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Synthesis of New Chelating Agents: Association of a Phosphaalkene Moiety with a Pyridine.

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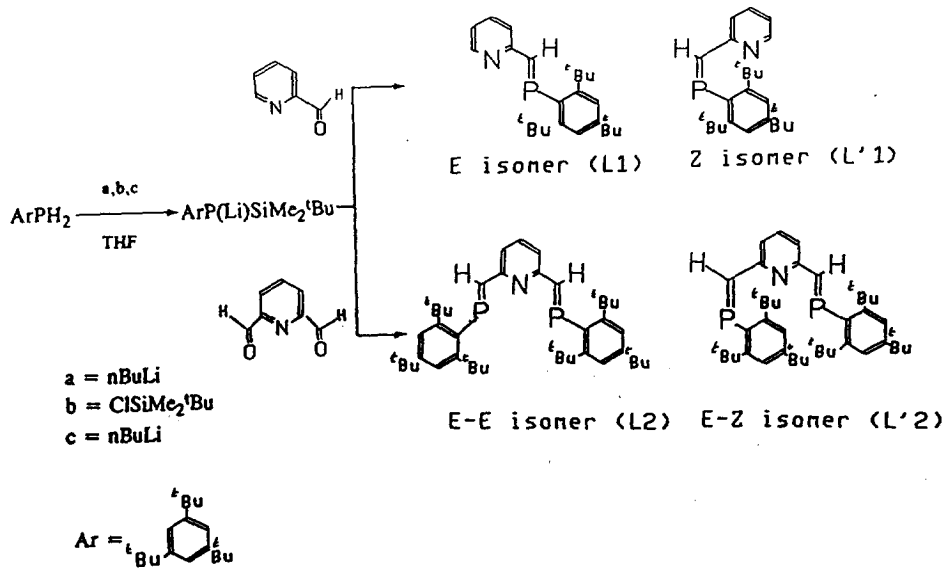
Abstract: *Molecules containing a pyridine ring located in α from one or two phosphaalkene moieties have been synthesized. The E isomer (L1) and the E,E isomer (L2) are well suited for acting as a bidentate and a tridentate ligand respectively. The crystal structure of the E isomer (L1) is determined.*

A large number of new stable organic molecules containing a dicoordinated trivalent phosphorus atom have been synthesized during the ten past years[1]. The phosphorus functional group (-P=C<, -P=P-, -P=N-...) confers interesting coordination properties on the molecules and many η^1 and η^2 complexes of phosphaalkenes with transition metals have been isolated[2]. Recently, we have synthesized a molecule containing two phosphaalkene groups and have shown that it can act as a tridentate ligand and form complexes with palladium[3].

We wish to report here the synthesis and the characterization of new molecules in which a pyridine fragment is associated with phosphaalkene moieties to form polydentate ligands (**L1** and **L2**)

The bonding of a pyridine ring to a phosphaalkene carbon has been achieved by adapting the procedure of Yoshifuji[4] and by reacting ArP(Li)SiMe$_2$^{t}Bu (where Ar: tri ^{t}BuPhenyl) with the appropriate pyridinecarboxaldehyde.

The reaction sequences are shown in Scheme 1:



Scheme 1

The crystal structure[5] of **L1** (*E* isomer) (Fig 1) shows that, as expected for a phosphaalkene molecule[1c], the atoms C7, P,C1, and C2 are almost coplanar (dihedral angle C7PC1C2= -177.7(8)°). This plane practically contains the pyridine ring (dihedral angle between mean planes=16.6(5)°) whereas it is perpendicular (90.0(3)°)to the phenyl ring (C1PC7C8 dihedral angle =-84.6°).

