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P,O-Ligands: 2-Hydroxyarylphosphines, Nickel Complexes and Use in Homogenous Catalysis

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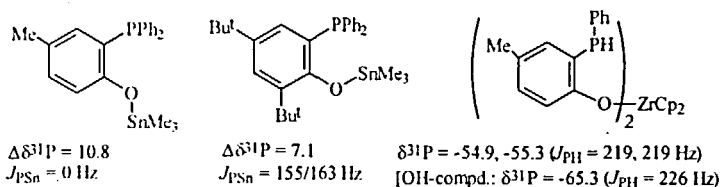
^a*Institut für Anorganische Chemie, Technische Hochschule Darmstadt, D-64287 Darmstadt,* ^b*Institut für Anorganische Chemie, Universität Greifswald, D-17487 Greifswald, Germany and* ^c*Institut für Technische und Petrochemie, Technische Hochschule Aachen, D-52056 Aachen, Germany*

Primary, secondary and tertiary 2-phosphinophenols were prepared by different organometallic routes using C,O-dilithium reagents and O-protected species, *o*-metallated alkoxymethyl ethers, or short-lived *o*-metallated 2-Li-arene-OP(X)R₂ compounds (X = O or lone electron pair) which rapidly rearrange to give 2-LiO-arene-P(X)R₂. The title compounds, being amphiphiles, exhibit a wide variety of reactions, some of which were presented on the XIIIth ICPC [1]. Here we focus on metallation, formation of nickel and organonickel complexes and type of coordination.

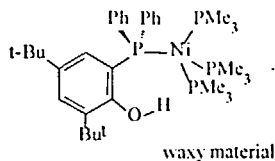
Metallation of *o*-phosphinophenols occurs at the oxygen atom. In PH/OH derivatives the equilibrium concentration of PLi is low. The phosphorus resonances are only slightly shifted, and slightly reduced P-H coupling constants compared to the OH derivatives indicate lack of P-coordination. This is apparent even in O-stannylated (soft metal) compounds, where P-Sn couplings are seen only if steric pressure induces a different conformation. The intramolecular P...Sn distance (337 pm) is much larger than a P-Sn bond but shorter than the van der Waals distance (400 pm). If lithium-*o*-phosphinophenolates were reacted with zirconocene dichloride, we observed neither significant coordination shifts of phosphorus nor changes of the proton shift of PH or of the one-bond

* Presenting author.

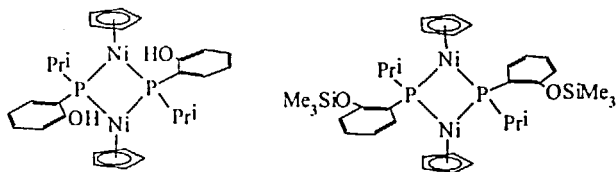
P-H coupling. It may be anticipated that hard d(0) metal ions coordinate mainly at oxygen. The P,O-chelate formation of a 6-*tert*-butyl substituted *o*-phosphinophenol with CpTiCl₃ by Willoughby *et al.* [2] is certainly due to steric pressure.



Efficient P-coordination of phosphinophenols or phosphinophenolates needs bond strengthening by back donation. Reaction of *o*-phosphinophenols with Ni(PMe₃)₄ (1:1) furnishes nickel(0) complexes which are η^1 -coordinated at phosphorus. The proton, phosphorus and carbon NMR spectra are consistent with a tetrahedral coordination and a free OH group. The increased acidity, as seen by the low-field shift, may be due to interactions with the basic Ni(PMe₃)₃ fragment.



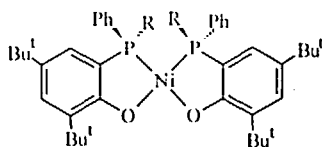
Another type of pure P-coordination was observed when secondary *o*-phosphinophenols were reacted with nickelocene. Phosphido-bridging dimers were formed which exhibit a negative coordination shift, much more for the OH than



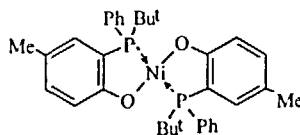
for O-silyl complexes. This feature and the different coupling pattern – triplets for C2 and C1 in the OH-complex and for C2 and C3 in the O-silyl complex – indicate different conformations. Weak donating properties of the OH groups towards nickel and increased back-donation could also contribute to the stronger shielding of the P-atom in this compound.

