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Coordination studies of nitrogen-containing aryl phosphine ligands P^N and P^N^N with rhodium

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The coordination behavior of the heterofunctional phosphine ligand $PPh_2NH(2\text{-}Py)$, $PPh_2(o\text{-}C_6H_4)CH{=}N\text{-}(CH_2)_nPh$ (n = 0–3) and $PPh_2(o\text{-}C_6H_4)CH{=}N\text{-}(CH_2)_n\text{-}(2\text{-}Py)$ (n = 1 or 2) towards Rh(I) and Rh(III) are reported and examples of neutral and cationic complexes containing bi-dentate P^N or tri-dentate P^N^N and N^N^C chelating modes of coordination are found. The synthesized complexes were characterized using different analytical and spectroscopic techniques including ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy IR spectroscopy, ESI mass spectrometry and elemental analysis. The crystal structure of representative compounds has been determined by X-ray diffraction methods. The fluxional behavior in solution of the rhodium(I) complexes of the type [RhCl(CO)(P^N)= has been investigated by NMR spectroscopy as well as the reactivity towards the oxidative-addition of MeI and I_2. It was found that rhodium (III) complexes of the general formula $[RhCl_2(P\hat{}N)_2]Cl$ formed three of the five possible stereoisomers and that different solvents induced isomerization between these stereoisomers, indicating hemilability of the P^N ligands.

1. Introduction

The bidentate and polydentate phosphines are important ligands in coordination chemistry and homogeneous catalysis. Special interest was given to compounds that have an aryl phosphine at one end to stabilize a low oxidation state of the metal ion, and a weakly coordinating nitrogen at the other end that can be substituted by a π-acceptor species. Among the functionalized phosphine ligands there are numerous examples where the nitrogen donors with the sp^2-N atom from pyridine or imine has been incorporated into a ligand (Fig. 1) [1–4].

Many studies have concerned on a simple pyridyl phosphines such as 2-(diphenylphosphino)pyridine (**A**). This P^N donor ligand can act as a monodentate ligand coordinated through the phosphorus or nitrogen atom, a bridging ligand in a dimeric and polymeric species or a chelating bidentate ligand [2,5]. The formation of mononuclear complexes where **A** ligand acts as four–membered chelate rings which are rather strained and unstable is less favored [5]. The pyridyl phosphines with the P atom separated from the pyridyl group by spacer atoms, capable of forming more stable five- and six-membered rings are expected to be the best chelate ligands. Some P^N ligands which contain N-H (**B**) [6,7], CH_2 (**C**) [8,9], $CH_2\text{-}CH_2$ (**D**) [10,11] and $CH_2\text{-}NH$ (**E**) [12–14] as spacer groups are shown in Fig. 1.

Potentially tridentate phosphine ligands P^N^N can contain two pyridyl N donor groups as in the $PPh(Py)_2$ [15], $PPh(CH_2CH_2Py)_2$ [11] or in the 6-(2-diphenylphosphinoetyl)-2-2′-bipyridine [26] and 6-diphenylphosphino-2-2′-bipyridine [16]. Phosphines with two different nitrogen donors included a pyridyl group and for example an imino [17] (**F**), pyrazolyl [18] or amino [19,20] groups have also been reported.

One of the more interesting chemical aspects of this type of ligands, lies in the fact that they can adopt different coordination modes i.e. mono-, bi- or tridentate, thus giving rise to different structures and steric encumbrances around the metal centers.

Following our interest in the synthesis and chemical properties of complexes with nitrogen containing phosphines [5,15] we have obtained and characterized some new rhodium complexes with the P^N, P^N^N and OP^N^N ligands (Chart 1):

2-(diphenylphosphino)aminopyridine (**PNH**),
N-[2-(diphenylphosphino)benzylidene]aniline (**PN0**),
N-[2-(diphenylphosphino)benzylidene]benzylamine (**PN1**),