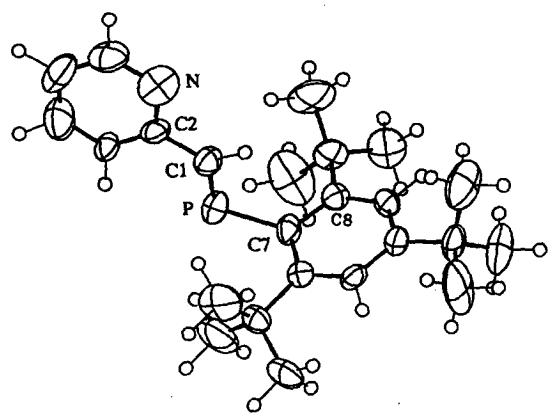


Figure 1. Crystal structure of **L1**

General procedure:

All reactions were carried out under an argon atmosphere. One equivalent of nBuLi was added, at room temperature, to a solution of $ArPH_2$ in THF. Then, one equivalent of $ClSiMe_2{}^tBu$ and another equivalent of nBuLi were successively added . After addition of the aldehyde the mixture was stirred during 1 hour. The resulting products were purified by silica-gel column chromatography by using CH_2Cl_2 as a solvent in the case of the monophosphaalkene compound and a mixture n-hexane/CH_2Cl_2 in the case of the diphosphaalkene. We have noticed partial decomposition of the two compounds on the column.

Characterization

The monophosphaalkene ligand **L1** (*E* isomer) was obtained as pale yellow crystals from a solution in pentane. Yield 45%; m_p=142-144°C; $^{31}P\{1H\}$-NMR ($CDCl_3$)/H_3PO_4: δ = 285.41 ppm, ^1H-NMR ($CDCl_3$) δ = 1.35 ppm (s,9H,^{t}Bu), 1.51ppm (s,18H,2^{t}Bu), 7.1 ppm (m,1H arom.), 7.34 ppm (m,1H arom), 7.43 ppm (s,2H arom.), 7.59 ppm (td,1H arom, J=8, 2 Hz), 8.08 ppm (d,1H, J_{PH}=25 Hz); 8.58 ppm (m,1H arom).

The diphosphaalkene **L2** (*E-E* isomer) forms a lemon yellow oil. Yield 30%; $^{31}P\{^1H\}$-NMR ($CDCl_3$) /H_3PO_4 δ=283.01 ppm; ^1H-NMR ($CDCl_3$) δ=1.35ppm (s,18H,2tBu),1.52ppm (s, 36H, 4 ^{t}Bu), 7.41ppm (s,4H arom), 7.58 ppm (m, 3H, arom), 8.1 ppm (d, 2H, P=CH, J_{PH}=25 Hz)

For the monophosphaalkene **L1** as well as for the diphosphaalkene **L2**, the last fractions of the column chromatography contains 5 to 10% of the other isomer : for the monophosphaalkene, the *Z* isomer **(L'1)** is characterized by δ=259.6 ppm (^{31}P-NMR), for the diphosphaalkene the *E-Z* isomer **(L'2)** is characterized by δ= 281.51 and δ= 256.9 ppm (^{31}P-NMR). The isolated compounds **L1** and **L2** are air stable and can be stored several weeks at -25°C.

All the structures of the compounds which have been synthesized here are consistent with their mass spectra and elemental analysis.

In order to confirm the expected chelating properties of **L1** we have reacted this compound with $Cu(NCCH_3)_4$ PF_6. Elemental analysis as well as $^{31}P\{^1H\}$ NMR spectroscopy (s, δ=245.23ppm) indicate that the resulting orange compound corresponds to $L_1Cu(NCCH_3)_2$, PF_6.

Acknowledgment

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5. *Crystal data E*,**L1**, $C_{24}H_{34}NP$, m=367.5, monoclinic, space group $P2_1/n$, a=9.794(3), b= 9.669(2), c= 23.643(5) Å, β=90.04(1)°, Z=4, D_c=1.09 gr.cm^{-3}, μ=0.125 mm^{-1}, Fooo=800, R= 0.062, ωR=0.059 ($\omega=1/\sigma^2(Fo)$) for 1386 observed reflections ($|Fo|>4\sigma(Fo)$). Data were collected at room temperature on an automatic four-circle Nonius CAD-4 diffractometer with monochromated MoKα radiation. The structure was solved by direct method[6] and refined by full matrix least-squares with XTAL 3.0 program[7]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

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