given in Table II. ^{31}P NMR spectra of nickel and palladium complexes, but not platinum complexes, show an AB quartet which is due to the presence of two non-equivalent phosphorous nuclei. In all these complexes, larger downfield chemical shifts were assigned to the phosphorus attached to fluorophenyl group, while the smaller values were assigned to the phosphorus attached to phenyl group. These chemical shift values were found to be in close agreement with the literature values published for the Ph₂PCH₂CH₂-PPh₂ [13] complexes of Ni(II), Pd(II) and Pt(II).

$^{31}P\{^1H\}$ NMR spectra of platinum complexes show an AB quartet and the presence of two satellites due to ^{195}Pt–^{31}P and ^{195}Pt–$^{31}P'$ couplings. The general appearance of an AB spectrum depends only on the ratio of $J(P-P')$ to $\nu_0\delta$ (the chemical shift difference between the non-equivalent phosphorous nuclei). Examination of the ^{31}P NMR data of the ligands shows that $\nu_0\delta$ is very small, 1.03 ppm for 1a and 2.28 ppm for 1b. This, together with large expected values for $J(P-P')$, 34.8 and 35.0 Hz for 1a and 1b respectively, means that the ratio $J(P-P')$: $\nu_0\delta$ will be very large and the expected spectrum must show two extremely large central components and two outer small components. The observed spectra of platinum complexes were found to be in accordance with the expectation (Fig. 1).
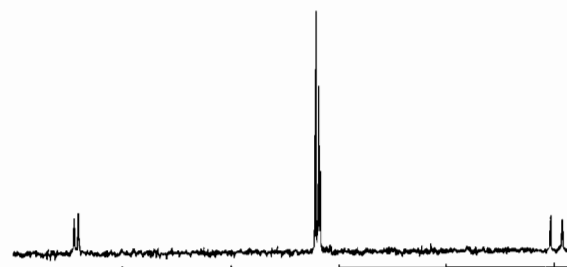

Fig. 1. Spectra for platinum complexes.

It has been shown [14] that $J(^{195}Pt$–$^{31}P)$ values depend on the Fermi contact term and can be written as

$$|^1J(Pt-P)| \propto \frac{\alpha Pt^2 \alpha P^2 \, [^SPt(6S)(0)] \, [^SP(3S)(0)]}{(\Delta E)}$$

where Y = Pt or P, Y^2 is the S character of the relevant bonding orbital of Y, $^SY(nS)(0)$ is the density of ns orbital at the Y nucleus and ΔE is a mean singlet triplet excitation energy. The difference

TABLE II. ^{31}P {^1H}NMR Data obtained for Ni(II), Pd(II) and Pt(II) Complexes in $CDCl_3$ at 25 °C

Compound	Chemical shift (ppm)		Coordination chemical shift (ppm)		$J(P-P')$ (Hz)	ΔR^a (ring coordination)	
	δPPh_2	δPR_2	ΔPPh_2	ΔPR_2		ΔPPh_2	ΔPR_2
[Ni(1a)Cl₂]	+58.12	+58.67	+70.25	+69.77	40.0		
[Ni(1a)Cl₂]	+65.28	+67.28	+77.41	+78.38	41.0		
[Ni(1a)I₂]	+79.65	+79.88	+91.78	+90.98	40.3		
[Ni(1a)(NCS)₂]	+23.65	+23.86	+35.78	+34.96	b		
[Pd(1a)Cl₂]	+65.35	+65.68	+77.48	+76.78	9.9	+34.78	+34.08
[Pd(1a)Br₂]	+64.45	+65.93	+76.58	+77.03	16.5	+33.88	+34.33
[Pd(1a)I₂]	+63.81	+64.55	+75.94	+75.65	15.3	+33.24	+32.95
[Pd(1a)(NCS)₂]	+66.38	+67.58	+78.51	+78.68	b	+35.81	+35.98
[Pt(1a)Cl₂ᶜ]	+43.69	+44.88	+55.82	+55.28	3.8	+33.52	+32.98
[Ni(1b)Cl₂]	+58.08	+58.12	+70.28	+72.60	39.5		
[Ni(1b)Br₂]	+64.52	+66.76	+76.72	+81.24	41.3		
[Ni(1b)I₂]	+78.97	+79.76	+91.17	+94.04	40.5		
[Ni(1b)(NCS)₂]	+23.65	+24.18	+35.05	+38.66	b		
[Pd(1b)Cl₂]	+65.56	+64.63	+76.76	+79.11	10.0	+34.06	+36.41
[Pd(1b)Br₂]	+65.21	+65.73	+77.41	+80.21	16.5	+34.71	+37.51
[Pd(1b)I₂]	+62.90	+64.75	+75.10	+79.23	15.1	+32.40	+36.53
[Pd(1b)(NCS)₂]	+66.56	+66.72	+78.76	+81.20	b	+36.06	+38.50
[Pt(1b)Cl₂ᵈ]	+42.32	+43.93	+54.52	+58.41	b	+32.22	+36.11