P-Tertiary 2-phosphinophenols prefer to form mono- and bis(P \rightarrow O-chelate) complexes. If diphenyl- or less bulky alkylphenylphosphinophenols were reacted with nickelocene in a 2:1 ratio, yellow to orange-brown bis(P,O-chelate) nickel complexes were formed. Another way is by reaction of phosphinophenols with Ni(PMe₃)₄ and stoichiometric amounts of oxygen. X-ray structure analyses of 3 alkylphenylphosphinophenolate nickel complexes show *cis*-arrangement of the two P-atoms with the ligands in *S,S*- and *R,R*-configuration in the two enantiomers. Solvated complexes of this type were readily formed in reactions of nickel salts with phosphinophenols in methanol or alcohol.

From *tert*-butylphenylphosphinocresole and nickel acetate in methanol a light green 2:1 complex is precipitated which is sparingly soluble and purely diamagnetic. On heating in a closed capillary above 120°C a stepwise reversible color change to yellow is observed. Solid state NMR



R: *i*-Pr, *t*-Bu, Ph

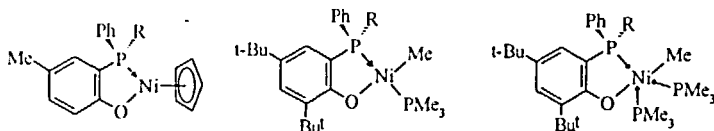


insoluble, $\delta^{31}\text{P CP MAS}$: 24.4 ppm (s)

studies indicate a structure with an inversion center, which is consistent with *trans*-configuration.

Reactions of P-tertiary *o*-phosphinophenols with nickelocene in benzene or toluene furnish semi-sandwich-P,O-chelates. The X-ray structure analysis of $[\eta^1\text{-CpNi}(2\text{-}i\text{PrPhP-4-MeC}_6\text{H}_3\text{O})]$ shows a centrosymmetric space group with equal populations of both enantiomers in the unit cell. The geometry at phosphorus is tetrahedral, the P-Ni-O-angle nearly 90° and the Cp-anion is η^5 -coordinated but the bond to the carbon in *trans*-position to oxygen is markedly shorter than the others by about 8-10 pm. Square planar and trigonal bipyramidal methylnickel-P,O-chelate complexes were synthesized by reactions of phosphinophenols with $[\text{Me}(\text{MeO})\text{Ni}(\text{PMe}_3)_2]$ and with $[\text{Me}_2\text{Ni}(\text{PMe}_3)_3]$, respectively. The square planar complex possess *trans*- phosphorus atoms as seen by two sharp doublets with P-P couplings of 316 Hz at -25°C. At 20°C the signals are broad. Since no signals for free trimethylphosphine were found,

a ligand migration leading to the pentacoordinate and a short-lived tri-coordinate species is assumed.



A methallylnickel–diphenylphosphinophenolate(P,O) chelate was obtained with methallylnickel bromide. This complex is thermally labile. On heating with ethylene under pressure polyethylene is formed. The close structural relationship to phosphinoenolato complexes, being the active species in the SHOPprocess [3], prompted us to investigate the (co)oligomerization of ethylene and other olefins in presence of $\text{Ni}(\text{COD})_2$ / phosphinophenol with a varying substitution pattern at phosphorus and the phenolic substituent to explore the electronic and steric influence on this reaction. Linear polyethylene and some copolymers were obtained. The general tendency found is that enhanced donor strengths at oxygen by *p*-methoxy or *tert*-butyl groups as well as increased donor strengths at phosphorus by an alkyl substituent or hydrogen increase the reactivity and the molecular weights of the polyethylene. Steric hindrance at sufficient basicity gave very active systems which are currently under closer investigation. Interestingly, oligomers were obtained in presence of Ph_3P . The ratio P,O-ligand / Ph_3P influences the average carbon number within the chain and the activity of the catalyst.

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