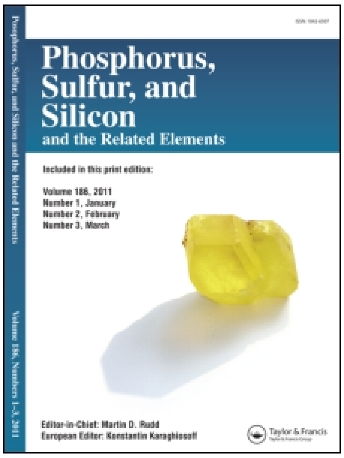

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o-PHOSPHINOPHENOLES - SYNTHESIS AND REACTIVITY

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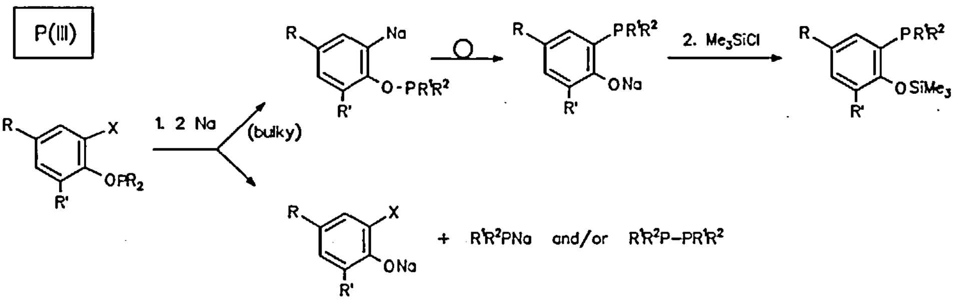
Abstract Single and bulky substituted o-phosphinophenoles, -naphtholes, -diphenyl-2'-oles and -dinaphthyl-2'-oles are prepared and their preferred conformations studied. Substitution reactions at OH- and PH-groups, cyclization reactions to give P-E-O and P=E-O heterocycles as well as formation of nickel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

Keywords: hydroxyaryl phosphine ligand, heterocycle, phosphen, aroxydiphosphine

By reaction of appropiate 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-phosphinophenoles, -naphtholes 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



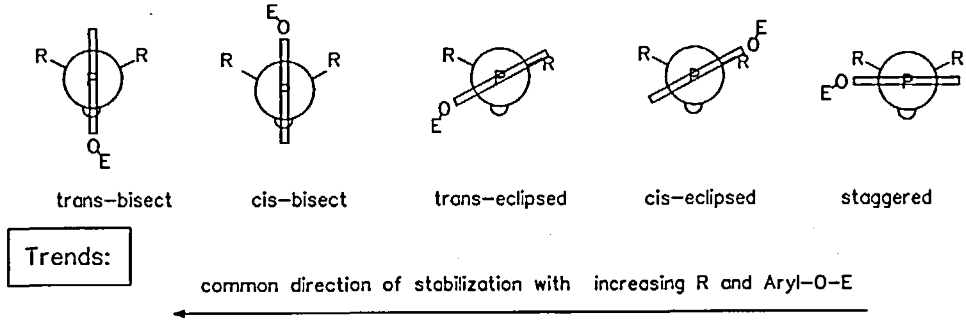
yields of phosphinophenoles:

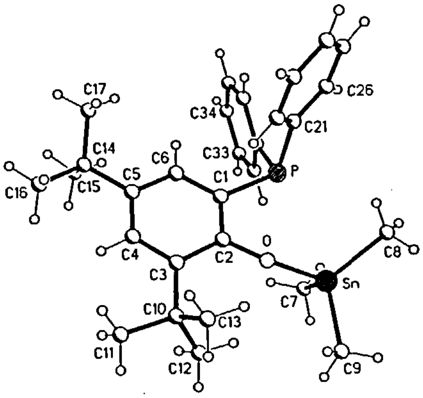
R=R = t-Bu (NMe$_2$)$_2$ NMe$_2$Ph (>80%)

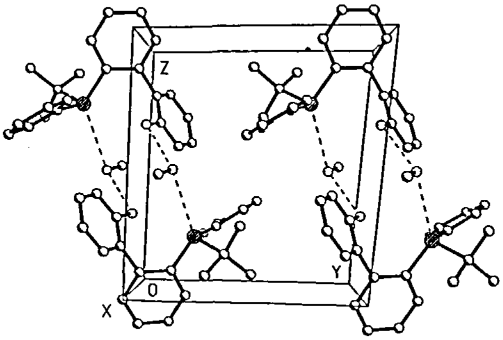
R=R = H (NMe$_2$)$_2$ > t-BuMe (i-Pr)$_2$ > (Et)$_2$ > Me$_2$ > Ph$_2$
(80%) (65%) (50%) (25%) (–)

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: $^{2}J_{PC1}$ 22-14, $^{2}J_{PC3}$ 0-5 Hz), the hindered 2,6-di(t-butyl)derivatives favour for the free phenoles cis-bisect (e.g. $P(NMe_2)_2$: $^{2}J_{PC1}$ 9, $^{2}J_{PC3}$ 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 ($^{4}J_{PP}$ ca. 140-150 Hz; $^{4}J_{PSn}$ ca. 160 Hz) and even $^{6}J_{PSiMe3}$ 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-$SiMe_3$-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

