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A NEW FAMILY OF AROMATIC POLYIMINE CHELATES SUBSTITUTED WITH TWO DIPHENYLPHOSPHINES

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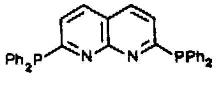
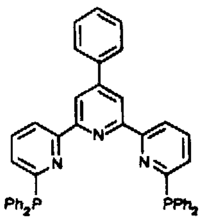
Summary. Reaction of lithium diphenylphosphide with vicinal nitrogen disubstituted polyimines such as 1,8-naphtyridine, 4'-phenyl-2,2',6',2"-terpyridine, 2,2'-bipyridine or 1,10-phenanthroline produces in high yield a new series of heterodifunctional ligands.

The use of homo- and heteronuclear polymetallic complexes in catalysis is of current interest[1] and ligands promoting the formation of such species are thus highly desirable[2]. The substitution of chelating polyimines with atoms like P, As, Si, S ... could lead to the controlled coordination of different metals[3], thus forming new soluble catalysts for the simultaneous activation of mixed substrates such as carbon dioxide and hydrogen[4]. In addition, varying the distance between the two phosphine substituents as well as their size is of importance respectively for the selective preparation of early-late transition metal complexes and for the modification of the basicity of the phosphine entity.

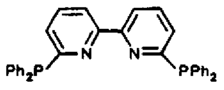
We have recently found that the ligand 6,6'-bis(diphenylphosphino)-2,2'-bipyridine forms with rhodium(I) large ring binuclear complexes which are efficient hydroformylation catalysts[5]. This prompted us to develop a general synthetic method for the difunctionalisation of a variety of aromatic polyimines, with diphenylphosphino or diphenylphosphinomethyl substituents.



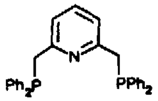
L_1



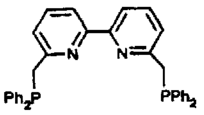
L_2



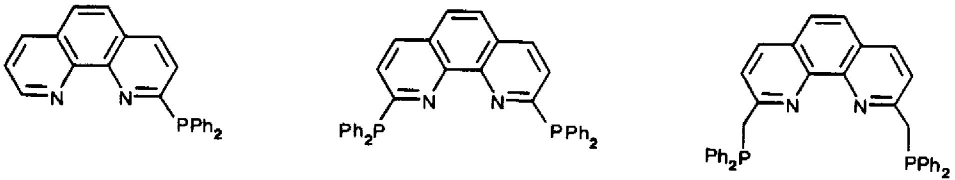
L_3



L_4



L_5



L_6 L_7 L_8

FIGURE 1

Ligands were typically prepared on one gram scale by reaction of two equivalents of PPh_2Li[6] with one equiv. of the dibromo or dichloro substituted starting compound, under *strictly air-free conditions* (Schlenk techniques). After 5 hours reaction time at 0°C (-40°C for the phenanthroline ligands), the solution was quenched with degassed ethanol and precipitation of the product occured after slow evaporation of the solvent. The new compounds were purified by chromatography under argon (alumina, dichloromethane/hexane) followed by crystallization in a degassed dichloromethane/pentane solution. The pure ligands were obtained as white crystals and characterized by ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ nmr, mass and electronic spectra, infrared and C, H, N, P elemental analysis. All data are consistent with the proposed structures (see Table and figure 1). The observed phosphorus chemical shifts are in good agreement with those reported for functionalized phosphines[7].

TABLE : Synthesis and selective data for ligands L_1 to L_8

Starting Compound	Ligand	Isolated Yield (%)	Melting point (°C)	$^{31}P\{^{1}H\}$ (ppm)[a]	Mass spectra[b] m/e (g)
2,7-dichloro-naphtyridine[8]	L_1	92	190	+1.96	498
6,6''-dibromo-4'-phenyl-2,2',6',2''-terpyridine[9]	L_2	84	253/4	-0.62	677
6,6'-dibromo-2,2'-bipyridine[10]	L_3[4,11]	92	198	-1.65	524
2,6-bis(bromomethyl)-pyridine[12]	L_4	70	144	-9.20	475
6,6'-bis(bromomethyl)-2,2'-bipyridine[13]	L_5	62	134	-9.32	552
2-chloro-1,10-phenanthroline[14]	L_6	94	121/2	-0.83	363/4
2,9-dichloro-1,10-phenanthroline[15]	L_7	91	186/7	+0.52	547/8
2,9-bis(bromomethyl)-1,10-phenanthroline[16]	L_8	54	118/20	-12.74	575/6