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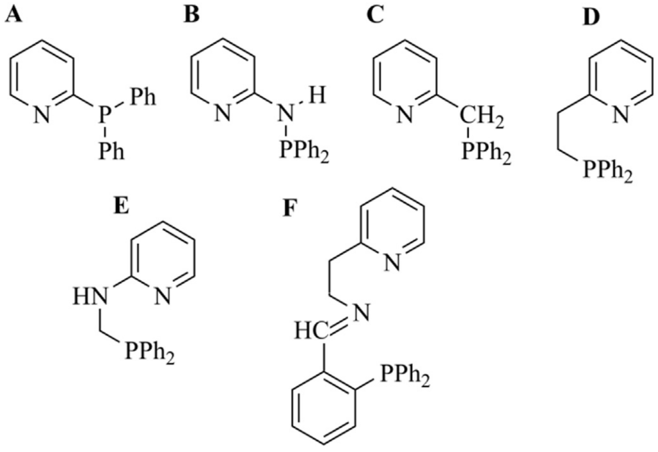

Fig. 1. Examples of known pyridyl and imine phosphines.

N-[2-(diphenylphosphino)benzylidene]-2-phenylethylamine (**PN2**),
N-[2-(diphenylphosphino)benzylidene]-3-phenylpropylamine (**PN3),**
N-[2-(diphenylphosphino)benzylidene]-2-(2-pyridyl)methylamine (**PNN1**),
N-[2-(diphenylphosphino)benzylidene]-2-(2-pyridyl)ethylamine (**PNN2**) and
N-[2-(diphenylphosphinooxide)benzylidene]-2-(2-pyridyl)ethylamine (**OPNN2**).

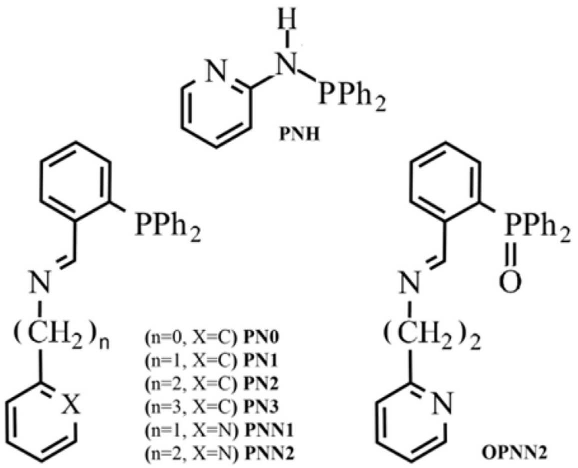

Chart 1. Structures of ligands used for complexation.

2. Experimental

2.1. Physical measurements

IR spectra were recorded on a Bruker IFS113v. Electrospray mass spectra were performed on a Finnigan MAT TSQ 700 triple stage quadrupole mass spectrometer. The ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on Bruker AMX 300 and Avance 500 spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. ^{31}P{^{1}H} NMR was referenced externally using H_3PO_4 (85% in D_2O) in a capillary. Elemental analyses were carried out with a CHNS Vario EL III analyzer.

2.2. Synthesis

All reactions were carried out under a nitrogen atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques. The solvents were dried following standard procedures and stored under nitrogen prior to use.

2-(diphenylphosphino)aminopyridine (**PNH**) [20] and the starting complex $[Rh(CO)_2Cl]_2$ [21] was prepared according to the literature procedures. $RhCl_3 \cdot 3H_2O$ (Sigma-Aldrich) were used as received. Following iminophosphine ligands were synthesized from the Schiff's base condensation reaction from the 2-diphenylphosphinobenzaldehyde (Sigma-Aldrich) and corresponding amines as described in the literature: N-[2-(diphenylphosphino)benzylidene]aniline (**PN0**) [22], N-[2-(diphenylphosphino)benzylidene]benzylamine (**PN1**) [23], N-[2-(diphenyl phosphino)benzylidene]-2-phenylethylamine (**PN2**) [24], N-[(2-diphenylphosphino) benzylidene]-2-(2-pyridyl) methylamine (**PNN1**) [25] and N-[2-(diphenylphosphino) benzylidene]-2-(2-pyridyl)ethylamine (**PNN2**) [26].