[a]Coordination chemical shift of chelate complex – coordination chemical shift for equivalent non-chelate complex: $cis[PdCl_2$-$\{P(Ph_2Et)_3\}_2] = 42.7$, $cis[PtCl_2 \{P(Ph_2Et)_3\}_2] = 22.3$; Ref. 16.   [b]$(J(P-P')$ could not be observed due to broad peaks. [c]$J(^{195}Pt-^{31}PPh_2) = 3607$ Hz and $J(^{195}Pt-^{31}P(C_6H_4F-m)_2 = 3643.0$ Hz.   [d]$J(^{195}Pt-^{31}PPh_2) = 3596.0$ Hz and $J(^{195}Pt-^{31}P$-$(C_6H_4F-p)_2 = 3636.79$ Hz.

in coupling constants is probably largely determined by variation in the αPt^2 and αP^2 terms, which in turn will be strongly affected by variation in the angle $P-Pt-P$ and $Pt-P-CH_2$.

Complex [Pt(1a)Cl₂] shows two coupling constants, 3643.0 Hz and 3607.0 Hz, which may be assigned to $J(^{195}Pt-^{31}P(C_6H_4F-m)_2)$ and $J(^{195}Pt-^{31}P Ph_2)$ respectively. In case of [Pt(1b)Cl₂], 3636.8 Hz and 3596.9 Hz values were assigned to $J(^{195}Pt-^{31}P(C_6H_4F-p)_2)$ and $J(^{195}Pt-^{31}P Ph_2)$ respectively. The values of these coupling constants confirm the cis configuration of the complexes and are in close agreement with the literature values for analogous complexes [14]. The observed increasing trend of coupling constants along the series–$PPh_2 < -P-(C_6H_4F-p)_2 < -P-(C_6H_4F-m)_2$ may be related to the increased electron withdrawing ability of substituents attached to the phosphorus [15].

The values of phosphorus–phosphorus coupling constants were found to be highest for nickel complexes and lowest for platinum complexes (Table II). The observed P–P' coupling constant $|J_{P-P'}$, observed| might be expected to include contributions due to transmissions through both the ligand backbone $(J_{PP'}B)$ and the metal atom $(2J_{PMP})$ i.e. $|J_{PP}$ observed| $= |J_{PP'}B + J_{PMP'}|$. We believe that in the complexes studied, the fundamental change in coupling through

the metal atom is responsible for the observed decrease in $|(J_{PP'}$ observed)| values down the series Ni > Pd > Pt.

It has been noted recently that the phosphorous atom present in five-membered rings exhibits an anomalously large coordination chemical shift (Δ) [16]. Such values are anomalous in the sense that they cannot be predicted from the linear relationship between the chemical shift of free ligand (δF) and the coordination chemical shift (i.e. $\Delta = A \delta F + B$) which has been shown to the valid for a variety of transition metal complexes [17]. The term 'ring contribution' (ΔR) has been introduced to explain the anomalous coordination chemical shifts. The values of ΔR have been calculated for palladium and platinum complexes in Table II. ΔR is the difference between the coordination chemical shifts Δ of a chelate complex and of cis-substituted equivalent non-chelate complex.

The elemental analysis, far IR and UV data have been given in Table 1. The far IR data are consistent with the C_{2v} symmetry of the molecule [18, 19], giving two infrared active bands (due to A_1 and B_2 modes) which confirm the cis-nature of the complexes. All these complexes exhibit a band at ~885, confirming the chelating behaviour of the ligand [20]. An increase in frequency and intensity of the

ligand band at ~1095 cm^{-1} was also observed; this can be taken as a good evidence for the coordination of phosphorus to metal [21]. The nature of the N-bonded thiocyanate complex was confirmed by the presence of two peaks at 2092 cm^{-1} and 2065 cm^{-1} [22] in the complexes [Ni(1a)(NCS)$_2$] and [Ni(1b)-(NCS)$_2$], respectively.

The electronic spectra of nickel complexes depict an intense absorption in the 400–500 nm in acetone solution, confirming the square-planar geometry of the complexes [23]. These absorptions may be assigned to the transitions which have 'd' orbital characteristic $d_{xy} - d_{x^2-y^2}$. These bands move to higher energy in the series I$^-$ < Br$^-$ < Cl$^-$ < NCS$^-$. The nickel iodide complex tends to be tetrahedral and show square planar tetrahedral equilibria.

Acknowledgements

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