

Phosphorus, Sulfur, and Silicon and the Related Elements

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o-Phosphinophenoles - Synthesis and Reactivity

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o-PHOSPHINOPHENOLS - SYNTHESIS AND REACTIVITY

JOACHIM HEINICKE, RENAT KADYROV, MANUELA KOESLING AND
 ULRICH JUX

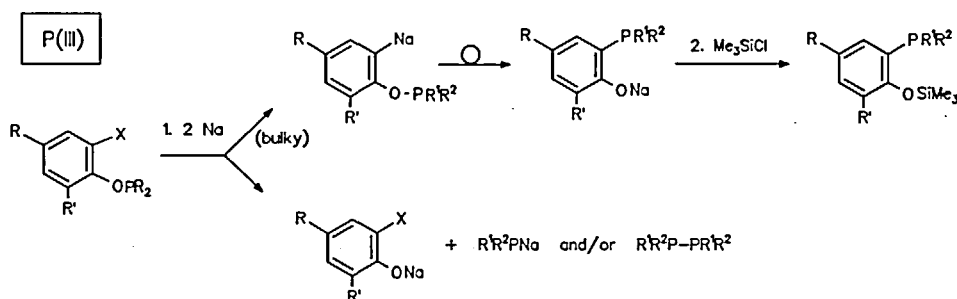
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Abstract Single and bulky substituted o-phosphinophenols, -naphthols, -diphenyl-2'-oles and -dinaphthyl-2'-oles are prepared and their preferred conformations studied. Substitution reactions at OH- and PH-groups, cyclization reactions to give P-E-O and P=E-O heterocycles as well as formation of nickel chelate complexes are described.

Keywords: hydroxyaryl phosphine ligand, heterocycle, phosphen, aroxydiphosphine

By reaction of appropriate dilithium reagents with chlorophosphines, subsequent treatment with Me_3SiCl and alcoholysis or by a metallation rearrangement procedure of o-bromo-aroxyphosphines (Scheme 1) a number of o-phosphinophenols, -naphthols as well as some diphenyl-2'-oles and dinaphthyl-2'-oles were prepared. Problems by side reactions and limits of the methods are discussed.

Scheme 1

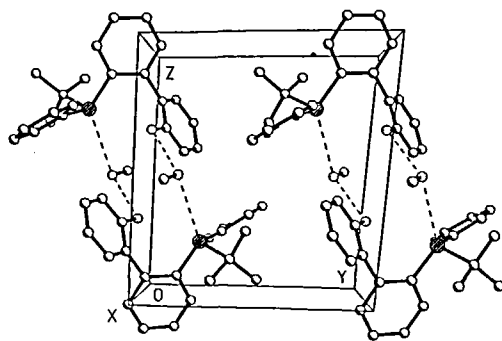
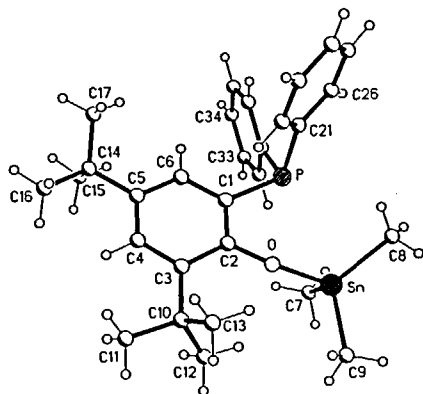
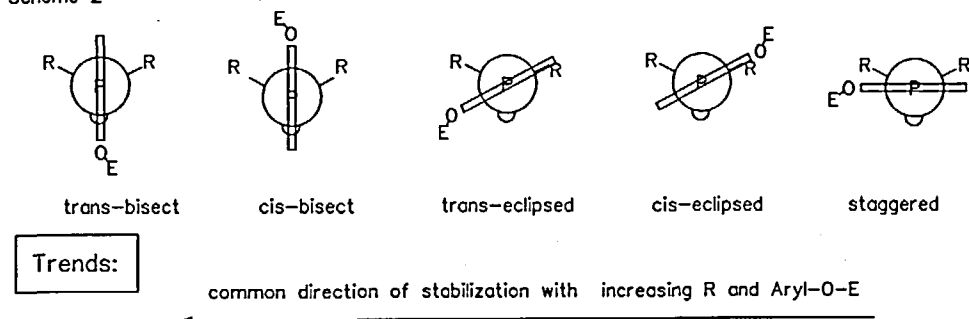


yields of phosphinophenols:

R=R = t-Bu	(NMe ₂) ₂	NMe ₂ Ph	(>80%)
R=R = H	(NMe ₂) ₂	t-BuMe (i-Pr) ₂	(65%)
	(80%)	(Et) ₂	(50%)
		Me ₂	(25%)
		Ph ₂	(-)

Special structural features were found for bulky derivatives. Simple phosphinophenoles and their silyl ethers prefer trans-conformations (Scheme 2) as shown by the ^{13}C - ^{31}P coupling constants of the vicinal carbons (average at 25°C: $^2J_{\text{PC1}}$ 22-14, $^2J_{\text{PC3}}$ 0-5 Hz), the hindered 2,6-di(*t*-butyl)derivatives favour for the free phenols cis-bisect (e.g. $\text{P}(\text{NMe}_2)_2$: $^2J_{\text{PC1}}$ 9, $^2J_{\text{PC3}}$ 40 Hz) and for O-substituted derivatives severely distorted trans-conformations (e.g. **A**) with trans-annular interactions. These cause strong P-CC-OE coupling constants ($^4J_{\text{PP}}$ ca. 140-150 Hz; $^4J_{\text{PSn}}$ ca. 160 Hz) and even $^6J_{\text{PSiMe}_3}$ couplings. In the 1-phosphinonaphth-2-oles the steric stress comes from the opposite site (CH8) and turns the favored conformations to trans-bisect for OH- and cis-bisect for O-SiMe₃-compounds in solution as well as in the crystals. The peculiarity of the 2-phosphinodiphenyl-2'-oles is the formation of methanol adducts by strong hydrogen bonds to OH and weakly to PR_2 and the nearly perpendicular distortion of the phenyl planes leading to diastereoisomers for P-asymmetric species (e.g. **B**) [1].