2.2.1. Synthesis of the ligands

N-[2-(diphenylphosphino)benzylidene]-3-phenylpropylamine (**PN3**) - 3-phenylpropyl-1-amine (344 μl; 2.41 mmol) in 10 mL of toluene was added drop-wise to a mixture of (2-(diphenylphosphino))-benzaldehyde (0.7 g; 2.41 mmol) and anhydrous magnesium sulfate (1.6 g) in toluene (10 mL). The reaction was stirred under reflux for 3 h. Resulting in a light yellow mixture. After filtration a yellow oil was obtained upon elimination of the solvent under reduced pressure. Twice the treatment with hexane (10 mL) resulted in a purification of the product, which however did not crystallize. Yield: 97%. ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz): δ (ppm) = 8.86 (d, J = 4,65 Hz, 1H, HC=N-), 7.98–7.94 (m, 1H, aromatic), 7.38–7.04 (m, 17H, aromatic), 6,87-6,83 (m, 1H, aromatic), 3.48 (t, J = 6.65 Hz, 2H, =NCH_2-), 2.44–2.39 (m, 2H, -CH_2-Ph), 1.84–1.75 (m, 2H, -CH_2-). ^{31}P{^{1}H} ($CDCl_3$, 298 K): δ (ppm) = −13.80. ESI-MS ($CHCl_3$ after treatment of H_2O_2) m/z: 424.2 [OPN3 + H]$^{+}$.

N-[(2-diphenylphosphinooxidebenzylidene)]-2-(2-pyridyl) ethylamine (**OPNN2**). To a solution of **PNN2** (0.100 g, 0.254 mmol) in methanol (10 mL) was added aqueous H_2O_2 (30% w/w 0.2 cm^{3}). The solution was stirred for 34 h. Solvent was evaporated under vacuum, and dichloromethane (2.0 mL) was added with stirring. Addition of the diethyl ether (20 mL) and hexane (20 mL) gave a solid which was collected by filtration and dried under vacuum. Yield 83%. Anal. Calc. (%) for $C_{26}H_{23}N_2OP$: C, 76.08; H, 5.65; N, 6.83. Found: C, 75.7; H, 5.55; N, 24.76. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ (ppm) = 8.98 (s, 1H, HC=N-), 8.45(d, J = 4.91 Hz, 1H, pyH^{6}), 8.12 (dd, J = 7.55, 3.78 Hz, 1H, BzH^{2}), 7.65–7.04 (m, 16H, aromatic), 3.74 (t, J = 7.36 Hz, 2H, =NCH_2-), 2.90 (t, J = 7.36 Hz, 2H, -CH_2-Ph), ^{31}P{^{1}H} ($CDCl_3$, 295 K, 121 MHz): δ = 31.84 (s) ppm. ESI-MS ($CHCl_3$) m/z: 411.17 [M + H]$^{+}$. IR (KBr): 1643 cm^{-1} ν(N=CH), 1178 cm^{-1} ν(P=O).

2.2.2. Synthesis of rhodium (I) complexes

[RhCl(CO)(PNH-*P,N*)] (1) $[Rh(CO)_2Cl]_2$ 0.02 g (0.05 mmol) was dissolved in anhydrous ethanol (5 cm^{3}) and to this 0.03 g (0.1 mmol) of the **PNH** in ethanol (5 cm^{3}) was added dropwise with the constant stirring under nitrogen atmosphere at room temperature. The orange color of the solution was immediately discharged to give a yellow solution which deposited a yellow powder over 10 min. The complex **1** was filtered washed with ether and dried in vacuum (yield 0.26 g, 57%). Anal. Calc. (%) for $C_{18}H_{15}ClN_2$ OPRh: C, 48.62; H, 3.40; N, 6.30; Cl, 7.97; P, 6.97. Found: C, 48.46; H, 3.20; N, 6.28; Cl, 8.19; P, 7.05. ESI-MS ($CHCl_3$, m/z): 409.9 - [Rh(CO)(PNH) + H]$^{+}$, 382.0 - [Rh(PNH) + H] $^{+}$; ($(CH_3)_2CO$, m/z): 853.0 - $[Rh_2Cl(CO)_2(PNH)_2]^{+}$, 825.0 - $[Rh_2Cl(CO)(PNH)_2]^{+}$, 797.0 -