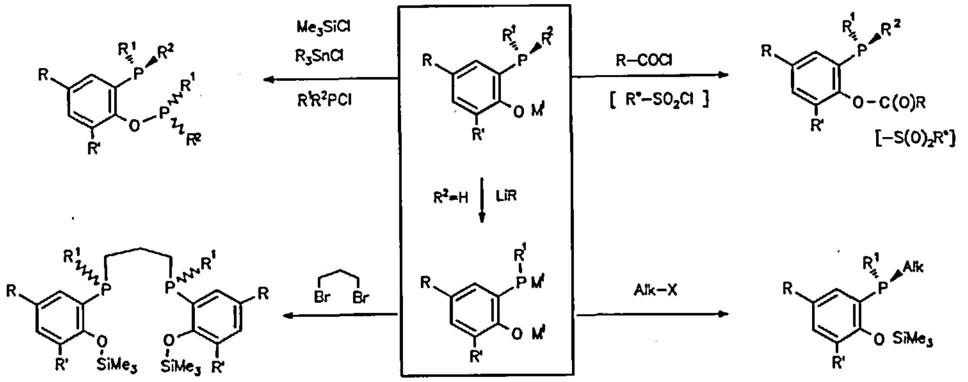




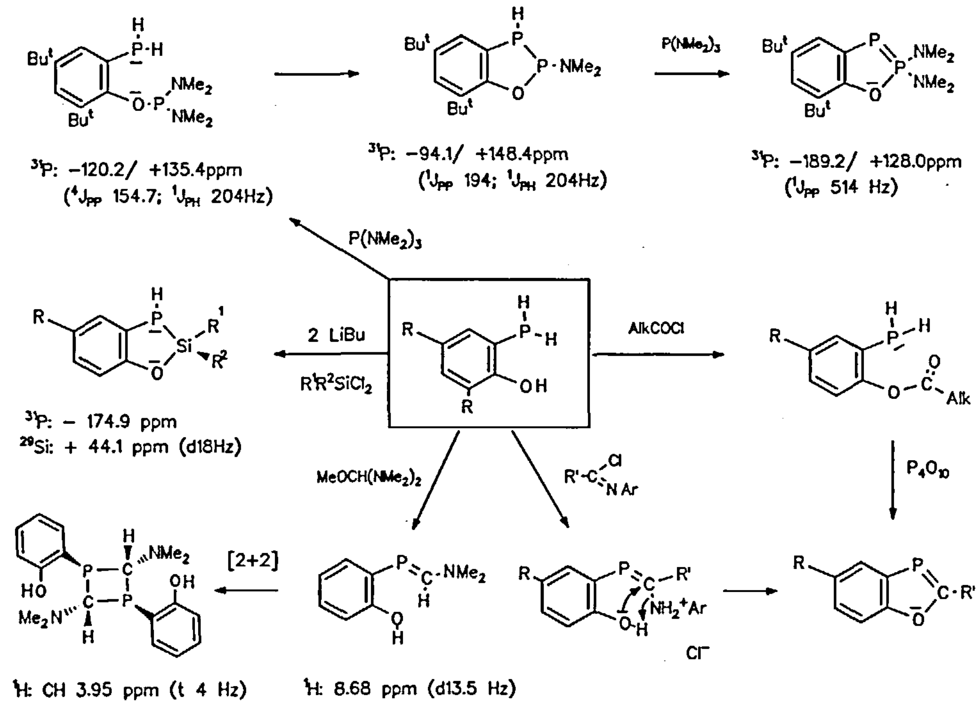


o-Hydroxyarylphosphines are ambident ligands with a hard and a soft Lewis-base center. After monometallation most electrophiles react at oxygen (Scheme 3). Alkylation proceeds in acceptable yields only on dimetallation or substitution of oxygen. The dilithium-phosphidophenolates were also tried to synthesize 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 phosphinophenoles thus allow the synthesis of cycles with low-coordinated phosphorus like the earlier studied benzoxaphospholes [2] or the new benzoxadiphospholes with a $P^{III}{=}P^{V}$ [3] structural unit (Scheme 4).

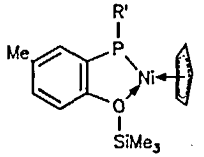
Scheme 3



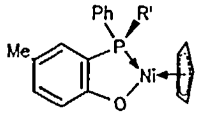
Scheme 4



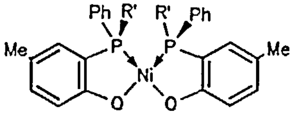
P-Tertiary [4], but also secondary o-hydroxyarylphosphines tend to form stable chelate complexes. From phosphinocresoles and nickel salts or ionic complexes we obtained green, but diamagnetic bis(chelate) complexes, probably in trans-configuration. $Ni(acac)_2$ reacts to give orange-brown soluble cis-bis(chelate)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



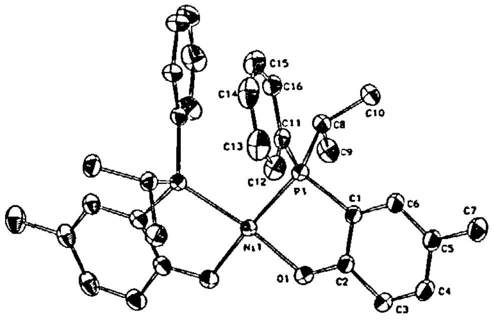
δ ^{31}P: − 88.9 ppm
($\Delta\delta$ = − 52.8 ppm)



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



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



Complexes formed from alkylarylphosphinophenoles and $Ni(COD)_2$ were found to be usable as homogenous catalysts for the polymerization and oligomerization of ethylene [6]. $Rh(CO)_2acac$ 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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