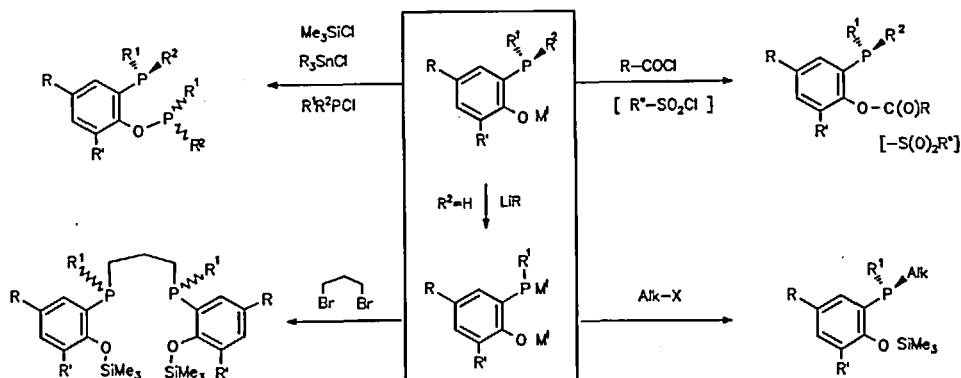
Scheme 2



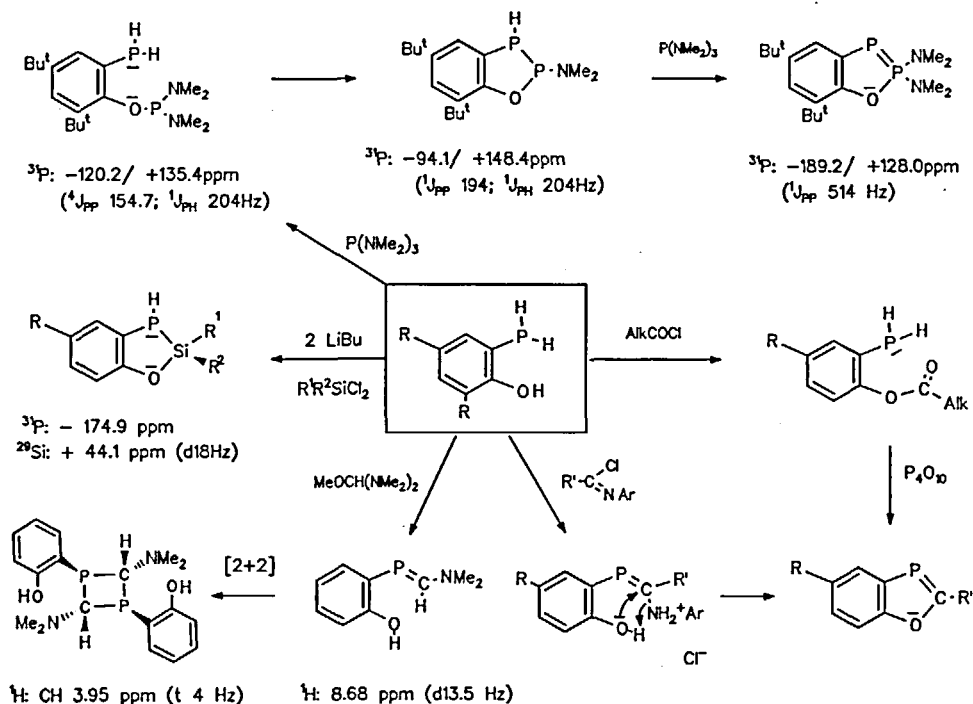
o-Hydroxyarylphosphines are ambident ligands with a hard and a soft Lewis-base center. After monometallation most electrophiles react at oxygen (Scheme 3). Alkylation proceeds in acceptable yields only on dimetallation or substitution of oxygen. The dilithium-phosphidophenolates were also tried to synthesize heterocycles but were found

to be here of limited use only. Heterocycles were obtained, however, by the more selective condensation of free P-H/O-H derivatives with element amides. Primary phosphinophenols thus allow the synthesis of cycles with low-coordinated phosphorus like the earlier studied benzoxaphospholes [2] or the new benzoxadiphospholes with a $\text{pIII}=\text{pV}$ [3] structural unit (Scheme 4).

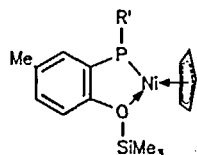
Scheme 3



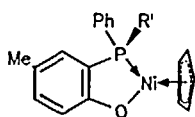
Scheme 4



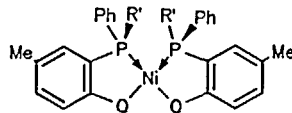
P-Tertiary [4], but also secondary o-hydroxyarylphosphines tend to form stable chelate complexes. From phosphinocresoles and nickel salts or ionic complexes we obtained green, but diamagnetic bis(chelate) complexes, probably in trans-configuration. $\text{Ni}(\text{acac})_2$ reacts to give orange-brown soluble cis-bis(chelate) complexes while nickelocene allows the mono- and bis-substitution to give CpNiL or cis- NiL_2 [5].



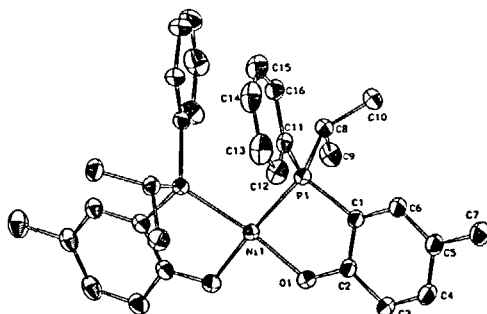
$\delta^{31}\text{P}$: - 88.9 ppm
($\Delta\delta$ = - 52.8 ppm)



$\delta^{31}\text{P}$: + 26 to +57 ppm
(R = Alk: $\Delta\delta$ = 75-81 ppm)
(R = Ph: $\Delta\delta$ = 61 ppm)



$\delta^{31}\text{P}$: + 21 to +51 ppm
(R = Alk: $\Delta\delta$ = 70-75 ppm)
(R = Ph: $\Delta\delta$ = 57.5 ppm)



Complexes formed from alkylarylphosphinophenoles and $\text{Ni}(\text{COD})_2$ were found to be usable as homogenous catalysts for the polymerization and oligomerization of ethylene [6]. $\text{Rh}(\text{CO})_2\text{acac}$ and P-asymmetric o-hydroxyarylphosphines give catalysts that allow the hydroformylation of vinylacetate [7], the separation of the ligands and the enantioselectivity remains to be studied.

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