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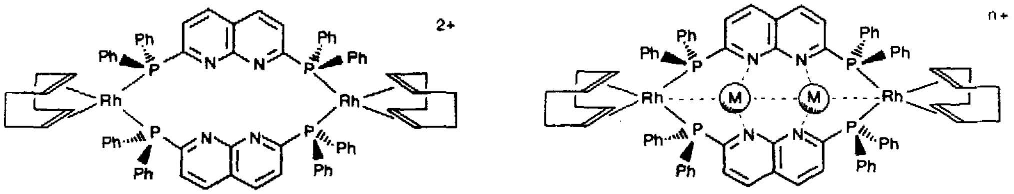
a) Chemical shifts are reported downfield and upfield of 85% H_3PO_4 and were measured in $CDCl_3$.

b) were obtained by electronic impact and revealed a molecular peak for all the ligands as well as an additional $(M-H)^+$ peak for ligands L_6, L_7 and L_8.

The free phosphines are moderately air-stable in the solid state, however they are oxygen-sensitive in solution forming the diphenylphosphine oxide analogues as detected by $^{31}P\{^1H\}$ nmr for the dramatic deshielding of the phosphorus resonance and by infrared spectroscopy. In order to further confirm the structure of the free phosphines we have prepared and isolated the diphenylphosphine oxides of ligands L_1 to L_8, by hydrogen peroxide oxidation[17]. Characteristic chemical shifts in $^{31}P\{1H\}$ nmr and vibrations in IR were observed for the phosphines oxides[18]. All the diphosphine oxides showed a downfield shift for the polyimine hydrogens, in the ^1H nmr spectra. These observations are similar to those reported for tri-2-pyridyl phosphine and its oxide[19]. The yields (Table) were high when an aromatic addition-elimination reaction (L_1-L_3 and L_6-L_7) was involved and lower in the case of an aliphatic substitution (L_4, L_5 and L_8). Of special interest is the synthesis of the rigid disubstituted naphtyridine L_1, and phenanthroline L_7 ligands which could form less fluxional complexes in solution compared with the bipyridine species L_3[5].

Preliminary complexation studies, using "$[Rh(acetone)_2COD]BF_4$"[5] (COD=1,5-cyclooctadiene) and ligands L_1 and L_2, have revealed the formation of large ring binuclear metal complexes, two ligands being mutually cis-coordinated and bridging the two rhodium(I) centers (complex $C_1 = [Rh_2(L_1)_2(COD)_2]^{2+}, 2BF_4^-$ is shown in figure 2 and complex $C_2 = [Rh_2(L_2)_2(COD)_2]^{2+}, 2BF_4^-$). Complexes C_1 and C_2 displayed characteristic phosphorus chemical shifts due to rhodium coordination : $^{31}P\{^1H\}$ nmr of C_1, CD_3CN, $\delta + 43.3$ ppm, d, $^1J_{P\text{-}Rh} = 169.2$ Hz and of C_2, CD_2Cl_2, $\delta + 25.6$ ppm, d, $^1J_{P\text{-}Rh} = 143.9$ Hz.



C₁

FIGURE 2

Molecular models indicate that the shortest internuclear metal distances are 8.4 Å and 10.1 Å for complexes C_1 and C_2 respectively, and 7.8 Å for the analogous complex with ligand L_3[5]. Moreover, CPK models of complex C_1 revealed an ideal cavity for the complexation of two additional transition metals (see right hand side of figure 2). The lack of flexibility of this complex is due to the rigidity of the naphtyridine ligand.

The longest metal-metal distance was estimated to be about 2.8 Å, being favourable for the formation of metal-metal bonds. For example, the Rh-Rh bond distance in the tris(μ-acetato)(2,7-bis(2-pyridyl)-1,8-naphtyridine)dirhodium(II) cation is 2.405(2)Å [20]. This observation is of interest in modelling heterogeneous catalytic surfaces with soluble complexes, especially with tetranuclear species (figure 2). Synthesis and characterization of such polynuclear complexes is currently in progress and will be reported elsewhere.

This synthetic method clearly represents a valuable high-yield route to a new family of multifunctionalized ligands which combine classical polyimines with phosphines. They have been used to prepare novel polynuclear transition metal complexes.

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18. ^{31}P{1H} nmr ($CDCl_3$) δ in ppm and IR ($CHCl_3$) g (s, P → 0) in cm^{-1} : +20.98 and 1180 for (L_1)ox.; +24.12 and 1185 for (L_2)ox.; +23.14 and 1190 for (L_3)ox.; +31.59 and 1185 for (L_4)ox.; +31.81 and 1190 for (L_5)ox.; +19.59 and 1185 for (L_6)ox.; +20.62 and 1185 for (L_7)ox; +25.41 and 11.90 for (L_8)ox..
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